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EVALUATION OF ISOTOPE MIGRATION - LAND BURIAL

WATER CHEMISTRY AT COMMERCIALLY OPERATED LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITES

STATUS REPORT THROUGH SEPTEMBER 30, 1979

ALLEN J. WEISS AND PETER COLOMBO

NUCLEAR WASTE MANAGEMENT DIVISION

DEPARTMENT OF NUCLEAR ENERGY, BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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Allen J. Weiss and Peter Colombo
Principal Investigators

Contributors

James H. Clinton
Kenneth S. Czyscinski
Sharon Dobbs
Robert F. Doering
A.J. Francis
Gregory G. Galdi
Sandra L. Garber
Catherine L. Green
Charles R. Iden
Beverly J. Nine
Richard F. Pietrzak
Joseph R. Steimers

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and
National Technical Information Service
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EXECUTIVE SUMMARY

The prime consideration for continued use of shallow land burial practices for the disposal of low-level radioactive waste is the containment of radionuclides from the enivronment. Before additional disposal sites for commercial low-level waste can be licensed, the existing sites must be evaluated in terms of their effectiveness for retaining radionuclides. A multidisciplined approach is required in this effort, one part of which is the study reported here.

In cooperation with the U.S. Geological Survey, a field and laboratory program was initiated to study the existing commercial low-level radioactive waste disposal sites. This investigation will provide source term data for radionuclides and other solutes in trench waters at the sites and will describe the physical, chemical, and biological properties of the geochemical system that control the movement of radionuclides. This study was also initiated to provide experimental research support to the U.S. Nuclear Regulatory Commission for development of criteria for the selection and licensing of solid low-level radioactive waste disposal sites.

The disposal sites sampled to date are located at West Valley, New York; Maxey Flats, Kentucky; Barnwell, South Carolina; and Sheffield, Illinois. Procedures for the collection, preparation and analysis (particularly under anaerobic conditions) of trench waters were developed, when necessary, to supplement standard procedures. Inorganic, organic, and radiochemical constituents in trench waters are measured and their relevance to movement of radionuclides is being evaluated. Water samples from test wells are being monitored to detect and characterize radionuclides along the flow paths of ground water.

A survey of the disposal sites was conducted to obtain an overview of the radioactivity in trench and well waters to select specific trenches for comprehensive study. Water samples were collected from: (a) 46 trenches and 5 wells at Maxey Flats, Kentucky, (b) 13 trenches and 3 wells at West Valley, New York, and (c) 27 test wells at Sheffield, Illinois, during the summer of 1977. The specific conductance, pH, and temperature of the water samples were measured in the field at the time of collection. Dissolved organic carbon (DOC), tritium, gross alpha, gross beta, and gamma radioactivity were measured in the laboratory (BNL). Tritium was the most abundant of the radionuclides found. Radioisotopes of americium and cesium cobalt were also found in a large number of trenches.

The trenches selected for further study were chosen based on extreme and average values of the parameters measured in this study. The final selection of trenches for sampling depended upon the availability of water in the trenches, location of new monitoring wells at the disposal sites, and local ground water flow paths.

More detailed radiochemical, inorganic, and organic analyses were performed on trench and well waters obtained during repeated sampling of the West Valley and Maxey Flats sites. Only one sampling of trenches at the Barnwell and Sheffield disposal sites has been performed. Some general conclusions can be made from these data in terms of source term information to be used in modeling efforts, as well as processes which may affect migration of radionuclides away from the trenches.

Trench waters are complex anoxic chemical systems which require more extensive investigation to assess their role in radionuclide retention and mobilization.

No overall systematic changes in any disposal site trenches were observed during the brief sampling interval. However, changes in some radionuclide and cation concentrations were observed in several trenches.

Tritium was the most abundant of the radionuclides and was found in all the trench waters. Chemically bound as HTO, tritium would be the most mobile radionuclide.

^{90}Sr, ^{238,239,240}Pu and ^{137}Cs were found as dissolved species in all trench waters and sorbed on suspended particulates at Maxey Flats and West Valley. Radionuclides measured as dissolved species in trench waters may be compared to the standard for release to an unrestricted area in 10CFR20, Appendix B, Table II, although it is understood that the waters in the trenches are <u>not</u> releases.

Tritium, ^{90}Sr, ^{137}Cs, and Pu in several trenches at Maxey Flats and West Valley exceeded the standard.

Only tritium in two trenches at Barnwell and ^{137}Cs and ^{90}Sr in one trench at Sheffield exceeded the standard.

Movement of radionuclide bearing suspended material through the hydrologic system may be a means by which radionuclides can migrate rapidly from disposal sites.

Numerous organic compounds were identified in the trench waters at Maxey Flats and West Valley, some of which have the potential for chelation with radionuclides.

The presence of radionuclides above background in well UB1 and UB1-A at Maxey Flats, together with organic compounds that are also found in nearby trenches, indicates communication between the wells and trench water leachates, and that migration of radionuclides from trenches has occurred.

The objectives of the microbiology study are: (i) to enumerate the abundance and distribution of microorganisms active in the trench leachates, and (ii) to determine the effects of various microbial processes on the transformation and migration of the buried radionuclides from the trenches into the environment.

Results of this study showed that aerobic, anaerobic, sulfate reducing, denitrifying, and methanogenic bacteria are present in the leachate samples, and are able to grow anaerobically in trench leachates, which indicates that the radionuclides and organics present in leachates are not toxic to these bacteria.

Methane bacteria present in the leachate samples produced appreciable amounts of tritiated and carbon-14 methane from the leachates. The presence of active microflora in the trench leachates suggest that they may play a significant role in the transformation of radionuclides and the organic constituents of the waste, and thus affect the long-term storage, mobility and migration of radionuclides from the waste disposal sites into the biosphere.

The geochemical aspects of radionuclide migration and retention treated in this report describe laboratory sorption studies involving batch experiments using site-specific materials and performed under conditions which simulate the field situation.

Sorption tests performed in this program have aimed at supplying relevant K_d numbers for use in the groundwater transport modeling studies of the commercial burial sites.

Solid phases used in the experiments were characterized in terms of parameters thought to influence sorptive properties. Laboratory experiments were performed to assess the effect on sorptive behavior of the following experimental variables: aqueous and solid phase compositional variations, contact time, water/soil ratio, and containers used in the experiments. Experimental results indicate that the observed K_d is a function of both solid and liquid phase compositional variations as well as contact time. The observation that the lowest K_d results are observed with anoxic trench waters and ultrasonicated soils points to the need to use site specific materials and experimental conditions which simulate in situ conditions as closely as possible.

Future sorption experiments will involve some batch experients, but also flow-through column experiments which more closely simulate the field situation. Batch experiments will be designed to allow comparison with column experiment results, and provide information of a mechanistic nature which will be useful in predictive applications.

Cores collected from below the disposal trenches at Barnwell, South Carolina, and Sheffield, Illinois will be analyzed radiochemically to determine the migration of radionuclides from the trenches and allow comparisons with laboratory studies.

Using laboratory sorption data to establish siting criteria involves determining mineral-pore water-radionuclide associations. Field verification of these associations requires a core analysis scheme more involved than a simple bulk radiochemical analysis as a function of depth. Both a bulk radiochemical analysis of the cored material and a further analysis based on mineral fractions will be performed on the trench cores. This analytical plan will permit detailed comparisons of laboratory results with the field situation.

EVALUATION OF ISOTOPE MIGRATION - LAND BURIAL

WATER CHEMISTRY AT COMMERCIALLY OPERATED LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITES

1 INTRODUCTION

1.1 Purpose of the Study

This study is designed to provide an understanding of and to monitor the behavior of existing low-level sites and to provide experimental research support to the U.S. Nuclear Regulatory Commission (NRC) for development of criteria for the selection and licensing of solid low-level radioactive waste disposal sites. One of the significant factors in the development of these criteria is the ability to make predictions on the rate of movement of radionuclides along the ground water flow path.

In cooperation with the U.S. Geological Survey (USGS), a field and laboratory program was initiated to study the existing commercial low-level radioactive waste disposal sites. This investigation will define the source terms (concentrations in solutions) of radionuclides and other solutes in trench waters at the sites, and will describe the physical, chemical, and biological properties of the geochemical system that control the movement of radionuclides.

1.2 Scope of the Study

1.2.1 Trench Water Analysis

Procedures for the collection, preparation and analysis of trench waters were developed, when necessary, to supplement standard procedures. Additional procedural improvements are made when necessary. Inorganic, organic, and radiochemical constituents in trench waters are being measured and their relevance to movement of radionuclides is being evaluated. Water from test wells in and around the disposal sites are being sampled to detect and characterize radionuclides along the flow paths of ground water.

1.2.2 Microbiological Processes

Microbial degradation of organic material buried in the trenches may contribute directly or indirectly to the migration of radionuclides. The consequences of the interaction of radionuclides present in the trenches with the products of microbial activity, e.g., gas generation, formation of soluble organo-radionuclide complexes, and bioaccumulation of radionuclides, are being measured and evaluated.

1.2.3 Geochemical Considerations

The geochemical aspects of radionuclide migration and retention treated in this portion of the program are limited to, (i) laboratory sorption studies and, (ii) radiochemical analyses of cores obtained by the U.S. Geological Survey from beneath waste disposal trenches. Laboratory sorption studies involve batch and column experiments using site-specific materials and are performed under conditions which simulate the field situation. Data and ideas developed from these studies will be compared to the results of the core analysis for field verification. Conclusions derived from these studies are expected to have direct application to modeling studies of some of the sites and to establish siting criteria and improved burial practices at future sites.

2 COMMERCIAL DISPOSAL OF LOW-LEVEL RADIOACTIVE WASTE

2.1 Introduction

Disposal of low-level radioactive wastes at commercially operated disposal sites began in 1962 at Beatty, Nevada. Since that time additional disposal sites were established in Maxey Flats, Kentucky; West Valley, New York; Richland, Washington; Sheffield, Illinois; and Barnwell, South Carolina, shown in Figure 2.1.

Figure 2.1. Commercial low-level radioactive waste disposal sites in the United States.

The disposal sites at West Valley, Maxey Flats, and Sheffield have discontinued operations leaving Barnwell as the only disposal site accepting commercial radioactive wastes in the Eastern U.S. Table 2.1 lists the existing disposal sites, the year licensed, and their current status.

Table 2.1

Commercial Low-Level Radioactive Waste Disposal Sites

Site	Year Licensed	Current Status
Beatty, Nevada	1962	open
Maxey Flats, Kentucky	1963	closed
West Valley, New York	1963	closed
Richland, Washington	1965	open
Sheffield, Illinois	1967	closed
Barnwell, South Carolina	1971	open

According to a recent study,(1) the total land presently available at the sites for shallow land burial is 660 acres. Based on current disposal practice which utilizes 50 percent of trench volume, 9.7×10^3 m^3 of packaged waste can be buried per acre of land. This results in a total capacity of 6.4×10^6 m^3 of waste that can be buried at the commercial sites. With moderate nuclear power growth and projected waste generation rates, it is calculated that the entire licensed land burial capacity will be used up by 1990(1,2,3). These estimates were based on the capacities of all six sites; and with three sites presently closed, the need to license additional acreage will be reached sooner than projected.

2.2 Low-Level Radioactive Waste

Low-level waste consists of a variety of laboratory, hospital, and reactor equipment, residues, and trash which are contaminated with radioactive materials. For the most part, the types of materials buried include clothing, plastics, paper, ion exchange resins, scintillation vials, animal carcasses, solidification agents, decontamination reagents, and other materials in small quantities.

Transuranic elements, e.g., plutonium, americium, neptunium, etc.. in concentrations greater than 10 nCi/g of waste are classified as TRU waste and are not accepted at commercial disposal sites. However, in the past, solid wastes contaminated with plutonium and other transuranic radionuclides were mixed with low-level wastes and buried at the commercial sites.(4)

Solid low-level radioactive wastes, such as those generated at commercial power plants, hospitals, research facilities, and universities, are usually buried in the containers in which they are shipped. The purpose of the package is to minimize personnel exposure and to prevent the loss of radioactive materials during shipment to the disposal site, according to regulations set forth by the Department of Transportation.

2.3 Site Characteristics

The disposal sites are located in sparsely settled areas that were considered suitable for shallow land burial of low-level radioactive wastes (Table 2.2). The sites' geohydrological characteristics are considered the primary containment for radioactive wastes buried there. These characteristics were believed to afford isolation of the buried radionuclides by sorption and ion exchange processes which attach the radionuclides to the soil or rocks in which they are in contact.

Table 2.2

Hydrogeological Characteristics of Commercial Disposal Sites

Site	Geologic Material Containing Trenches	Distance of Water Table From Surface	Average Annual Rainfall[a]
Maxey Flats, Kentucky	weathered and unweathered shale (fractured)	10 meters or less to perched water table	113 cm/yr
West Valley, New York	glacial till (high clay content)	saturated or near saturated to the surface	104 cm/yr
Sheffield, Illinois	glacial loess (silts and clays with interbedded sand lens)	10 meters	89 cm/yr
Barnwell, South Carolina	sandy clay coastal plain sediment (sand, silts and clays)	10 meters	118 cm/yr
Beatty, Nevada	alluvium (sand and silts)	85 meters	12 cm/yr

[a] Rainfall data obtained at burial sites or at weather bureau stations located several miles from the sites.

2.4 Shallow Land Burial

Burial practices at the commercial disposal sites are similar. Typically, solid wastes are buried in shallow rectangular trenches with varying dimensions, ranging from 60-150 m long, 8-15 m wide, and 6 m deep. The trench floor is sometimes sloped toward one or more sumps, and riser pipes are provided for routine observation of water levels and for removal of water. Solid wastes are buried in an assortment of containers, such as cardboard and wooden boxes, plastic bags, cement casks, steel drums, and steel bins.

When filled with waste, the trench is backfilled with previously excavated earth, compacted, and covered with capping material. Generally, the compacted cap contains clay that expands when moist, to retard infiltration of rain water. The finished trench is covered with soil and planted with shallow rooted ground cover to prevent soil erosion. Rain or ground water that enters a trench may leach the contents of the buried containers that have failed either during burial operations or through corrosion and decomposition processes. A prime concern of burial operation is that the leached material may be carried to the environment around the trenches by the infiltrated water.

In this report, the terms "trench water" and "trench leachate" are used interchangeably to identify water that resides in a trench, and that may be removed via sumps or test wells in the trench.

2.5 References

1. U.S. Nuclear Regulatory Commission, "NRC Task Force on Review of the Federal/State Program for Regulation of Commercial Low-Level Radioactive Waste Burial Grounds," USNRC Report NUREG-0217, March 1977.[a]

2. M. F. O'Connell and W. F. Holcomb, "A Summary of Low-Level Radioactive Wastes Buried at Commercial Sites Between 1962-1973, with Projections to the Year 2000," Radiation Data and Reports, Vol. 15, No. 12, (December 1974).[b]

3. W. F. Holcomb, "A Summary of Shallow Land Burial of Radioactive Wastes at Commercial Sites Between 1962 and 1976 with Projections," Nuclear Safety, Vol. 19, No. 1, p. 50 (January-February 1978).[b]

4. U.S. Nuclear Regulatory Commission," Regulation of Federal Radioactive Waste Activities - Report to Congress on Extending the Nuclear Regulatory Commission's Licensing or Regulatory Authority to Federal Radioactive Waste Storage and Disposal Activities," USNRC Report NUREG-0527, September 1979.[a]

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[a] Available for purchase from National Technical Information Service, Springfield, Va. 22161.

[b] Available in public technical libraries.

3 PRELIMINARY STUDY

3.1 Introduction

Water samples were initially obtained from the Maxey Flats, Kentucky, disposal site in April 1976 to gain experience in the collection, handling, and analyses of trench waters. The first samples were collected jointly with the USGS, State of Kentucky, BNL, and with the assistance of Nuclear Engineering Company (NECO) personnel at the site.

Field measurements and sample filtration were performed on the site, in a laboratory provided by NECO, within an hour after sample collection. The samples were packed in ice and brought to BNL for chemical and radiochemical analyses.

3.2 Trench Water Collection

Trench water samples were obtained by lowering flexible Tygon tubing into the trench via a riser pipe and pumping the water with a peristaltic pump (Figure 3.1). Initially, some water was diverted to a waste tank to clean out the lines before collecting a sample. Samples were collected from eight trenches selected by USGS on the basis of previous experience at Maxey Flats. Samples obtained for inorganic and radiochemical analyses were collected and stored in plastic containers, while samples for organic analyses were kept in glass bottles.

Figure 3.1. Portable unit used for pumping water from trenches at Maxey Flats.

3.3 Trench Water Filtration

The water samples contained solid materials including suspended particulates and sediment that were stirred up when the tubing was lowered to the bottom of the sump. These particulates were removed from the sample by filtration through a 0.45 μm membrane filter. It is generally accepted that material in "solution" will pass through a 0.45 μm filter. However, it is understood that true solution is not defined by this arbitrary cut-off limit.

The procedure used for filtering the trench waters is in accordance with standard USGS field methods.(1) Figure 3.2 shows the filtration equipment used at Maxey Flats.

3.3.1 Iron Precipitation

The initially clear trench waters become cloudy with the formation of a brown iron hydroxide precipitate after being exposed to air. Water samples from trenches at the West Valley, New York, disposal site were shown to have a high Fe^{2+}/Fe^{3+} ratio(2). Ferrous iron, which is more soluble than ferric iron in the pH range normally found in trench waters, is oxidized to the latter by air. This phenomenon is commonly observed in water obtained from land fills containing buried iron drums.

3.4 Sample Analysis

Inorganic, organic, and radiochemical analyses of the samples were performed to measure the concentrations of selected constituents dissolved in the trench waters (source term). The constituents of interest in these samples are listed in Table 3.1.

Table 3.1

Constituents of Interest in Water Samples Taken From Maxey Flats, Kentucky, Disposal Site, April 1976

Field Measurements	Metals	Non Metals	Radionuclides
pH	calcium	bicarbonate	gross alpha
temperature	iron	carbon	gross beta
specific conductance	lithium	carbonate	gamma scan (Ge(Li))
	magnesium	chloride	^{241}Am
	manganese	dissolved organic carbon (DOC)	^{238}Pu
	potassium	nitrate	$^{239,240}Pu$
	sodium	nitrite	^{90}Sr
		silica	
		sulfate	
		residue	

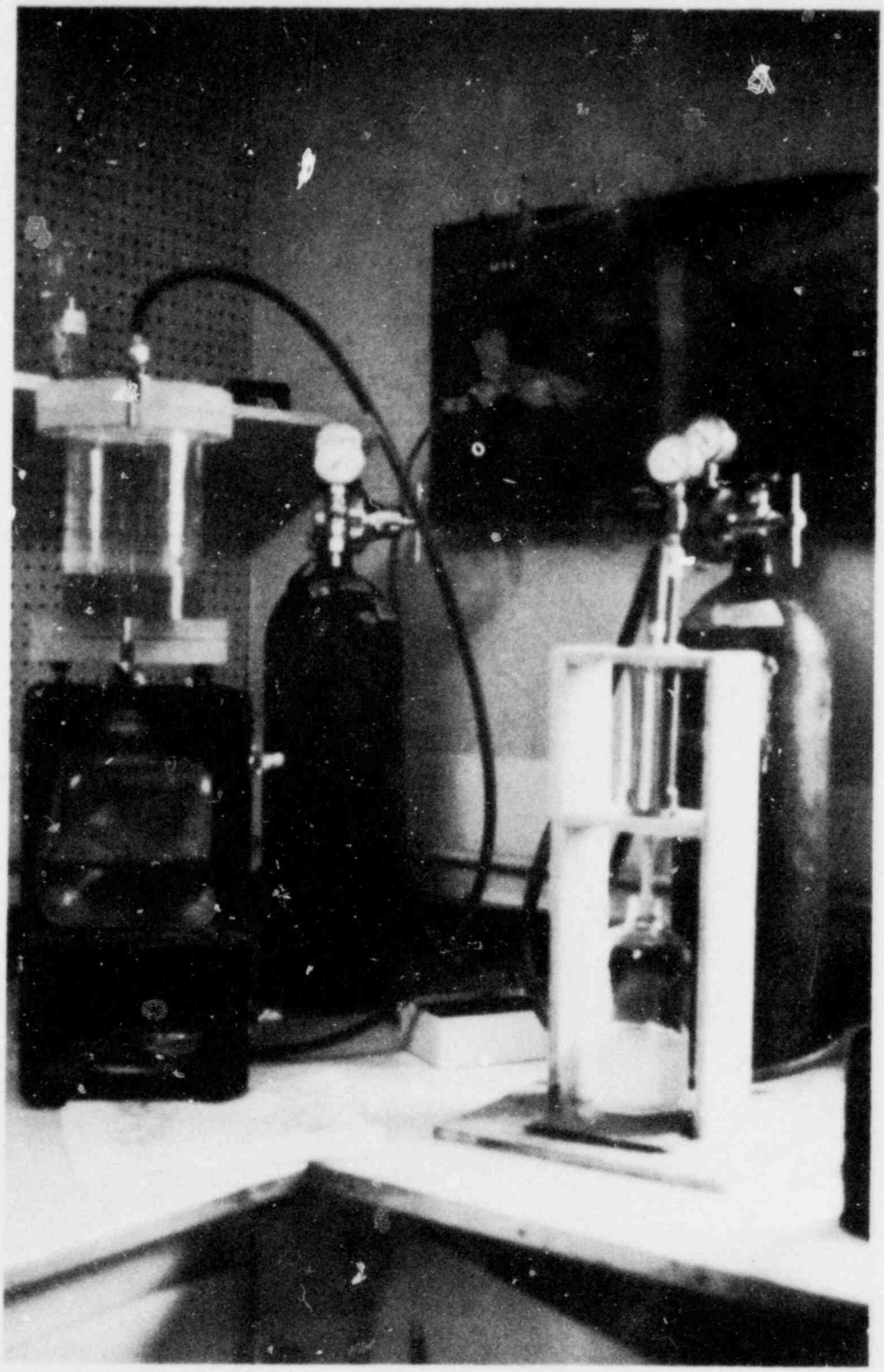

Figure 3.2. Filtration equipment used at Maxey Flats.

3.5 Discussion

The iron that precipitated from the trench waters and was subsequently filtered from the samples contained material that was originally dissolved in the water. Radionuclides and other solutes that were originally in solution in the trench environment may have been adsorbed onto, or coprecipitated with, the iron hydroxide. Therefore, the results of these analyses are not representative of the trench condition and are not reported here. These data are available in a previous report of this program.(3)

Procedures were developed to prevent air from coming in contact with trench water samples during collection and filtration. These anoxic procedures are described in Chapter 5 and Appendix B. The analytical procedures, including modifications made to conventional standard methods, that are employed in this study are also fully described in Chapter 5 and Appendices C and D.

3.6 References

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2. L. Husain, J.M. Matuszek, J. Hutchinson, and M. Wahlen, "Chemical and Radiochemical Character of a Low-Level Radioactive Waste Burial Site", in Management of Low-Level Radioactive Waste, M.W. Carter, et al., Ed. (Pergamon Press, N.Y., 1979), Vol. 2, p. 888.

3. P. Colombo, A.J. Weiss, and A.J. Francis, Brookhaven National Laboratory, "Evaluation of Isotope Migration - Land Burial, Water Chemistry at Commercially Operated Low-Level Radioactive Waste Disposal Sites", USNRC Report BNL/NUREG 50623, March 1977. Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C.

4 SURVEY STUDY OF LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITES

(G.G. Galdi, S. Garber, C. Green, B. Nine, J. Steimers, and A.J. Weiss)

4.1 Introduction

A survey of the commercial low-level radioactive waste disposal sites was conducted to obtain an overview of the radioactivity in trench waters and well waters for selecting specific trenches for comprehensive study. Water samples were collected from: (a) 46 trenches and 5 wells at Maxey Flats, Kentucky, (b) 13 trenches and 3 wells at West Valley, New York, and (c) 27 test wells at Sheffield, Illinois, during the summer of 1977. Samples were not collected from Barnwell, South Carolina, at that time due to the absence of water in the trenches during the summer. However, six trench and six well water samples were obtained from the Barnwell site in the winter of 1978 during the rainy season in South Carolina. Surface and ground water samples were also collected from areas adjacent to the Maxey Flats and West Valley sites.

The specific conductance, pH, and temperature of the water samples were measured in the field at the time of collection. Dissolved organic carbon (DOC), tritium, gross alpha, gross beta, and gamma radioactivity were measured in the laboratory (BNL).

4.2 Sample Collection

United States Geological Survey personnel conducting hydrogeological studies at the disposal sites collected the water samples for this survey study. Samples were obtained from most trenches and wells that contained water. The procedures adopted by USGS and BNL personnel for conducting the survey study are described in Appendix A.

Briefly, trench water samples were obtained by lowering plastic tubing into established riser pipes in the trenches and lifting the water with a peristaltic pump. Some trench and well water samples were obtained with a bailer when the water levels were below the lift capability of a peristaltic pump. A 500-mL non-filtered sample, for radiochemical analysis, and a 50-mL filtered sample, for organic analysis, were collected from each sampling location.

The sample for radiochemical analysis was acidified with 35 mL concentrated nitric acid immediately after collection to prevent iron hydroxide precipitation and was stored at ambient temperature in a polyethylene bottle. The radioactivity of this sample represents the total activity (dissolved plus particulate solids) in the water.

The procedure in Appendix A describes steps for obtaining a sample for DOC analyses by in-line filtration of trench water. However, in-line filtration in the field was not accomplished due to rapid clogging of the filter by particulate material in the water. Also, the pressure available from the peristaltic pump, after lifting the water from the trench, was insufficient for filtering. Instead, the organic sample was obtained by filling a stainless steel filtration unit directly from the outflow of the peristaltic pump, or from the bailer, and pressurizing the unit with a portable nitrogen cylinder. A 50-mL sample was filtered through a 0.45 μm silver membrane into a glass bottle and was kept at ∿ 4°C until the DOC analysis was completed.

4.3 Analyses

4.3.1 Dissolved Organic Carbon (DOC)

Carbon analysis was determined on the filtered, non-acidified sample using the Beckman Total Carbon Analyzer which measured both total and inorganic carbon. The organic carbon content was obtained by difference with a detection limit ≃ 1-2 mg/L.

4.3.2 Tritium

Tritium as HTO was determined on the filtered, non-acidified sample. One mL of a distilled aliquot of water sample in 15 mL of liquid scintillation fluid was counted in a Beckman LS8100 liquid scintillation counter. Trench water samples were counted for 1 minute, whereas well and stream samples were generally counted for 10 minutes. With these counting times, and with a background count of approximately eight counts/min, the detection limit for tritium is 8,000 pCi/L for trench water and 2,000 pCi/L for wells and streams. This study was intended to survey a large number of samples in a limited time, therefore the detection limit is somewhat higher than commonly achieved in environmental monitoring studies. Because well waters from the Sheffield, Illinois, and Barnwell, South Carolina, sites were not expected to contain much tritium, if any, a larger aliquot was counted for a longer time. The detection limit for tritium is 240 pCi/L, when 7 mL of sample plus 9 mL of liquid scintillation fluid is counted for 100 minutes.

4.3.3 Gross Alpha-Gross Beta

Gross alpha and gross beta activities were measured on an aliquot of the acidified non-filtered water sample. A 3-mL aliquot of trench water was heated to dryness in a 50 mm diameter planchette and counted with a Nuclear Chicago two-channel, low-level, proportional flow counter for 10 minutes. Well and stream samples were concentrated from 50 mL to 3 mL, dried in a 50 mm diameter planchette, and counted for 20 minutes. The alpha detection limits for these counting conditions are 200 pCi/L for trench water and 6 pCi/L for wells and streams. Beta detection limits for these conditions are 700 pCi/L for trench water and 30 pCi/L for wells and streams. The gross beta concentrations reported do not include tritium radioactivity, which is reported separately.

4.3.4 Gamma

The gamma activities of the acidified, non-filtered samples were measured by scintillation counting with a NaI(Tl) detector. Gross gamma activity, without energy discrimination, was determined with a 76-x 76-mm NaI(Tl) well crystal in a Searle 1185 gamma counting system. A 10-mL aliquot of water sample was counted for 20 minutes in an energy window between 15 and ∞ keV. This counting method was used to obtain relative gamma activities of a large number of trench water samples in a short period of time.

In addition to NaI(Tl) counting, 15-mL and 250-mL aliquots of these samples were counted for 1000 minutes with a 2 keV resolution Ge(Li) gamma ray spectrometer system to identify and measure the individual gamma emitting radionuclides present. Detection limits for the individual radionuclides varied from sample to sample because of Compton continuum variations resulting from different combinations of radionuclides in the samples.

4.3.5 Detection Limits

The detection limits reported here and elsewhere in the report are based on the premise that the minimum detectable activity is that activity which, in the same counting time, gives a count which is different from the background count by three times the standard deviation of the background count.

4.4 Maxey Flats, Kentucky, Site

4.4.1 Collection

Water samples were collected from 46 trenches and 5 wells at the Maxey Flats, Kentucky, disposal site. Figure 4.1 shows the location of trenches and wells at Maxey Flats. Some trenches have one or more riser pipes for water removal. They are identified by a riser number or letter following the trench number. Trench 34 has four riser pipes, trench 31 has risers in its east and west ends, and trenches 40, 43, and 44 have risers in the north and south ends. The "33L trench" is a group of side by side slit trenches each having one or more riser pipes.

The inside of new Tygon tubing was flushed with approximately three gallons of trench water before a sample was collected. Due to a shortage of new tubing, it was necessary to sample trenches 33L-17, 33L-13, 1, 5S, and 23 in sequence with the same tubing. The outside of the used tubing was wiped clean before it was inserted into the next riser pipe, and the inside was then flushed with at least five gallons of trench water before the sample was collected.

Water samples from trenches 40N, 42, and 44N were collected with new PVC bailers which had been washed with detergent and rinsed with approximately one half gallon of distilled water before taking the sample. All on-site well water samples were taken with separate copper bailers. Trenches 12L, 13L, 28, 29, 33L-2, 33L-5, 33L-7, 33L-14, 33L-15, 34-2, 34-3, 40S, 41, 43N, and 43S were not sampled because of insufficient water or badly bent sump pipes.

Ten samples from wells and streams in the vicinity of the disposal site were also collected. Locations of the off-site sampling positions in relation to the trench area at the disposal site are shown in Figure 4.2 and described in Table 4.1. The off-site samples were taken directly in glass bottles, except at: (a) location 5, which was obtained in a metal bucket and then poured into a glass bottle, and (b) location 6, which was collected in a glass bottle from a kitchen tap.

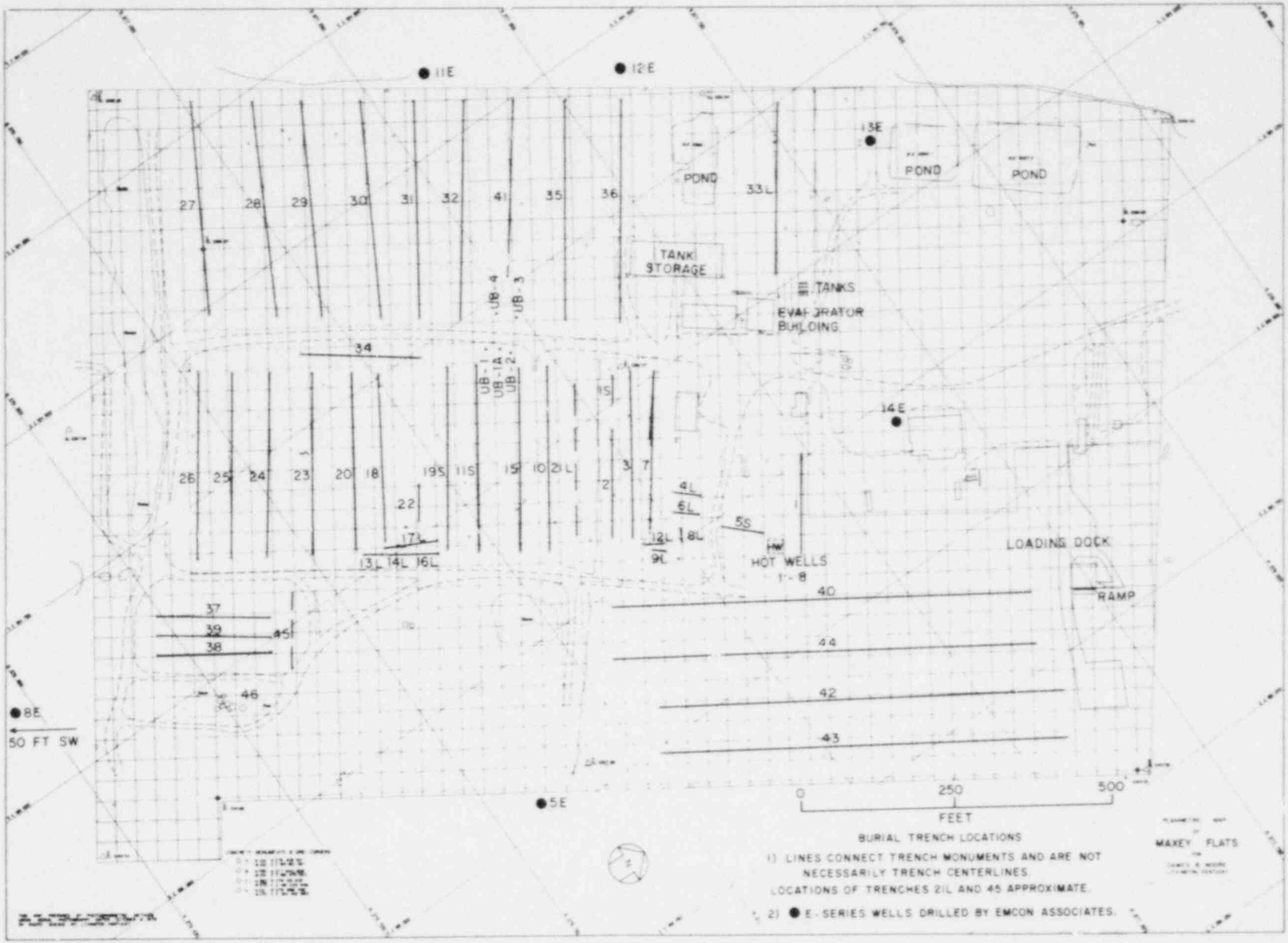

Figure 4.1. Map of burial trench locations at the Maxey Flats, Kentucky, radioactive waste disposal site (adapted from drawing supplied by J. Clancey, Dames & Moore).

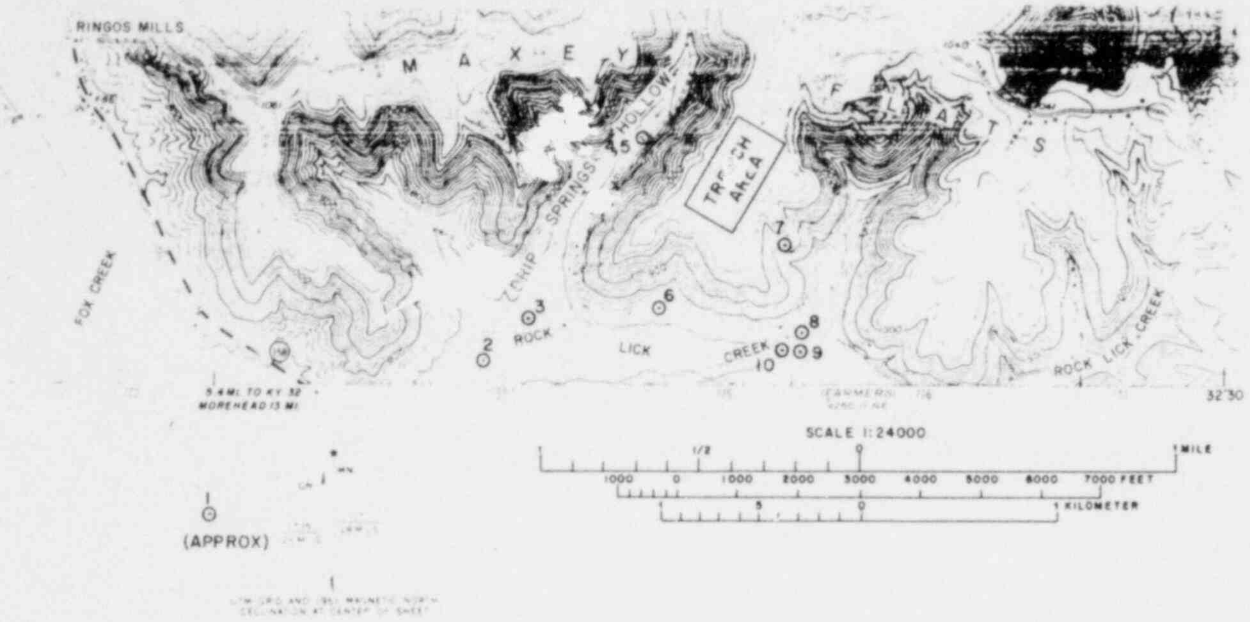

Figure 4.2. Sampling locations near the Maxey Flats, Kentucky, disposal site (adapted from topographical map obtained from H. Zehner, USGS).

Table 4.1

Sampling Locations in the Vicinity of Maxey Flats, Kentucky, Disposal Site, Survey Study 1977

Sampling Position[a]	Location
# 1	Fox Creek below Rock Lick Creek
# 2	Rock Lick Creek at USGS Gaging Station
# 3	Drip Springs Hollow above Rock Lick Creek
# 4	Drip Springs Hollow at McRoberts House
# 5	McRoberts Well in Drip Springs Hollow
# 6	Skaggs Well - South of Trench Area
# 7	KDHR[b] Sample Point 13 in Site Main Drainage
# 8	No-Name Hollow above Rock Lick Creek
# 9	Rock Lick Creek above No-Name Hollow
#10	Rock Lick Creek below No-Name Hollow

[a] Position numbers correspond to circled locations shown in Figure 4.2, except #1, which is approximately three quarter mile SW of area shown.

[b] Kentucky Department of Human Resources sample point.

4.4.2 Results

The ranges of pH, specific conductance, DOC, gross alpha, gross beta, gross gamma, and tritium measured in the trench water samples taken from the disposal site are shown in Table 4.2.

Table 4.2

Ranges of Measurements of Water Samples Taken From Maxey Flats, Kentucky, Disposal Site, Survey Study 1977

Measurement	Range
pH	2.2 - 12.4
Specific conductance (μmho/cm at 25°C)	2.8 E2 - 3.9 E4
DOC (mg/L)	<1 E0 - 6.0 E3
Gross alpha (pCi/L)	<2 E2 - 6.4 E5
Gross beta (pCi/L)	8 E2 - 5.7 E7
Gross gamma (relative cpm)	<1 E1 - 1.6 E4
Tritium (pCi/L)	2.5 E5 - 7.4 E9

Field measurements of pH, temperature, and specific conductance of individual water samples taken from the disposal site and vicinity are given in Table 4.3. These measurements were generally made less than five minutes after collecting a sample. When there was greater than five minutes delay in making the measurements, the elapsed time is indicated in parenthesis after the temperature. Since the water temperature was not measured immediately after sampling, the value should not be taken as the actual ground water temperature. The specific conductance of the on-site samples ranged from 280 to 38,500 μmho/cm at 25°C. The specific conductance of the off-site waters are in a narrow range between 128 and 428 μmho/cm at 25°C. Since specific conductance is related to the amount of dissolved solids in the trench water, any iron hydroxide that precipitated before making the measurement would have caused a reduction of the measured value.

The pH of the trench samples varied from 2.2 to 12.4 indicating differences in chemical composition of the trench waters. The pH of the off-site water samples are in a range between 4 and 7.

Table 4.3

Field Measurements of Water Samples Taken From Maxey Flats, Kentucky, Disposal Site and Vicinity, Survey Study 1977

Sampling Location[a]	Date Sampled	pH	Temperature (°C)	Specific Conductance (μmho/cm at 25°C)
Trench 1	6/16/77	7.0	21.0 (15)[b]	2.30 E3
Trench 2	6/9/77	7.1	17.0 (30)	3.85 E4
Trench 3	6/6/77	6.6	22.0 --[c]	1.75 E3
Trench 5S	6/16/77	6.6	23.0 (12)	1.83 E3
Trench 7	6/6/77	7.1	28.0 --	2.33 E3
Trench 8	6/6/77	8.2	25.0 --	2.68 E4
Trench 9L	6/6/77	7.0	25.0 --	2.78 E2
Trench 14L	6/7/77	6.5	25.5 --	4.23 E2
Trench 17L	6/7/77	5.8	22.5 --	1.32 E4
Trench 18	6/9/77	7.2	16.5 (25)	4.35 E3
Trench 19S	6/9/77	6.8	18.0 (35)	2.32 E3
Trench 22	6/7/77	7.0	20.0 --	9.42 E2
Trench 23	6/16/77	7.2	23.0 (13)	5.20 E3
Trench 24	6/8/77	6.9	15.5 --	3.38 E3
Trench 25	6/8/77	6.9	15.0 --	2.36 E3
Trench 26	6/8/77	7.0	14.5 --	2.72 E3
Trench 27	6/8/77	5.7	16.5 --	1.63 E4
Trench 30	6/9/77	___	___	___
Trench 31E	6/9/77	7.4	17.0 (25)	3.18 E3
Trench 31W	6/9/77	7.6	17.0 (30)	7.46 E3
Trench 32	6/8/77	7.3	17.0 --	5.55 E3
Trench 33L-1	6/16/77	7.2	22.0 (10)	1.09 E3
Trench 33L-3	6/16/77	5.3	19.5 (10)	1.22 E4
Trench 33L-4	6/9/77	12.4	16.0 (15)	7.23 E3
Trench 33L-6	6/16/77	7.0	19.5 (7)	8.19 E3
Trench 33L-8	6/14/77	6.6	19.5 --	1.06 E3
Trench 33L-9	6/14/77	5.8	19.5 --	6.49 E3
Trench 33L-10	6/16/77	6.6	19.0 (13)	1.26 E3
Trench 33L-11	6/16/77	12.0	19.0 (7)	3.00 E3
Trench 33L-12	6/16/77	6.7	19.0 (10)	1.50 E3
Trench 33L-13	6/16/77	6.9	19.0 (8)	7.62 E2
Trench 33L-16	6/9/77	12.4	18.0 --	9.14 E3
Trench 33L-17	6/16/77	12.2	20.0 (12)	4.00 E2
Trench 33L-18	6/16/77	2.2	19.0 (19)	1.10 E4
Trench 34-1	6/7/77	7.0	18.5 --	7.55 E2
Trench 34-4	6/7/77	6.7	17.0 --	1.38 E3
Trench 35	6/8/77	7.9	16.0 --	5.50 E3
Trench 36E	6/8/77	8.6	16.0 --	5.80 E3
Trench 36W	6/8/77	7.3	16.0 --	2.84 E3
Trench 37	6/9/77	6.1	16.5 (20)	8.66 E3
Trench 38	6/7/77	6.9	16.0 --	1.67 E3

Cont. →

Table 4.3, continued

Field Measurements of Water Samples Taken From Maxey Flats, Kentucky, Disposal Site and Vicinity, Survey Study 1977

Sampling Location	Date Sampled	pH	Temperature (°C)	Specific Conductance (umho/cm at 25°C)
Trench 39	6/7/77	6.3	17.5 --	1.53 E3
Trench 40N	6/17/77	7.2	20.0 (10)	6.33 E3
Trench 42	6/17/77	7.1	20.0 (10)	2.83 E3
Trench 44N	6/17/77	6.4	19.0 --	1.16 E4
Trench 44S	6/17/77	6.6	19.5 (10)	2.32 E3
Well 5E	6/10/77	7.5	16.0 --	1.12 E4
Well 8E	6/10/77	7.0	16.0 --	1.20 E3
Well 12E	6/10/77	7.1	15.0 --	1.81 E3
Well 13E	6/10/77	7.4	15.5 --	2.10 E3
Well 14E	6/10/77	6.9	16.0 --	1.83 E3
#1[d]	6/15/77	7.0	22.5 --	2.10 E2
#2	6/15/77	6.7	24.5 --	1.86 E2
#3	6/15/77	6.6	22.5 --	1.83 E2
#4	6/15/77	5.6	25.0 --	1.85 E2
#5	6/15/77	4.9	19.0 --	2.40 E2
#6	6/15/77	4.0	20.5 --	3.45 E2
#7	6/15/77	5.0	21.0 (10)	4.28 E2
#8	6/15/77	5.6	23.0 --	1.62 E2
#9	6/15/77	5.8	24.0 (10)	1.28 E2
#10	6/15/77	6.1	26.5 (10)	1.33 E2

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[a] Sampling locations correspond to positions indicated in Figure 4.1.

[b] Numbers in ( ) are minutes between sampling and measurement.

[c] -- Indicate less than five minutes between sampling and measurement.

[d] Sampling location numbers (#1-#10) correspond to locations in Figure 4.2 as described in Table 4.1.

Radionuclide and DOC concentrations in the trench, well, and stream samples are given in Table 4.4. Gross alpha, gross beta, and tritium concentrations are given in pCi/L; gross gamma is reported as relative counts/min above laboratory background. The numbers in parenthesis represent 2σ percent counting uncertainty. It should be noted that the radiochemical samples were not filtered; therefore, the reported radionuclide concentrations include the activity of any particulate material in the water samples.

Tritium was measured in all samples; the highest concentration was 4.8 x 10^9 pCi/L in trench 27. Well 13E contains a considerable amount of tritium (6.1 x 10^6 pCi/L). Gross beta was found in all trenches and gross alpha was found in most trenches. Two of the five on-site wells, 8E and 12E, contained small but detectable amounts of gross alpha and gross beta activity. The presence of alpha and beta radioactivity in these wells is not necessarily a consequence of radionuclide migration from adjacent trenches. Traces of radioactivity in these wells could have resulted from (a) cross contamination during previous water sampling, (b) contamination during drilling, (c) contamination of surface water runoff seeping from the ground surface down the cement grout and well bore interface,(1) or (d) natural radioactivity from the rock.

Dissolved organic carbon was found in all trench waters except in trench 22 and ranged in concentration from 7.4 mg/L to 6,000 mg/L. Analyses for DOC in the on-site well waters were performed prior to the present study by USGS laboratories. The values obtained from samples taken March 2, 1977, and April 26, 1977, are given in Table 4.4.

The concentrations of gamma-ray emitting radionuclides identified in trench water samples are given in Table 4.5. Cobalt-60 was found in most trench waters; cesium-134, cesium-137 and americium-241 were found in many samples; manganese-54 and sodium-22 were found in a few samples. No gamma-ray emitting radionuclides were detected in any of the five on-site well samples or in the ten off-site water samples collected.

The pH, specific conductance, DOC, tritium, gross alpha, gross beta, and gross gamma data from Tables 4.3 and 4.4 are presented in Figure 4.3 showing the distribution of these measurements among the trenches. The bar graphs list the trench numbers that fall within ranges of these measurements.

Based on the data obtained from this survey of the Maxey Flats, Kentucky, disposal site, trenches 2, 19, 26, 27, 32, 33L-4, 33L-18, and 37 have been identified for further studies. These trenches represent extreme and average values of the parameters measured in this study. The final selection of trenches for sampling will depend upon availability of water in the trenches, location of new monitoring wells at the disposal site, and local ground water flow paths.

Table 4.4

Radionuclide and DOC Concentrations in Water Samples Taken From Maxey Flats, Kentucky, Disposal Site and Vicinity, Survey Study 1977

Sampling Location	Gross Alpha (pCi/L)	Gross Beta (pCi/L)	Tritium (pCi/L)	Gross Gamma[a] (counts/min)	DOC (mg/L)
Trench 1	1.4 E3 (41)[b]	1.2 E4 (17)	3.7 E6 (3.5)	<1 E1	1.0 E2
Trench 2	6.4 E3 (17)	3.4 E4 (15)	1.9 E7 (1.6)	1.2 E2	5.0 E1
Trench 3	5 E2 (69)	2.8 E4 (9.7)	1.3 E7 (1.9)	<1 E1	2.6 E2
Trench 5S	4.8 E5 (2.2)	5.7 E7 (<1)	1.5 E8 (<1)	1.6 E4	3.6 E2
Trench 7	7.4 E4 (5.8)	8.8 E6 (<1)	3.6 E8 (<1)	3.0 E3	3.2 E2
Trench 8	1.4 E3 (41)	8.9 E4 (5.3)	6.4 E5 (8.4)	7.4 E2	6.0 E3
Trench 9L	<2 E2	2.3 E3 (44)	7.9 E5 (7.6)	<1 E1	2.5 E2
Trench 14L	7 E2 (59)	2.4 E4 (10)	2.5 E5 (13)	<1 E1	7.4 E0
Trench 17L	1.5 E4 (12)	3.2 E6 (<1)	8.9 E6 (2.3)	1.0 E3	5.6 E3
Trench 18	1.6 E3 (35)	1.6 E5 (3.4)	4.5 E8 (<1)	1.9 E2	4.6 E2
Trench 19S	1.8 E5 (3.6)	9.6 E5 (2.2)	8.4 E7 (<1)	2.8 E2	4.0 E2
Trench 22	<2 E2	3.3 E3 (33)	1.8 E6 (5.1)	1.1 E1	<1 E0
Trench 23	9.3 E4 (5.2)	2.0 E5 (4.7)	1.0 E9 (<1)	2.6 E2	8.0 E2
Trench 24	1.2 E4 (15)	4.6 E5 (2.3)	1.9 E8 (<1)	1.4 E2	1.1 E3
Trench 25	6 E2 (62)	5 E3 (35)	8.0 E8 (<1)	<1 E1	9.6 E2
Trench 26	2.8 E4 (8.5)	1.1 E5 (5.7)	1.1 E8 (<1)	5.9 E1	6.8 E2
Trench 27	8.6 E4 (5.3)	5.7 E5 (2.3)	4.8 E9 (<1)	4.3 E2	7.0 E2
Trench 30	3.7 E3 (25)	2.7 E5 (2.9)	7.4 E9 (<1)	6.8 E2	3.5 E2
Trench 31E	2.3 E4 (10)	5.8 E4 (8.8)	4.8 E8 (<1)	7.0 E1	1.7 E3
Trench 31W	9.3 E3 (16)	1.3 E5 (4.8)	4.7 E9 (<1)	2.2 E2	7.0 E2
Trench 32	2.8 E4 (9.5)	1.3 E6 (<1)	1.9 E9 (<1)	3.9 E2	8.9 E2
Trench 33L-1	<2 E2	3 E3 (38)	3.7 E6 (3.5)	<1 E1	6.2 E1
Trench 33L-3	1.2 E4 (13)	1.7 E5 (3.8)	4.6 E7 (1.0)	9.0 E2	4.5 E3
Trench 33L-4	3.9 E3 (24)	6.7 E4 (6.4)	5.9 E7 (1.3)	2.5 E1	1.7 E3
Trench 33L-6	<2 E2	7.9 E3 (21)	7.4 E6 (2.5)	<1 E1	8.6 E2
Trench 33L-8	1.5 E3 (40)	2 E3 (90)	1.3 E6 (5.1)	2.2 E1	3.9 E1
Trench 33L-9	1.8 E4 (11)	2.8 E4 (15)	2.6 E7 (1.3)	5.3 E1	4.1 E3
Trench 33L-10	<2 E2	6.8 E3 (22)	7.4 E5 (7.8)	<1 E1	4.3 E1
Trench 33L-11	<2 E2	3.2 E3 (36)	2.2 E7 (1.4)	<1 E1	4.4 E2
Trench 33L-12	6 E2 (63)	1.1 E4 (16)	2.4 E7 (1.3)	4.7 E2	5.7 E1
Trench 33L-13	<2 E2	4.2 E3 (32)	5.7 E5 (8.9)	<1 E1	2.7 E1
Trench 33L-16	4 E2 (72)	6.7 E4 (5.8)	1.3 E8 (<1)	<1 E1	1.0 E3
Trench 33L-17	1.9 E3 (36)	7.1 E3 (24)	1.4 E7 (2.6)	<1 E1	3.2 E2
Trench 33L-18	6.4 E5 (1.8)	1.6 E5 (13)	5.0 E7 (<1)	6.6 E2	5.8 E3
Trench 34-1	1.1 E4 (15)	1.8 E6 (1.5)	1.9 E6 (4.9)	6.7 E2	2.5 E1
Trench 34-4	3.9 E3 (24)	2.8 E5 (2.8)	9.9 E6 (2.2)	1.7 E3	2.5 E1
Trench 35	3.5 E3 (24)	3.7 E4 (8.8)	2.4 E9 (<1)	<1 E1	8.1 E2

Table 4.4, continued

Radionuclide and DOC Concentrations in Water Samples Taken
From Maxey Flats, Kentucky, Disposal Site and Vicinity, Survey Study 1977

Sampling Location	Gross Alpha (pCi/L)	Gross Beta (pCi/L)	Tritium (pCi/L)	Gross Gamma[a] (counts/min)	DOC (mg/L)
Trench 36E	5.7 E3 (18)	1.0 E4 (24)	5.3 E8 (<1)	<1 E1	1.1 E2
Trench 36W	9.5 E3 (15)	2.8 E4 (12)	5.1 E7 (<1)	8.7 E1	2.9 E2
Trench 37	8.2 E3 (17)	9.4 E4 (5.5)	9.8 E6 (2.2)	2.9 E2	3.0 E3
Trench 38	1.3 E3 (39)	1.9 E4 (12)	3.3 E7 (1.2)	2.5 E1	1.7 E2
Trench 39	<2 E2	4.1 E3 (29)	7.5 E5 (7.8)	<1 E1	1.7 E1
Trench 40N	1.3 E4 (13)	3.4 E5 (2.7)	6.6 E8 (<1)	1.0 E3	4.4 E2
Trench 42	4 E2 (80)	3.0 E4 (9.1)	1.6 E7 (1.7)	3.4 E1	3.3 E2
Trench 44N	8.8 E3 (17)	1.0 E6 (1.6)	1.0 E8 (<1)	6.2 E3	3.0 E3
Trench 44S	8 E2 (55)	2.0 E3 (58)	1.4 E7 (1.8)	2.1 E1	5.6 E1
Well 5E	<6 E0	<3 E1	1.8 E3 (4.0)	<1 E1	3.3, 3.1[c]
Well 8E	6 E1 (33)	2.1 E2 (25)	1.4 E4 (18)	<1 E1	3.5, 5.3[c]
Well 12E	5 E1 (36)	1.8 E2 (29)	1.8 E4 (15)	<1 E1	6.0, 2.7[c]
Well 13E	<6 E0	<3 E1	6.1 E6 (<1)	<1 E1	13, 13[c]
Well 14E	<6 E0	<3 E1	2.4 E4 (12)	<1 E1	2.2, 2.7[c]
#1[d]	<1 E1	<4 E1	8.6 E3 (17)	<1 E1	2.9 E0
#2	<1 E1	<4 E1	2.2 E4 (13)	<1 E1	4.2 E0
#3	<1 E1	<4 E1	2.4 E4 (12)	<1 E1	<3.5 E0
#4	<1 E1	<4 E1	2.3 E4 (12)	<1 E1	1.8 E0
#5	<1 E1	<4 E1	1.4 E4 (15)	<1 E1	<1 E0
#6	<1 E1	8 E1 (63)	1.5 E4 (14)	<1 E1	1.3 E0
#7	<1 E1	1.3 E2 (63)	2.9 E4 (11)	<1 E1	<2 E0
#8	<1 E1	1.7 E2 (38)	3.8 E4 (10)	<1 E1	3.3 E0
#9	<1 E1	<4 E1	2.0 E4 (13)	<1 E1	<1.5 E0
#10	<1 E1	<4 E1	1.4 E4 (15)	<1 E1	<2 E0

[a] Relative counting rate.

[b] Number in ( ) = 2σ percent counting uncertainty.

[c] DOC analyses performed by USGS on samples taken 3/2/77 and 4/26/77.

[d] Sampling location numbers (#1-#10) correspond to locations in Figure 4.2 as described in Table 4.1.

Table 4.5

Concentration of Gamma-Ray Emitting Radionuclides in Water Samples Taken From Maxey Flats, Kentucky, Disposal Site, Survey Study 1977

Sampling Location	^{241}Am (pCi/L)	^{134}Cs (pCi/L)	^{137}Cs (pCi/L)	^{60}Co (pCi/L)
Trench 1	<1.7 E2	<1.3 E2	<1.9 E2	<2.7 E2
Trench 2	4.7 E3 (6.2)[a]	<1.7 E2	<2.3 E2	1.9 E4 (3.1)
Trench 3	<1.9 E2	<1.4 E2	<2.0 E2	1.9 E3 (12)
Trench 5S	<1.7 E2	<2.2 E2	<2.9 E2	9 E2 (24)
Trench 7	<6.7 E2	<2.5 E2	3.3 E3 (12)	8.5 E4 (1.4)
Trench 8	<2.7 E2	<2.6 E2	9 E2 (29)	1.2 E5 (1.2)
Trench 9L	<4.0 E1	<1.6 E1	<2.0 E1	<2.0 E1
Trench 14L	<1.7 E2	<1.4 E2	<1.7 E2	<1.6 E2
Trench 17L	<1.9 E2	<1.2 E2	<1.5 E2	<1.5 E2
Trench 18	<2.2 E2	<1.6 E2	4.8 E3 (6.8)	2.3 E4 (2.8)
Trench 19S	<2.8 E2	<1.2 E2	4.6 E3 (5.2)	1.3 E3 (13)
Trench 22	<1.8 E2	<1.2 E2	<1.7 E2	1.5 E3 (13)
Trench 23	<1.8 E2	<1.1 E2	<1.6 E2	<1.6 E2
Trench 24	9 E2 (34)	<1.4 E2	4.3 E2 (19)	1.2 E3 (15)
Trench 25	<1.7 E2	<1.3 E2	3.8 E2 (15)	<1.2 E2
Trench 26[b]	1.0 E3 (9.5)	7 E1 (29)	4.4 E3 (2.0)	4.6 E2 (8.6)
Trench 27[c]	2.7 E3 (10)	5.7 E2 (16)	5.6 E3 (2.1)	1.3 E4 (1.4)
Trench 30	<2.8 E2	<2.9 E2	9.2 E4 (1.1)	3.0 E4 (2.4)
Trench 31E	3 E2 (62)	<1.4 E2	7.6 E3 (4.0)	3.6 E3 (7.7)
Trench 31W	7 E2 (23)	9.9 E2 (6.1)	4.0 E4 (<1)	1.9 E2 (13)
Trench 32	<3.0 E2	<1.6 E2	4.2 E3 (5.7)	2.2 E3 (13)
Trench 33L-1	<1.7 E2	<1.2 E2	<1.3 E2	1.5 E3 (4.2)
Trench 33L-3	1.8 E3 (17)	3.3 E3 (18)	4.6 E4 (1.7)	9.7 E4 (1.4)
Trench 33L-4[d]	2 E2 (47)	<1.0 E2	<2.0 E1	<1.8 E2
Trench 33L-6	<1.5 E2	<1.0 E2	<1.2 E2	3.7 E2 (8.5)
Trench 33L-8	<1.9 E2	<1.7 E2	<2.2 E2	5.5 E3 (2.2)
Trench 33L-9	<1.7 E2	<1.4 E2	2.8 E3 (7.6)	1.9 E3 (13)
Trench 33L-10	<1.5 E2	<1.2 E2	<1.7 E2	1.1 E3 (14)
Trench 33L-11	<1.5 E2	<1.2 E2	<1.8 E2	1.0 E3 (19)
Trench 33L-12	<1.9 E2	<1.8 E2	<2.5 E2	3.4 E4 (2.4)
Trench 33L-13	<4.1 E1	<1.8 E1	<2.1 E1	1.3 E3 (4.5)
Trench 33L-16	<5.4 E1	<1.6 E1	<1.8 E1	<2.5 E1
Trench 33L-17	<1.5 E2	<1.1 E2	<1.8 E2	1.3 E3 (16)
Trench 33L-18	4.7 E3 (10)	2.6 E3 (12)	3.6 E4 (1.8)	8.3 E3 (5.0)
Trench 34-1	<3.4 E2	1.6 E3 (21)	2.8 E4 (2.0)	1.0 E4 (4.3)
Trench 34-4	<3.6 E2	<3.9 E2	<5.2 E2	2.7 E5 (<1)
Trench 35	2.4 E2 (33)	<1.7 E2	5.1 E2 (12)	<2.9 E2

Table 4.5, continued

Concentration of Gamma-Ray Emitting Radionuclides in Water Samples Taken From Maxey Flats, Kentucky, Disposal Site, Survey Study 1977

Sampling Location	^{241}Am (pCi/L)	^{134}Cs (pCi/L)	^{137}Cs (pCi/L)	^{60}Co (pCi/L)
Trench 36E	<1.7 E2	<1.3 E2	<2.0 E2	1.4 E3 (16)
Trench 36W[e]	<1.8 E2	3 E2 (90)	6.7 E3 (4.2)	2.4 E3 (11)
Trench 37[f]	9.3 E3 (4.0)	8 E2 (46)	4.1 E3 (6.9)	3.5 E4 (2.2)
Trench 38[g]	5 E2 (57)	<1.3 E2	1.8 E3 (10)	1.8 E3 (12)
Trench 39	<4.1 E1	<1.5 E1	2.6 E2 (18)	<1.9 E1
Trench 40N	<3.2 E2	2.2 E4 (2.8)	1.7 E5 (<1)	2.8 E3 (11)
Trench 42[h]	<1.6 E2	<1.2 E2	<1.8 E2	2.8 E3 (9.2)
Trench 44N[i]	<6.4 E2	7 E3 (32)	1.5 E4 (7.2)	8.4 E5 (<1)
Trench 44S[j]	<4.1 E1	<1.8 E1	<2.7 E1	4.7 E2 (7.8)
Well 5E[k]	<3.9 E1	<1.6 E1	<1.8 E1	<1.8 E1
Well 8E[k]	<3.9 E1	<1.6 E1	<1.8 E1	<1.8 E1
Well 12E[k]	<3.9 E1	<1.6 E1	<1.8 E1	<1.8 E1
Well 13E[k]	<3.9 E1	<1.6 E1	<1.8 E1	<1.8 E1
Well 14E[k]	<3.9 E1	<1.6 E1	<1.8 E1	<1.8 E1

[a] Number in ( ) = 2σ percent counting uncertainty.
[b] ^{22}Na in trench 26 = 1.3 E2 (21).
[c] ^{54}Mn in trench 27 = 3 E2 (34).
[d] ^{22}Na in trench 33L-4 = 1.3 E2 (20).
[e] ^{54}Mn in trench 36W = 2.1 E3 (14).
[f] ^{54}Mn in trench 37 = 1.8 E3 (26).
[g] ^{54}Mn in trench 38 = 9 E2 (28).
[h] ^{54}Mn in trench 42 = 6 E2 (33).
[i] ^{54}Mn in trench 44N = 1.9 E5 (1.3).
[j] ^{54}Mn in trench 44S = 1.7 E2 (24).
[k] Minimum detectable level < 1.7 E1 for ^{22}Na and ^{54}Mn.

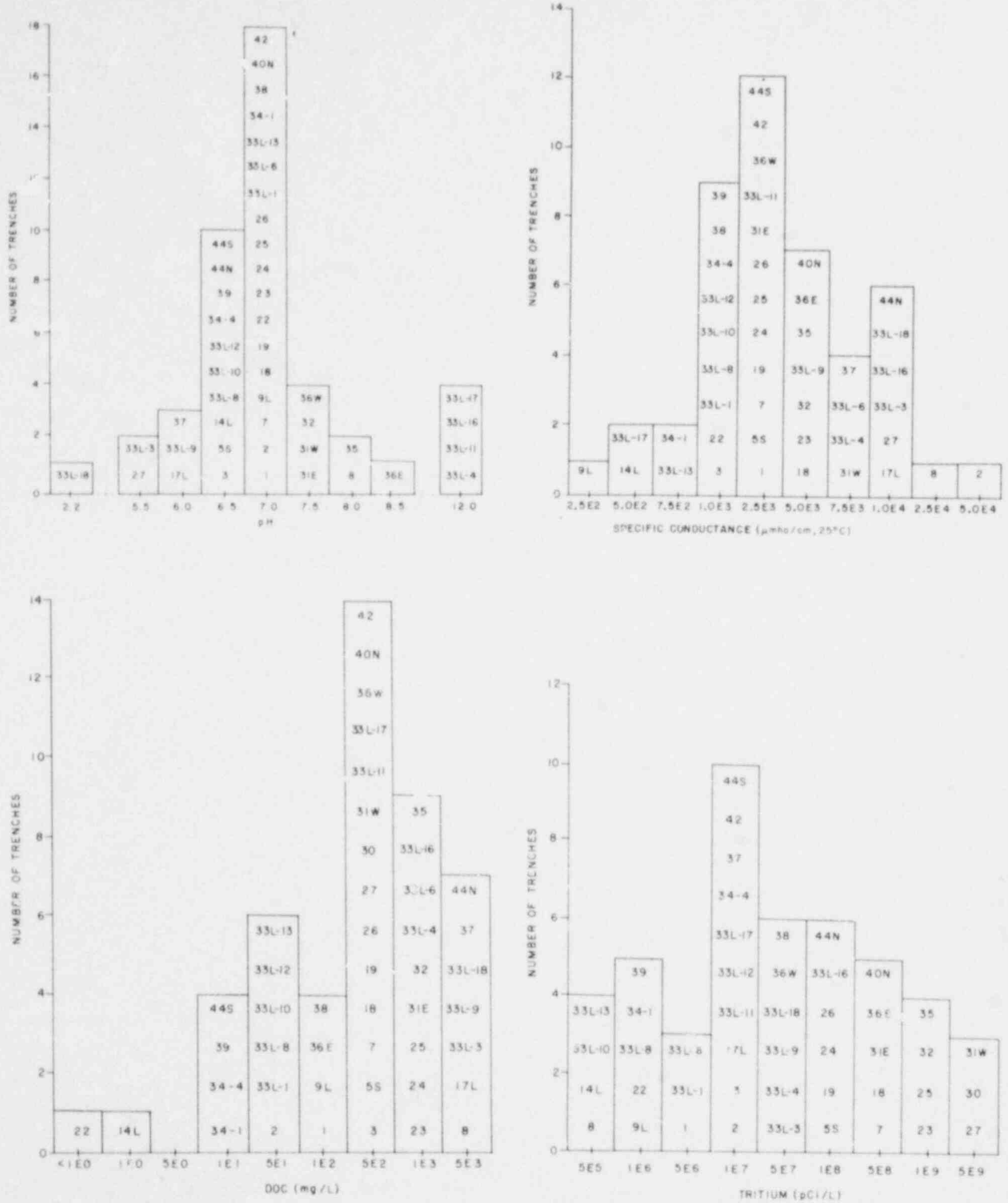
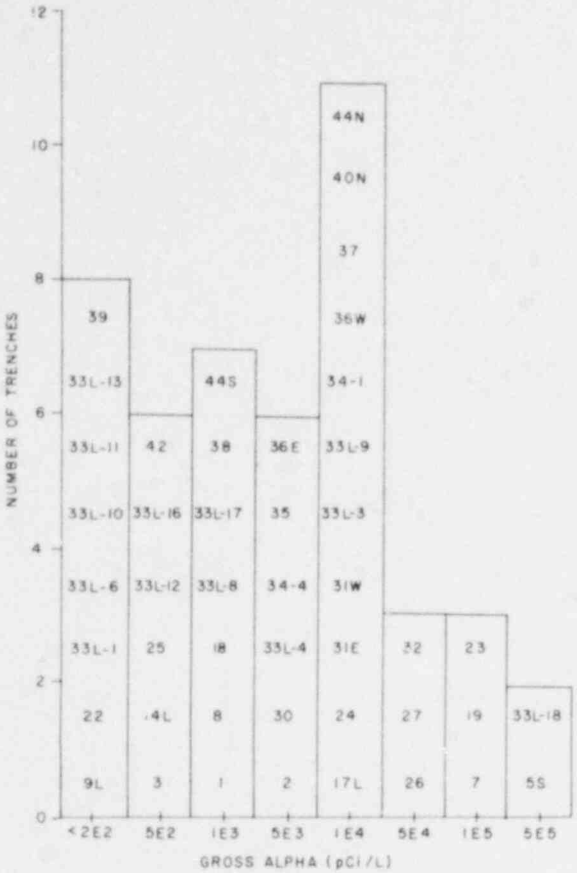


Figure 4.3 (on this and facing page). Distribution of pH, specific conductance, DOC, tritium, gross alpha, gross beta, and gross gamma among trench waters taken from Maxey Flats, Kentucky, disposal site (1977).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10
8
6
4
2
0
NUMBER OF TRENCHES
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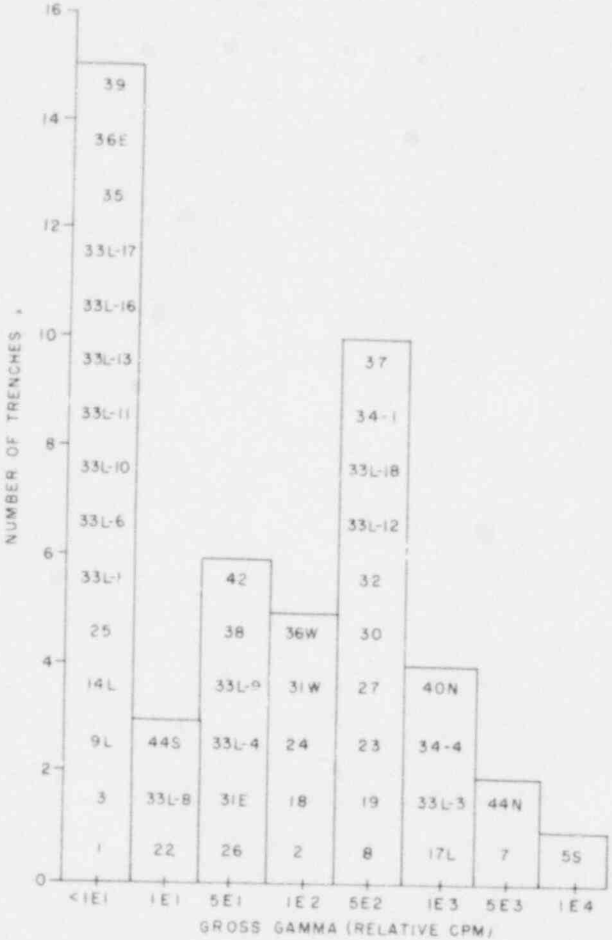
33L-11
33L-10
33L-6
33L-1
22
9L
42
33L-16
33L-12
25
14L
3
44S
38
33L-17
33L-8
18
8
1
36E
35
34-4
33L-4
30
2
44N
40N
37
36W
34-1
33L-9
33L-3
31W
31E
24
17L
32
27
26
23
19
7
33L-18
5S
<2E2
5E2
1E3
5E3
1E4
5E4
1E5
5E5
GROSS ALPHA (pCi/L)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14
12
10
8
6
4
2
0
NUMBER OF TRENCHES
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36E
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33L-17
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33L-10
33L-6
33L-1
25
14L
9L
3
1
44S
33L-8
22
42
38
33L-9
33L-4
31E
26
36W
31W
24
18
2
37
34-1
33L-18
33L-12
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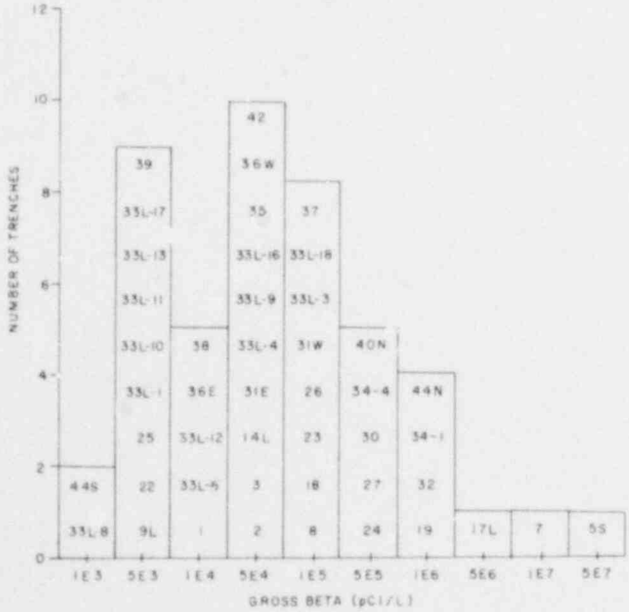
19
8
40N
34-4
33L-3
17L
44N
7
5S
<1E1
1E1
5E1
1E2
5E2
1E3
5E3
1E4
GROSS GAMMA (RELATIVE CPM)


12
10
8
6
4
2
0
NUMBER OF TRENCHES
44S
33L-8
39
33L-17
33L-13
33L-11
33L-10
33L-1
25
22
9L
38
36E
33L-12
33L-5
1
42
36W
35
33L-16
33L-9
33L-4
31E
14L
3
2
37
33L-18
33L-3
31W
26
23
18
8
40N
34-4
30
27
24
44N
34-1
32
19
17L
7
5S
1E3
5E3
1E4
5E4
1E5
5E5
1E6
5E6
1E7
5E7
GROSS BETA (pCi/L)

4.5 West Valley, New York, Site

4.5.1 Collection

Water samples were collected from 13 trench locations and 3 wells at the West Valley, New York, disposal site during June and July 1977. The locations of trenches and wells at the West Valley low-level disposal site are shown in Figure 4.4(2) with a description of the sampling points given in Table 4.6.

Table 4.6

Description of Sampling Points at West Valley, New York, Disposal Site, Survey Study 1977

Sampling Point[a]	Description
Trench 1	NFS/1975
Trench 2	NYGS/2-1A
Trench 3	8" Sump
Trench 4	NYGS/4-1A
Trench 5	8" Sump
Trench 8	NYGS/8-1B
Trench 9	New 6" Sump
Trench 10N	New 6" Sump
Trench 11	NYGS/11-1A
Trench 12	8" Sump
Trench 13	6" Sump
Trench 14	NYGS/14-1A
Trench 2	New Sump - samples taken after 1 hr, 7 hrs, and 24 hours of pumping
Well C2-1	USGS test hole, 15 feet from NW corner of trench 4
Well B-2	USGS test hole, 10 feet from north end of trench 2
Well D-1	USGS test hole, 8 feet from west side of trench 5

[a] Sampling points correspond to positions indicated in Figure 4.4.

Seven water samples from wells and streams outside of the disposal site were also taken. Figure 4.6 shows the approximate location of the off-site sampling positions in relation to the trench area at the disposal site. The numbers adjacent to the arrows in Figure 4.6 correspond to sampling locations described in Table 4.7.

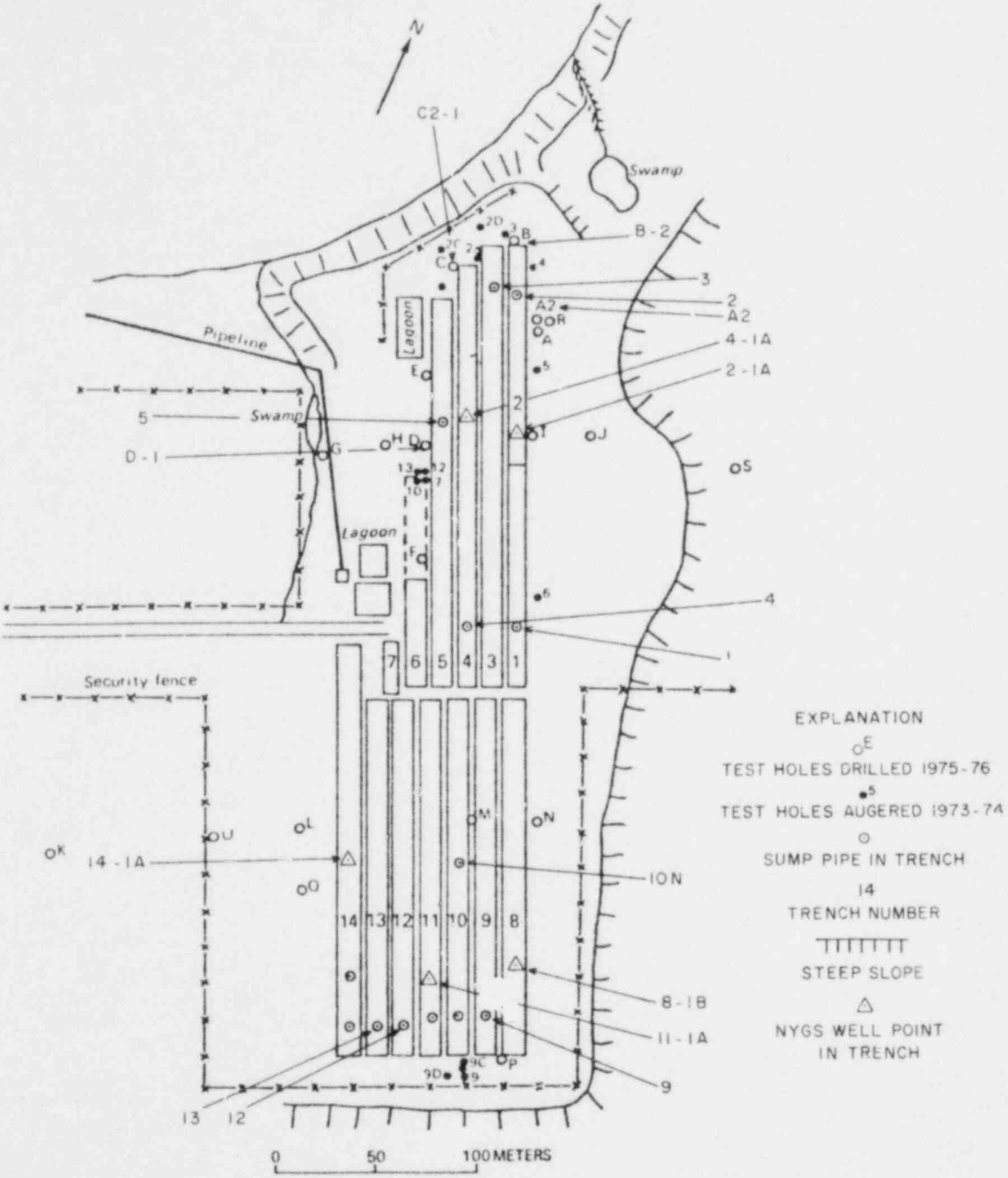


Figure 4.4. Sketch of the West Valley, New York, radioactive waste disposal site indicating sampling points (updated from sketch by USGS).(2)

Table 4.7

Sampling Locations in the Vicinity of West Valley, New York, Disposal Site, Survey Study 1977

Sampling Position[a]	Location/Description
#1	Well PAH-1: USGS test hole, 1200 feet south of burial ground; water enters iron casing from gravel layer 19-23 feet beneath till.
#2	Spring near PAH-16: 900 feet NE of burial ground, across Erdman Brook, 80 feet inside site security fence.
#3	Erdman Brook Upstream: Immediately upstream from RR track, south of site security fence.
#4	Erdman Brook at Gage: Waterfall above plunge pool at USGS gage.
#5	Buttermilk Creek at BM Road: Riffle approximately 100 feet upstream from abandoned bridge on Buttermilk Road.
#6	Buttermilk Creek at Thomas Corners Road: Riffle approximately 300 feet upstream from bridge on Thomas Corners Road.
#7	Ehmke Well: Unused flowing 10 inch well on Rock Springs Road, 1 mile south of burial ground.

[a] Position numbers correspond to location indicated in Figure 4.5.

All samples were obtained with new plastic tubing except well D-1 where the same tubing from well B-2 was used. During the filtration of samples for DOC analyses, it was discovered that the filtration assembly was not operating properly; and that some part of the sample may have by-passed the silver filter. Samples that are suspect are from trenches 3, 4, 5, 10, 11, 12, 14, and from well D-1, well PAH-1, and spring near PAH-16. It should be assumed that the organic carbon values reported in these trenches are total organic carbon instead of DOC.

4.5.2 Results

The ranges of pH, specific conductance, DOC, gross alpha, gross beta, gross gamma, and tritium measured in the trench water samples taken from the disposal site are shown in Table 4.8.

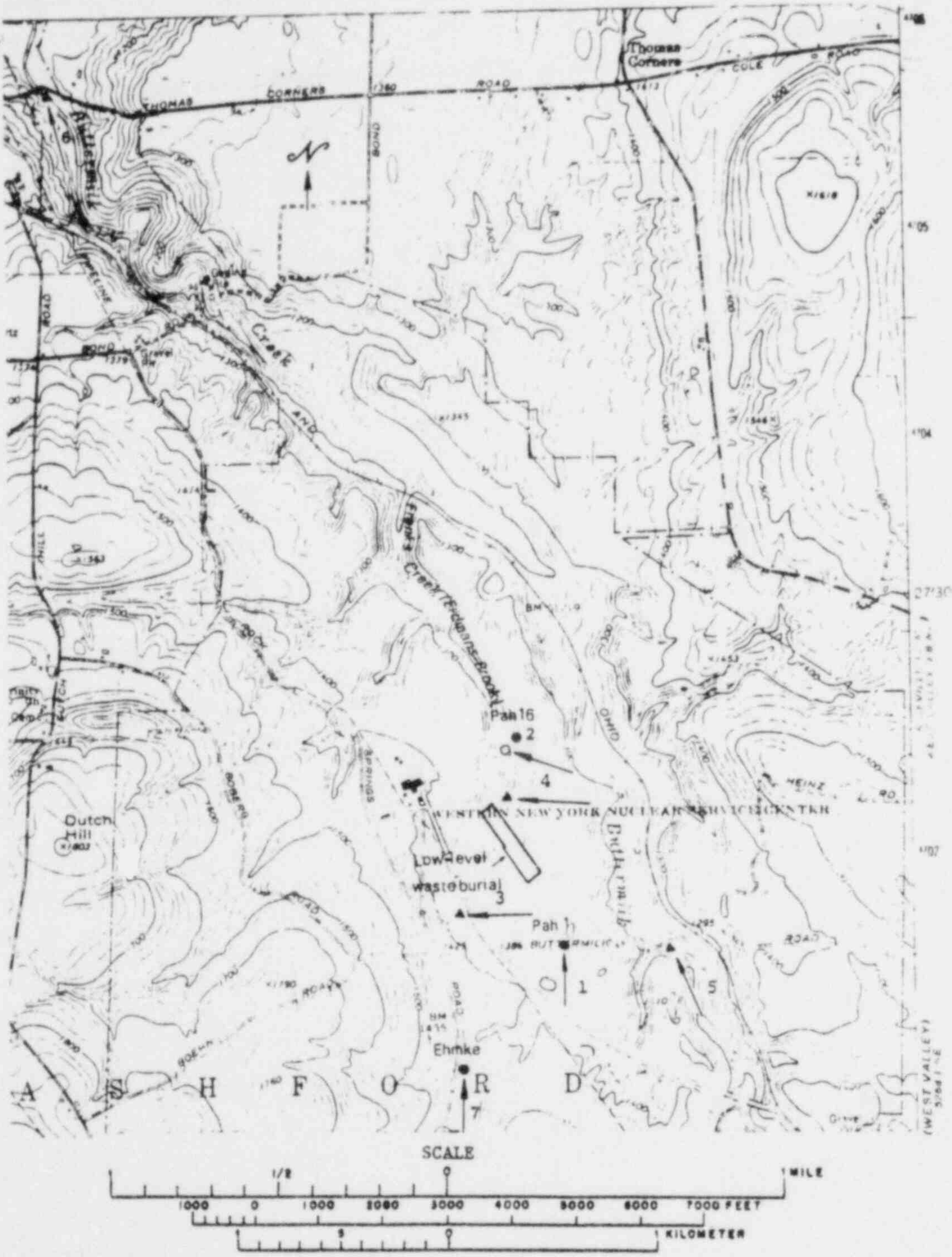


Figure 4.5. Approximate sampling locations near the West Valley, New York, disposal site (Ashford Hollow, New York, 1964, Base from USGS, obtained from D. Prudic).

Table 4.8

Ranges of Measurements of Water Samples Taken From West Valley, New York, Disposal Site, Survey Study 1977

Measurement	Range
pH	6.5 - 11.1
Specific conductance (μmho/cm at 25°C)	1.5 E3 - 1.7 E4
DOC (mg/L)	2.7 E2 - 4.9 E3
Gross alpha (pCi/L)	<2 E2 - 2.9 E6
Gross beta (pCi/L)	9.1 E4 - 3.1 E7
Gross gamma (relative counts/min)	<1 E1 - 7.3 E3
Tritium (pCi/L)	2.2 E5 - 5.6 E9

Field measurements of pH, temperature, and specific conductance of water samples taken from the disposal site and vicinity are given in Table 4.9. These measurements were generally made soon after collecting a sample. Since the water temperature was not measured in-line, the values should not be taken as the actual ground water temperature. The pH of the trench water samples ranged from 6.5-9.4, which is narrower than the pH range of 2.2-12.4 found at Maxey Flats. Water from well C2-1 has a pH of 11.1. This is probably a consequence of the well construction where the piezometer was set in a sand envelope and covered with cement grout.(2) In a well where there is little water movement, the hydrated cement contaminates the water resulting in an elevated pH. Because the till at West Valley is poorly permeable, the grout-contaminated water was not diluted by ground water adjacent to the well boring. The pH of the off-site water samples are in a range between 6.8 and 8.3.

Values of specific conductance of trench waters ranged from 1,500 to 17,000 μmho/cm at 25°C. Since specific conductance is related to the amount of dissolved solids in the water, any iron hydroxide that precipitated before making the measurement would have caused a reduction of the measured value. Specific conductance of the off-site waters are in a narrow range between 150 and 520 μmho/cm at 25°C and are between one and two orders of magnitude lower than the trench waters.

Radionuclide and DOC concentrations of trench, on-site well, and off-site water samples are given in Table 4.10. Gross alpha, gross beta, and tritium concentrations are given in pCi/L; gross gamma is reported as relative counts/min above laboratory background. Tritium is present in all trenches and on-site wells, and in nearly all the off-site samples. The highest tritium levels were found in trenches 8 and 10 with concentrations of 4.0x10^9 pCi/L and 5.6x10^9 pCi/L respectively. Gross beta was found in all trench samples and gross alpha was found in most trenches. Organic carbon was found in all on-site samples.

The concentrations of gamma-ray emitting radionuclides in trench water samples from the West Valley site are given in Table 4.11. Cobalt-60, cesium-134, and cesium-137 were found in many trench waters, while americium-241, sodium-22, and manganese-54 were found in only a few samples. No gamma-ray emitting radionuclides were detected in any of the on-site well samples or in the seven off-site water samples collected. The minimum detectable levels for off-site water samples are the same as the well samples given in Table 4.11.

Based on the data obtained from this survey of the West Valley, New York, disposal site, trenches 3, 4, 5, 8, 9, and 11 have been identified as candidates for further studies. The final selection will depend upon availability of water in the trenches, location of monitoring wells at the disposal site, and local ground water flow paths.

Table 4.9

Field Measurements of Water Samples Taken From West Valley, New York, Disposal Site and Vicinity, Survey Study 1977

Sampling[a] Location	Date Sampled	pH	Temperature (^{o}C)	Specific Conductance (μmho/cm at $25^{o}C$)
Trench 1	6/21/77	6.49	13.4	6.25 E3
Trench 2	6/21/77	7.16	15.5	6.60 E3
Trench 3	6/22/77	7.15	13.2	8.60 E3
Trench 4	6/22/77	6.89	14.1	1.71 E4
Trench 5	6/22/77	6.85	12.6	6.95 E3
Trench 8	7/27/77	6.82	11.7	8.10 E3
Trench 9	7/28/77	6.79	13.2	3.72 E3
Trench 10N	7/27/77	6.77	13.0	5.95 E3
Trench 11	6/23/77	9.35	16.0	1.53 E3
Trench 12	6/23/77	6.77	14.5	8.44 E3
Trench 13	6/23/77	6.71	13.9	1.26 E4
Trench 14	6/23/77	7.14	12.2	3.22 E3
Trench 2 New Sump				
1 hr	7/27/77	7.27	11.2	7.95 E3
7 hr	7/27/77	7.19	10.0	8.05 E3
24 hr	7/28/77	7.20	11.0	7.90 E3
Well C2-1	6/21/77	11.1	16.2	9.48 E2
Well B-2	6/22/77	7.90	12.6	4.90 E2
Well D-1	6/23/77	7.96	12.8	8.70 E2
#1 Well PAH-1	6/24/77	7.02	10.8	5.16 E2
#2 "Spring" near PAH 16	6/24/77	6.80	16.7	1.54 E2
#3 Erdman Brook Upstream	7/28/77	6.96	16.9	2.94 E2
#4 Erdman Brook at Gage	7/29/77	7.37	18.0	3.08 E2
#5 Buttermilk Creek at BM Road	7/29/77	8.25	20.4	2.97 E2
#6 Buttermilk Creek at Thomas Corner	7/29/77	8.29	22.0	3.12 E2
#7 Ehmke Well	7/29/77	7.44	10.2	4.95 E2

[a] Sampling locations correspond to positions indicated in Figures 4.4 and 4.5.

Table 4.10

Radionuclide and DOC Concentrations in Water Samples Taken From West Valley, New York, Disposal Site and Vicinity, Survey Study 1977

Sampling Location	Gross Alpha (pCi/L)	Gross Beta (pCi/L)	Tritium (pCi/L)	Gross Gamma[a] (counts/min)	DOC (mg/L)
Trench 1	2.2 E4 (11)[b]	9.1 E4 (5.9)	2.2 E5 (14)	1.9 E1	2.6 E3
Trench 2	1.6 E3 (35)	1.5 E5 (4.2)	1.2 E8 (<1)	1.4 E2	2.7 E2
Trench 3	2.0 E4 (10)	4.1 E6 (<1)	4.4 E8 (<1)	1.9 E3	1.6 E3[c]
Trench 4	<2 E2	2.4 E7 (<1)	4.5 E8 (<1)	7.3 E3	6.9 E2[c]
Trench 5	6 E3 (18)	6.5 E5 (1.8)	1.4 E9 (<1)	3.3 E2	2.6 E3[c]
Trench 8	6.3 E4 (4.4)	4.5 E5 (<1)	4.0 E9 (<1)	7.6 E2	3.1 E3
Trench 9	1.1 E3 (9.2)	1.7 E5 (<1)	4.8 E8 (<1)	2.3 E2	1.7 E3
Trench 10N	2.3 E5 (<1)	8.8 E5 (<1)	5.6 E9 (<1)	4.3 E2	2.6 E3[c]
Trench 11	<2 E2	1.4 E5 (4.6)	2.6 E8 (<1)	<1 E1	6.8 E2[c]
Trench 12	1.8 E4 (11)	2.3 E6 (<1)	3.6 E8 (<1)	4.4 E3	4.9 E3[c]
Trench 13	2.9 E6 (<1)	3.1 E7 (<1)	4.8 E7 (<1)	1.7 E2	2.5 E3
Trench 14	8.5 E3 (16)	1.5 E6 (<1)	1.2 E8 (<1)	1.7 E3	1.7 E3[c]
Trench 2 New Sump					
1 hr	1.2 E3 (9.5)	2.0 E5 (<1)	9.5 E7 (<1)	1.6 E2	5.6 E2
7 hrs	9.4 E2 (9.7)	1.7 E5 (<1)	——	1.6 E2	——
24 hrs	1.1 E3 (9.5)	1.8 E5 (<1)	——	1.7 E2	——
Well C2-1	<6 E0	6 E1 (52)	3.4 E4 (11)	——	6.8 E1
Well B-2	<6 E0	<3 E1	3.6 E4 (10)	<1 E1	6.9 E0
Well D-1	2 E1 (70)	6.3 E2 (11)	3.5 E7 (1.2)	<1 E1	2.5 E1[c]
#1[d]	<6 E0	8 E1 (45)	<2 E3	<1 E1	4.0 E1[c]
#2	<6 E0	5 E1 (63)	2.0 E4 (13)	<1 E1	2.2 E0[c]
#3	<6 E0	<3 E1	9.7 E3 (3.6)	<1 E1	1.0 E1
#4	<6 E0	6 E1 (61)	2.2 E4 (13)	<1 E1	7.6 E0
#5	<6 E0	<3 E1	2.0 E4 (2.5)	<1 E1	2.7 E0
#6	<6 E0	<3 E1	1.8 E4 (2.7)	<1 E1	2.3 E0
#7	<6 E0	<3 E1	<2 E3	<1 E1	2.1 E0

[a] Relative counting rate.

[b] Number in ( ) = 2σ percent counting uncertainty.

[c] Filter assembly was not operating properly. Some samples may have by-passed the filter.

[d] Sampling location numbers correspond to locations in Figure 4.4 as described in Table 4.5.

Table 4.11

Concentration of Gamma-Ray Emitting Radionuclides in Water Samples Taken From West Valley, New York, Disposal Site, Survey Study 1977

Sampling[a] Location	^{241}Am (pCi/L)	^{134}Cs (pCi/L)	^{137}Cs (pCi/L)	^{60}Co (pCi/L)
Trench 1	<1.7 E2	<1.1 E2	<1.6 E2	<1.1 E2
Trench 2	<2.1 E2	<1.2 E2	2.4 E4 (2.2)[b]	<1.2 E2
Trench 3	<5.1 E2	<1.9 E2	1.6 E5 (<1)	1.0 E4 (4.5)
Trench 4	<1.1 E3	<1.9 E2	2.6 E4 (2.2)	<1.9 E2
Trench 5[c]	<2.7 E2	2.6 E3 (12)	3.8 E4 (1.7)	3.9 E2 (23)
Trench 8	5.2 E2 (83)	1.4 E3 (26)	1.3 E5 (<1)	<1.8 E2
Trench 9[d]	<2.2 E2	2.7 E3 (12)	4.0 E4 (1.6)	9 E2 (18)
Trench 10N[e]	1.1 E3 (30)	8 E2 (40)	9.9 E3 (3.5)	<1.8 E2
Trench 11	<1.8 E2	<1.3 E2	<2.2 E2	2.7 E3 (10)
Trench 12[f]	<6.1 E2	1.3 E4 (6.0)	9.0 E5 (<1)	6.2 E3 (6.4)
Trench 13[g]	<2.4 E2	6 E2 (49)	4.9 E3 (5.2)	2.8 E3 (10)
Trench 14[h]	<4.2 E2	3.3 E4 (2.2)	2.4 E5 (<1)	1.4 E3 (14)
Trench 2 New Sump				
1 hr	<2.2 E2	<1.3 E2	3.2 E4 (1.8)	5 E2 (24)
7 hrs	<2.2 E2	<1.3 E2	2.9 E4 (1.9)	8 E2 (21)
24 hrs	<2.2 E2	<1.3 E2	2.9 E4 (1.9)	7 E2 (18)
Well C2-1[i]	<3.9 E1	<1.6 E1	<1.8 E1	<1.8 E1
Well B-2[i]	<3.9 E1	<1.6 E1	<1.8 E1	<1.8 E1
Well D-1[i]	<3.9 E1	<1.6 E1	<1.8 E1	<1.8 E1

[a] Sampling dates and location same as in Table 4.9.
[b] Number in ( ) = 2σ percent counting uncertainty.
[c] ^{22}Na in trench 5 = 4 E2 (45).
[d] ^{22}Na in trench 9 = 9 E2 (25).
[e] ^{22}Na in trench 10N = 3.7 E3 (8.7).
[f] ^{22}Na in trench 12 = 1.1 E3 (24); ^{54}Mn = 1.1 E3 (34).
[g] ^{22}Na in trench 13 = 8 E2 (25).
[h] ^{22}Na in trench 14 = 4 E2 (32); ^{54}Mn = 3.1 E3 (34).
[i] Minimum detectable level < 1.7 E1 for ^{22}Na and ^{54}Mn.

4.6 Sheffield, Illinois, Site

4.6.1 Collection

Water samples were collected from 27 test wells at the Sheffield, Illinois, disposal site during June, July, and November 1977. Samples from 8 wells (512, 517, 518, 524, 525, 527, 528, 529) were obtained by peristaltic pumping as described earlier. The other 19 samples were collected with separate copper - brass bailers, each dedicated to a well. Figure 4.6 shows the approximate location of the wells, some of which are adjacent to disposal trenches, and some outside of the trench area. The boundaries of three trench areas are shown with ++++. The "E" and "N" markings on the two axes are State of Illinois coordinates representing 500 feet between coordinates. Due to the absence of accumulated water in the trenches at the site, no trench water samples were obtained for analysis.

4.6.2 Results

The ranges of pH, specific conductance, DOC, gross alpha, gross beta, and tritium measured in the well water samples taken from the disposal site are shown in Table 4.12.

Table 4.12

Ranges of Measurements of Water Samples Taken From Sheffield, Illinois, Disposal Site, Survey Study 1977

Measurement	Range
pH	6.2 - 12.1
Specific conductance (μmho/cm at 25°C)	2.2 E2 - 7.0 E3
DOC (mg/L)	1.2 E1 - 6.6 E3
Gross alpha (pCi/L)[a]	<6 E0 - 1 E1
Gross beta (pCi/L)	<3 E1 - 1.5 E3
Tritium (pCi/L)[b]	<2.4 E2 - 5.9 E3

[a] Gross alpha concentrations in two wells are slightly above background.

[b] Tritium was measured in three wells.

Field measurements of pH, temperature, and specific conductance of the well samples are given in Table 4.13. The pH range of 25 well waters is between 6.2-8.5 which is comparable to well and ground water samples from Maxey Flats and West Valley. However, water from wells 512 and 519 show a pH of

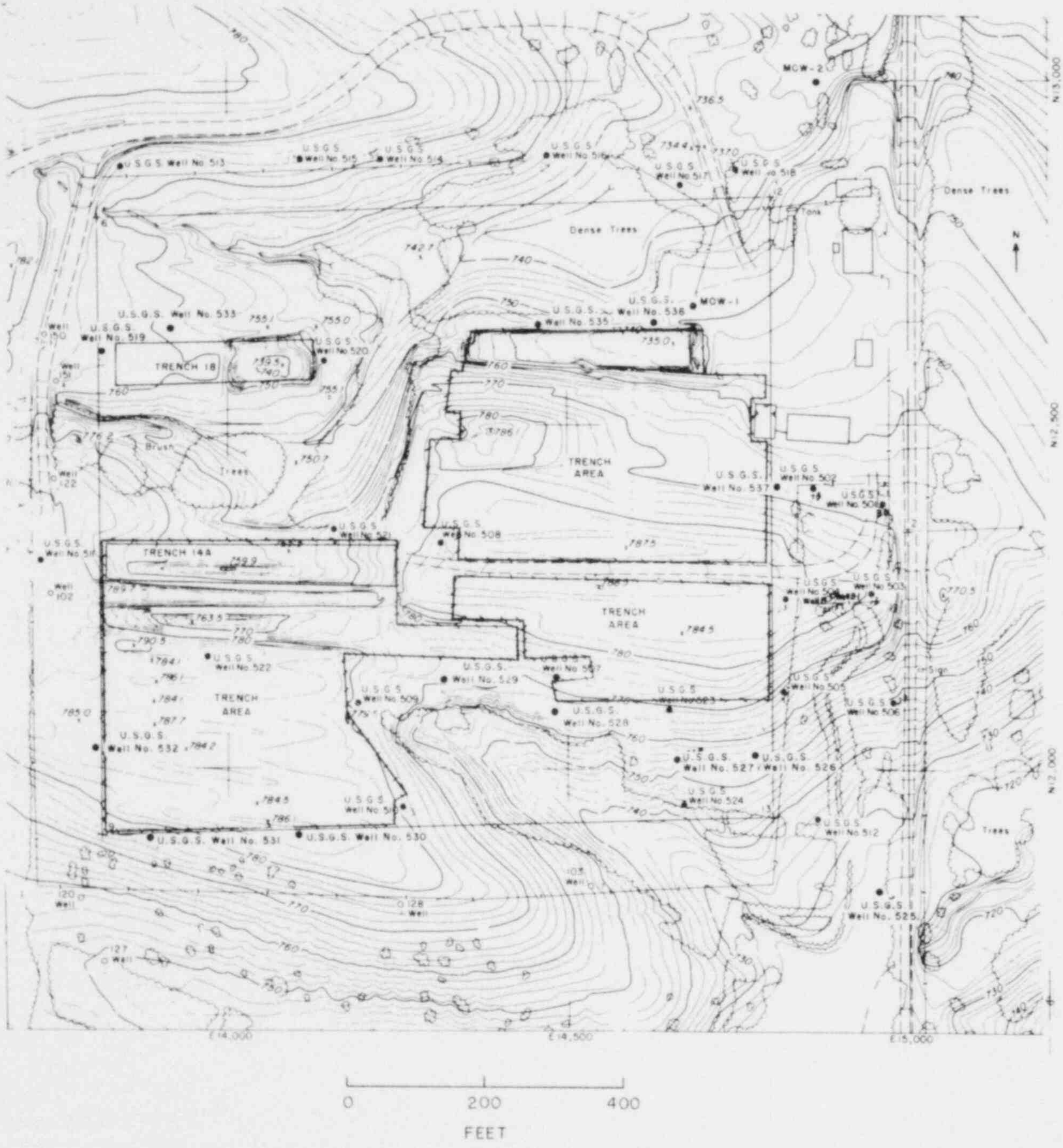


Figure 4.6. Sampling locations of wells at the Sheffield, Illinois, disposal site (adapted from topographical map, USGS, obtained from J. Foster).

Table 4.13

Field Measurements of Water Samples Taken From
Sheffield, Illinois, Disposal Site, Survey Study 1977

Sampling Location[a]	Date Sampled	pH	Temperature (°C)	Specific Conductance (μmho/cm at 25°C)
Well 507	7/8/77	7.0	13.0	1.48 E3
Well 510	6/29/77	8.5	12.0	7.00 E2
Well 511	6/29/77	7.0	17.5	7.65 E2
Well 512	6/29/77	10.8	14.0	5.60 E2
Well 513	6/28/77	7.0	17.0	8.10 E2
Well 515	6/27/77	6.8	20.0	5.20 E2
Well 516	6/27/77	7.1	16.0	5.10 E2
Well 517	6/27/77	7.3	22.0	1.05 E3
Well 518	7/7/77	7.4	17.5	7.25 E2
Well 519	6/28/77	12.1	15.0	7.00 E3
Well 520	6/28/77	6.8	19.0	8.90 E2
Well 521	7/7/77	7.1	15.0	7.20 E2
Well 522	6/28/77	7.1	16.0	6.70 E2
Well 523	7/8/77	6.8	20.0	1.26 E3
Well 524	7/8/77	7.8	18.0	4.55 E2
Well 525	7/8/77	6.3	10.8	7.60 E2
Well 527	11/18/77	7.9	10.4	8.25 E2
Well 528	7/7/77	6.7	20.0	1.24 E3
Well 529	7/7/77	6.9	16.0	9.20 E2
Well 530	7/8/77	7.2	15.0	1.51 E3
Well 531	7/8/77	7.4	13.9	9.00 E2
Well 532	7/8/77	6.9	15.5	1.55 E3
Well 533	7/7/77	7.2	15.0	8.95 E2
Well 535	7/8/77	6.6	12.3	1.21 E3
Well 536	7/8/77	6.2	12.5	1.55 E3
Well MOW-1	7/7/77	7.0	14.5	8.85 E2
Well MOW-2	7/7/77	6.9	13.0	2.24 E2

[a] Sampling locations correspond to positions indicated in Figure 4.6.

10.8 and 12.1 respectively, which may be a result of contamination from cement grout around the well casing. The specific conductance of well 519 is also unusually high for ground water.

Radionuclide and DOC concentrations of these well samples are given in Table 4.14. DOC concentrations ranged from 1.2 E1-6.6 E3 mg/L. The concentrations in most of these wells are higher than in wells at the other sites and are comparable to concentrations normally present in trench waters.[a] Two samples contained alpha activity slightly above background, three samples contained

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[a] The DOC concentrations in well water samples collected in April 1979 (Section 5.3.3.3) showed a decrease of two orders of magnitude.

Table 4.14

Radionuclide and DOC Concentrations in Water Samples Taken From Sheffield, Illinois, Disposal Site, Survey Study 1977

Sampling[a] Location	Gross Alpha[a] (pCi/L)	Gross Beta[a] (pCi/L)	Tritium[b] (pCi/L)	DOC[a] (mg/L)
Well 507	<6 E0	<6 E1	4.8 E3 (8.0)	4.4 E2
Well 510	<6 E0	2.6 E2 (29)[c]	<2.4 E2	1.7 E2
Well 511	<6 E0	<6 E1	<2.4 E2	8.1 E2
Well 512	<6 E0	1 E2 (53)	<2.4 E2	4.8 E1
Well 513	<6 E0	<3 E1	<2.4 E2	1.5 E3
Well 515	<6 E0	<3 E1	<2.4 E2	3.5 E2
Well 516	<6 E0	<3 E1	<2.4 E2	1.5 E2
Well 517	<6 E0	8 E1 (50)	<2.4 E2	1.2 E1
Well 518	<6 E0	6 E1 (65)	<2.4 E2	1.8 E1
Well 519	<6 E0	1.6 E2 (29)	<2.4 E2	5.7 E2
Well 520	<6 E0	2.9 E2 (27)	<2.4 E2	3.4 E2
Well 521	<6 E0	<6 E1	——[d]	1.1 E3
Well 522	<6 E0	<6 E1	<2.4 E2	6.7 E2
Well 523	<6 E0	4.7 E2 (19)	——[d]	6.6 E3
Well 524	<6 E0	<3 E1	<2.4 E2	3.5 E1
Well 525	<6 E0	<6 E1	<2.4 E2	1.4 E3
Well 527[e]	——	——	5.9 E3 (6.1)	——
Well 528	1 E1 (70)	<3 E1	7 E2 (52)	9.6 E2
Well 529	<6 E0	2.9 E2 (27)	<2.4 E2	2.0 E2
Well 530	<6 E0	4 E1 (85)	<2.4 E2	3.3 E3
Well 531	<6 E0	<3 E1	<2.4 E2	1.1 E3
Well 532	<6 E0	6.2 E2 (16)	<2.4 E2	1.8 E3
Well 533	<6 E0	<3 E1	<2.4 E2	8.5 E2
Well 535	8 E0 (77)	6 E1 (58)	<2.4 E2	7.9 E2
Well 536	<6 E0	1.5 E3 (10)	<2.4 E2	4.5 E3
Well MOW I	<6 E0	6 E1 (57)	<2.4 E2	1.1 E3
Well MOW II	<6 E0	<3 E1	<2.4 E2	2.3 E2

[a] Sampling locations and dates same as in Table 4.13.
[b] Sampled 11/18/77.
[c] Number in ( ) = 2σ percent counting uncertainty.
[d] Not sampled.
[e] New well drilled after July 1977.

small amounts of tritium, and beta activity was detected in approximately half the samples. Sample 536, which contained the highest beta activity, did not contain any measurable gamma emitting radionuclides when counted with a Ge(Li) system. Gamma counting was not performed on the other well samples due to the very low alpha and beta activity levels measured.

Any trenches that accumulate sufficient water for sampling will be collected for analyses.

4.7 Barnwell, South Carolina, Site

4.7.1 Collection

Water samples were collected from 6 trenches and 6 wells at the Barnwell, South Carolina, site in February and March 1978. Water is usually not present in the trenches at the Barnwell site, except during the winter rainy season. The location of trenches and wells which were sampled are shown in Figure 4.7. Wells CN-3, WW5, WW6, and WW7 are approximately 30 feet west of the trenches TR-5, TR-6, and TR-7. Well CN-4 is located at the southwest edge of trench TR-8, and well CN-1 is located between the east ends of trenches TR-13 and TR-16. Trench TR-11 is adjacent to and south of trench TR-13. All samples were collected with bailers because the water level was greater than 30 feet below ground level. Tritium concentrations in the wells were measured on unfiltered water samples collected November 1978.

4.7.2 Results

The ranges of pH, specific conductance, DOC, gross alpha, gross beta, and tritium measured in the trench water samples taken from the disposal site are shown in Table 4.15.

Table 4.15

Ranges of Measurements of Water Samples Taken From
Barnwell, South Carolina, Disposal Site, Survey Study 1978

Measurement	Range
pH	5.9 - 6.7
Specific conductance (μmho/cm at 25°C)	4.5 E1 - 1.4 E3
DOC (mg/L)	<1 - 2.8 E2
Gross alpha (pCi/L[a]	6 E1 - 1.0 E3
Gross beta (pCi/L)	3 E2 - 3.6 E3
Tritium (pCi/L)	1.0 E6 - 6.4 E8

[a] Gross alpha found only in trench 7D1.

Field measurements of pH, temperature, and specific conductance of the trench and well samples are given in Table 4.16. The pH of the trench waters ranged from 5.9 to 6.7, whereas the pH of the well waters ranged from 5.9 to 11.4. The probable cause of the high pH in some well samples is contamination from the cement grout used in construction of the wells. Specific conductance of the well waters are comparable to well waters from the other disposal sites.

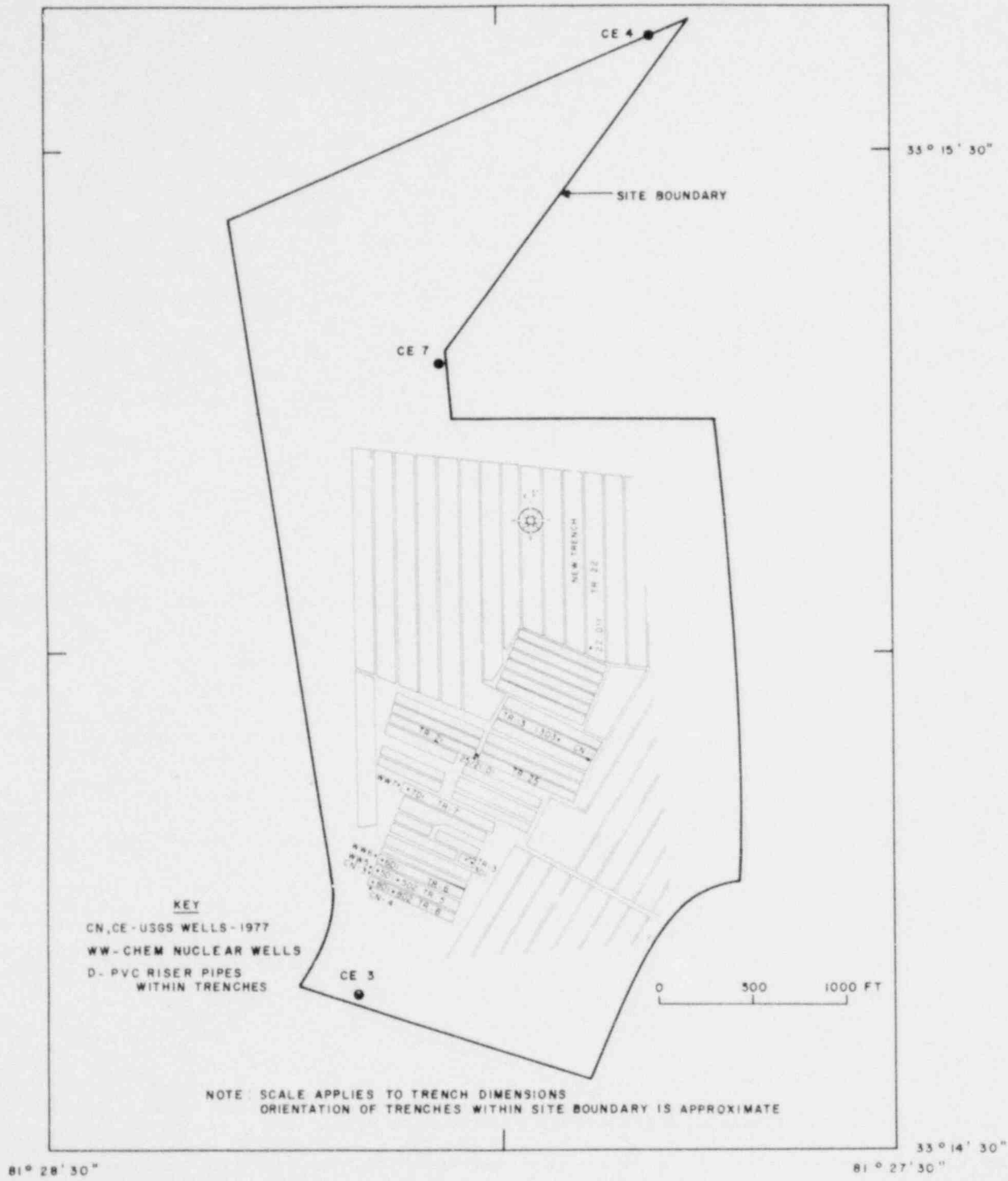

Figure 4.7. Sampling locations of trenches and wells at the Barnwell, South Carolina, waste disposal site (updated from sketch by USGS, obtained from J. Cahill).

Table 4.16

Field Measurements of Water Samples Taken From Barnwell, South Carolina, Disposal Site, Survey Study 1978

Sampling[a] Location	Date Sampled	pH	Temperature (^{o}C)	Specific Conductance (μmho/cm at 25^{o}C)
Trench 5D1	2/22/78	5.9	14	5.80 E2
Trench 6D1	2/22/78	5.9	13	3.60 E2
Trench 7D1	2/23/78	6.5	17	1.37 E3
Trench 8D1	2/22/78	6.3	15	7.50 E2
Trench 13D3	2/23/78	6.3	17	3.80 E2
Trench 22D11	2/23/78	6.7	14	4.5 E1
Well WW5	3/1/78	8.4	18	2.3 E1
Well WW6	3/1/78	6.8	18	3.5 E1
Well WW7	2/23/78	5.9	30	3.0 E1
Well CN-1E	3/1/78	9.6	18	1.64 E2
Well CN-3N	3/1/78	11.4	18	1.60 E3
Well CN-4W	3/1/78	10.4	18	2.05 E2

[a] Sampling locations correspond to positions indicated in Figure 4.7.

Radionuclide and DOC concentrations of trench and well samples are given in Table 4.17. The DOC concentrations fall within the DOC ranges found in trenches and wells at the Maxey Flats and West Valley sites. Tritium was found in all trenches and wells. The concentrations in the trenches are also comparable to the levels found at the Maxey Flats and West Valley sites. Only well sample CN-4W contains a significant amount of tritium and has detectable amounts of alpha and beta activities; only trench water sample 7D1 has detectable alpha activity. Three of the trenches show low levels of beta activity between 7.9 E2-1.4 E3.

Table 4.17

Radionuclide and DOC Concentrations in Water Samples Taken
From Barnwell, South Carolina, Disposal Site, Survey Study 1978

Sampling[a] Location	Gross Alpha (pCi/L)	Gross Beta (pCi/L)	Tritium (pCi/L)	DOC (mg/L)
Trench 5D1	<6 E1	1.4 E3 (21)[b]	1.3 E7 (<1)	130
Trench 6D1	<6 E1	<3 E2	1.0 E6 (<1)	6.1
Trench 7D1	1.0 E3 (21)	3.6 E3 (10)	6.4 E8 (<1)	3.0
Trench 8D1	<6 E1	8 E2 (32)	3.5 E7 (<1)	180
Trench 13D3	<6 E1	<3 E2	1.7 E6 (<1)	280
Trench 22D11	<6 E1	<3 E2	1.2 E6 (<1)	1
Well WW5	<6 E0	<2 E1	9.7 E2 (28)[c]	2-3.7
Well WW6	<6 E0	<2 E1	1.4 E3 (21)[c]	1
Well WW7	<6 E0	<2 E1	1.1 E3 (24)[c]	2-3.9
Well CN-1E	<6 E0	<2 E1	1.5 E3 (20)[c]	15
Well CN-3N	<6 E0	<2 E1	9.7 E2 (28)[c]	4.5
Well CN-4W	3 E1 (33)	1.2 E2 (15)	1.9 E5 (<1)[c]	11

[a] Sampling dates and locations same as in Table 4.16.
[b] Number in ( ) = 2σ percent counting uncertainty.
[c] Unfiltered samples collected 11/16/78.

The concentrations of gamma-ray emitting radionuclides in the trench water and well water samples from the Barnwell site are given in Table 4.13. Four trench water samples contain cesium-137, two contain cobalt-60, and one contains manganese-54. No gamma activity was detected in any of the well water samples. The limits of detection for the radionuclides of interest are shown in Table 4.18.

Any trenches that accumulate sufficient water for sampling will be collected for analyses.

Table 4.18

Concentration of Gamma-Ray Emitting Radionuclides in Water Samples Taken From Barnwell, South Carolina, Disposal Site, Survey Study 1978

Sampling[a] Location	^{137}Cs (pCi/L)	^{60}Co (pCi/L)
Trench 5D1[b]	1.8 E2 (13)[c]	2.8 E2 (12)
Trench 6D1	<1.8 E1	<1.8 E1
Trench 7D1	3.6 E1 (28)	<1.8 E1
Trench 8D1	<1.8 E1	7 E1 (24)
Trench 13D3	1.1 E2 (18)	<1.8 E1
Trench 22D11	8 E1 (24)	<1.8 E1
Well WW5	<1.8 E1	<1.8 E1
Well WW6	<1.8 E1	<1.8 E1
Well WW7	<1.8 E1	<1.8 E1
Well CN-1E	<1.8 E1	<1.8 E1
Well CN-3N	<1.8 E1	<1.8 E1
Well CN-4W	<1.8 E1	<1.8 E1

[a] Sampling dates and locations same as in Table 4.16.
Minimum detectable levels: ^{241}Am < 3.9 E1, ^{134}Cs < 1.6 E1, ^{22}Na < 1.7 E1, ^{54}Mn < 1.6 E1.

[b] ^{54}Mn in trench 5D1 = 1.3 E2 (20).

[c] Number in ( ) = 2σ percent counting uncertainty.

4.8. References

1. D.M. Montgomery, H.E. Kolde, and K.L. Blanchard, "Radiological Measurement at the Maxey Flats Radioactive Waste Burial Site 1974-1975", EPA-520/5-76/020, 1977. Available from U.S. Environmental Protection Agency, Office of Radiations Programs, Cincinnati, OH. 45268. Available from National Technical Information Service, Springfield, Va. 22161.

2. D.E. Prudic and A.D. Randall, "Ground-Water Hydrology and Subsurface Migration of Radioisotopes at a Low-Level Solid Radioactive-Waste Disposal Site, West Valley, New York", in Management of Low-Level Radioactive Waste, Vol. 2, M.W. Carter, A.A. Moghissi and B. Kahn, Eds. (Pergamon Press, London, 1979), pp. 853-882. Available in public technical libraries.

5 TRENCH WATER ANALYSIS

5.1 Introduction

The objective of the analytical program is to measure the concentration of radionuclides and other chemical species present in trench waters at the commercial low-level radioactive waste disposal sites. This source term information is essential in evaluating potential radionuclide migration along ground water flow paths, and modeling of existing disposal sites. Such information will contribute to the evaluation of radionuclide retention at the existing sites and the establishment of criteria and standards for shallow land burial of radioactive waste.

Water samples were obtained from trenches and wells at the commercial radioactive waste disposal sites located in Maxey Flats, Kentucky; West Valley, New York; Barnwell, South Carolina; and Sheffield, Illinois, between September 1976 and September 1979. Collection procedures were developed to maintain anoxic conditions in ground waters, while measuring pH, Eh, conductance, dissolved oxygen and temperature in situ.

Trench waters were analyzed for major inorganic constituents using ion specific electrodes, colorimetric, and atomic absorption methods. Organic compounds were determined by gas chromatographic and mass spectrometric analyses.

Radiochemical analyses of components dissolved in the trench waters and sorbed on suspended particulates in the waters were performed. Gross alpha, gross beta, tritium, strontium-90, plutonium-238,239,240 and gamma-ray emitting radionuclides were measured.

An overview of the analytical scheme is given in Figure 5.1.

5.2 Procedures

The following is a summary of the procedures that were developed and employed for the collection and analysis of trench water samples from the low-level radioactive waste disposal sites. The details of each procedure are found in the appendices as indicated.

5.2.1 Anoxic Collection (J.H. Clinton, G.G. Galdi, R.F. Pietrzak, and A.J. Weiss)

Procedures were designed to maintain the anoxic nature of the trench waters. Oxygen leaking into the samples will result in the formation of an iron (ferric) hydroxide precipitate.

After collection, the water samples are stored in 4-liter borosilicate glass bottles designed to maintain the trench water environment. The anoxic collection procedure allows samples to be stored for months without visible signs of the reddish-brown ferric hydroxide. A schematic diagram of the anoxic water sample collection system is shown in Figure 5.2. A photograph of the anoxic collection apparatus employed at the disposal sites is shown in

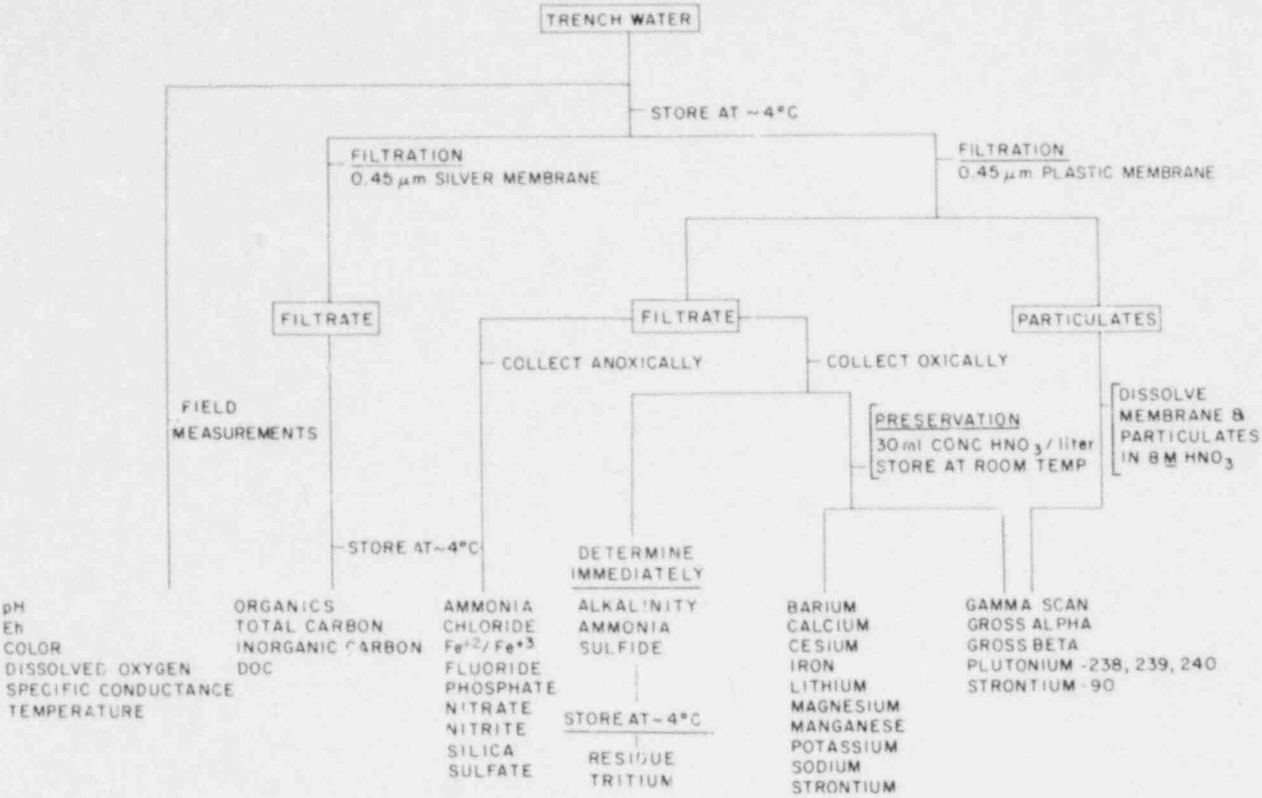

Figure 5.1. Scheme for partitioning water samples for analysis.

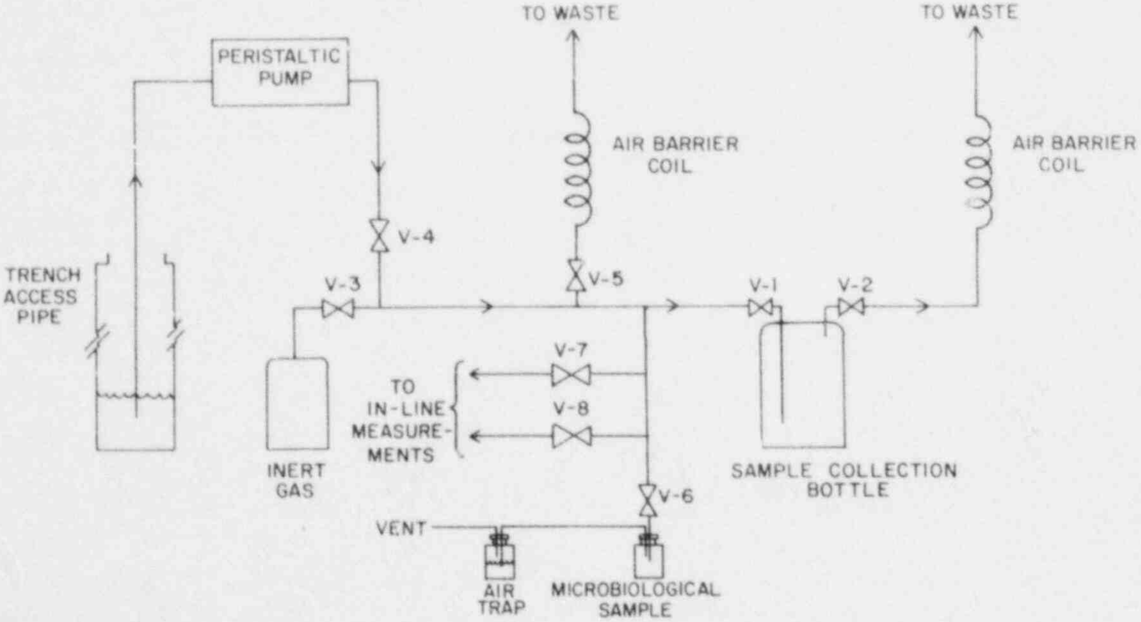

Figure 5.2. Schematic diagram of the system for anoxic collection of water.

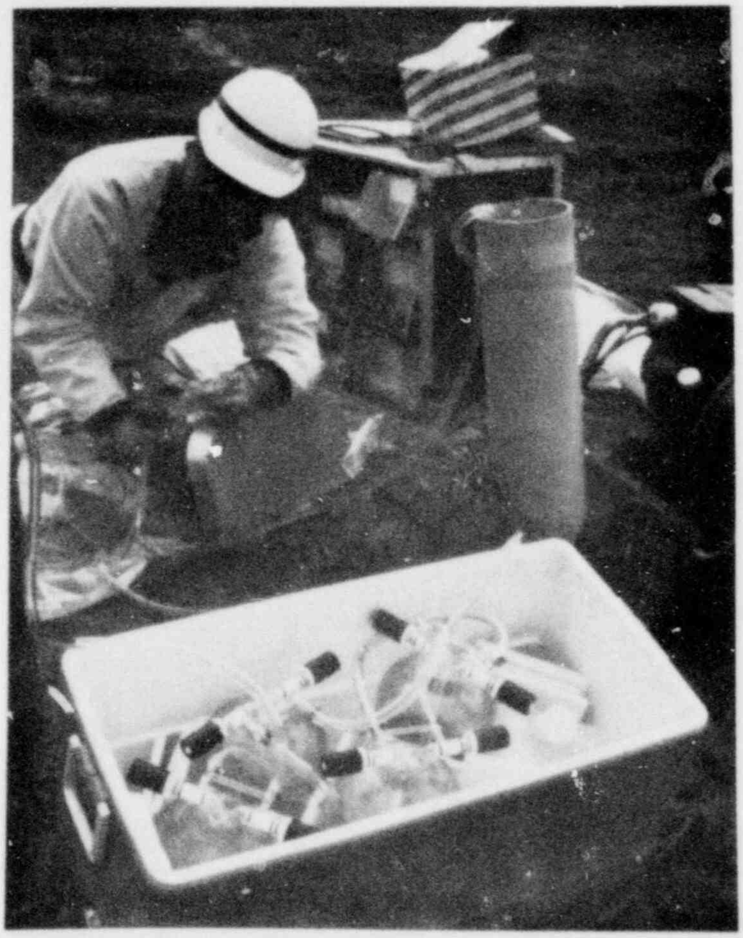

Figure 5.3. Portable anoxic collection system used to sample trench water from low-level radioactive waste disposal sites.

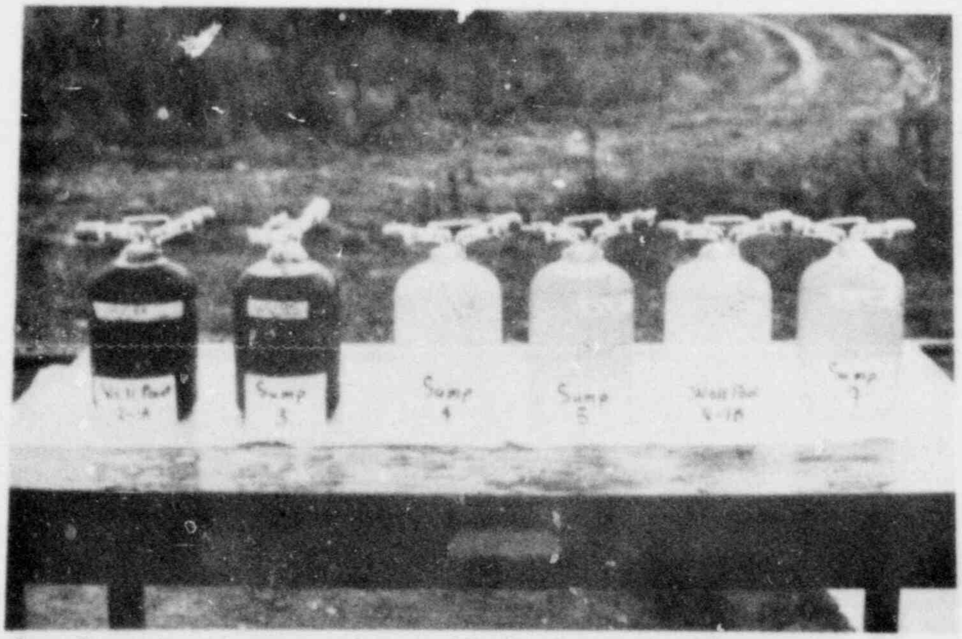

Figure 5.4. Trench water samples collected anoxically at the West Valley, New York, low-level radioactive waste disposal site, November 1977.

Figure 5.3. Figure 5.4 shows trench water samples collected anoxically at one of the low-level radioactive waste disposal sites. The detailed collection procedure is described in Appendix B.

5.2.2 In-Line Probe Measurements

Physico-chemical characteristics of trench waters which are subject to change during storage are measured at the time of sample collection. The temperature, pH, redox potential (Eh), dissolved oxygen, and specific conductance of the trench water samples are measured in-line while the water sample is being collected. A description of the manifold containing the probes is given in Appendix B.

5.2.3 Anoxic Filtration

Upon arrival at BNL, the trench water samples are filtered through 0.45 μm membrane filters to remove particulate matter present in them. The filtering process is also done under an inert atmosphere to maintain the anoxic character of the waters. The detailed procedure developed to transfer and filter aliquots of trench water anoxically are described in Appendix B. The filtrate is divided into several fractions and processed according to the scheme shown in Figure 5.1. The dissolved fraction of each sample is analyzed for inorganic, organic, and radiochemical constituents. The particulate fraction is analyzed for radiochemical constituents only.

5.2.4 Inorganic Analyses (S. Garber)

The following is a brief summary of methods used to measure the dissolved chemical constituents in trench waters. A more complete description is given in Appendix C.

5.2.4.1 Alkalinity Titration

The alkalinity titration is performed with filtered trench water, immediately after filtration. Generally carbonate and bicarbonate concentrations in ground water are determined by titrating the water sample with a standard acid to pH 8.3 and pH 4.5, respectively. The equations that govern the reactions are:

$$CO_3^{=} + H^+ \rightleftarrows HCO_3^- \qquad (1)$$

$$HCO_3^- + H^+ \rightleftarrows H_2O + CO_2 \qquad (2)$$

The end points of these titrations are sharp in the absence of other ions that are in competition for the hydrogen ion. In the presence of salts of weak organic and inorganic acids the titration curve does not give a sharp endpoint due to buffering of the system. The titration alkalinity in this case is not a simple function of the carbonate-bicarbonate concentrations. The shape of an acid-base titration curve can yield useful information in addition to carbonate and bicarbonate relationships.

5.2.4.2 Chloride

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of non-ionic but soluble mercuric chloride. In the presence of ferric ion, the liberated thiocyanate forms a highly colored ferric thiocyanate whose concentration is proporticnal to the original chloride concentration. The intensity of the ferric thiocyanate is measured spectrophotometrically.

5.2.4.3 Dissolved Metals

Dissolved metals in the acidified aliquot of filtered trench water are determined by atomic absorption spectroscopy.

5.2.4.4 Ferrous - Ferric Iron

Iron in the ferrous state is reacted with 1,10-phenanthroline between pH 3.2 and 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex which is measured spectrophotometrically. Ferric iron is determined by subtracting the ferrous iron concentration from the total iron concentration. Total iron is determined colorimetrically by reduction with hydroxylamine hydrochloride and subsequent reaction with 1,10-phenanthroline. Atomic absorption determination of total iron is a convenient check on this method.

5.2.4.5 Fluoride

Fluoride is determined with a specific ion electrode consisting of a single-crystal lanthanum fluoride membrane and an internal reference. The crystal is an ionic conductor in which only fluoride ions are mobile. The potential developed across the membrane in the Orion 94-09 probe is proportional to the fluoride ions in solution and is measured against an external reference with the Orion 407A specific ion meter.

5.2.4.6 Phosphate

The determination of orthophosphate depends upon the formation of molybdophosphoric acid with the addition of ammonium molybdate in acid medium. This is reduced to molybdenum blue by ascorbic acid at 37°C and is measured spectrophotometrically.

5.2.4.7 Nitrogen-Ammonia

A gas sensing electrode, containing a hydrophobic gas permeable membrane, allows dissolved ammonia generated in the sample to diffuse through the membrane until the partial pressure of ammonia is the same on both sides. The partial pressure of ammonia is proportional to its concentration according to Henry's law.

When sodium phenoxide and sodium hypochlorite are added to a solution containing an ammonium salt, the Berthelot reaction takes place with the formation of a green compound related to endophenol. The color intensity is measured spectrophotometrically which is proportional to the ammonia concentration.

Methods have been developed to perform this analysis in a nitrogen or argon environment.

5.2.4.8 Nitrogen-Nitrite

Nitrite reacts with sulfanilamide under acidic conditions to yield a diazo compound which couples with N-1-napthylethylene-diamine dihydrochloride to form a red colored compound. The color intensity measured spectrophotometrically is related to the concentration of nitrite.

5.2.4.9 Nitrogen-Nitrite plus Nitrate

Nitrate is reduced to nitrite when passed through a cadmium-copper column. The nitrite is then treated with sulfanilamide and N-1 naphthylenediamine dihydrochloride to form the red azo dye as above. When both nitrite and nitrate are present in a sample, the nitrate value is obtained by subtracting the nitrite value from the combined nitrite plus nitrate value.

5.2.4.10 Silica

Ammonium molybdate reacts with silica (SiO_2) in acid medium to form molybdosilicic acid. This is reduced to molybdenum blue by ascorbic acid and measured spectrophotometrically. Oxalic acid is added before the ascorbic acid to eliminate interference from phosphates.

5.2.4.11 Sulfate

When equimolar barium chloride and methylthymol blue are added to a sulfate-containing sample at pH 2.5-3.0, barium sulfate precipitates. After adjusting the pH to 12.5-13.0, the barium remaining in solution reacts with the methylthymol blue to form a chelate. The uncombined methylthymol blue remaining in solution is measured spectrophotometrically and is proportional to the sulfate initially present in the sample.

5.2.4.12 Sulfide

A silver-silver sulfide electrode used in conjunction with a reference electrode develops a potential which is a direct function of the logarithm of the activity of the sulfide ion.

5.2.5 Organic Analyses (A.J. Francis, B. Nine, C.R. Iden, and C. Chang)

5.2.5.1 Carbon Analyses

The total carbon and inorganic carbon content is determined using a Beckman Model 915 Total Carbon Analyzer. The difference between the total carbon and the inorganic carbon measurements is the dissolved organic carbon (DOC) of the sample.

5.2.5.2 Organic Compound Identification

A liquid extraction technique using methylene chloride is employed to isolate acidic, neutral, and basic organic compounds from the trench waters. These fractions are analyzed by gas chromatography and identified by mass spectrometry (GC/MS) methods. The details of these procedures are described in Appendix E.

5.2.6 Radiochemical Analysis (J.H. Clinton, G.G. Galdi, S.L. Garber, R.F. Pietrzak, and A.J. Weiss)

Radiochemical measurements are performed on the filtrate and particulates collected during filtration of each trench water sample. Except for tritium, all of the radiochemical measurements are made on an acidified aliquot of the filtrate. Tritium is measured on a non-acidified fraction of filtrate. The following is a brief summary of the procedures used to measure radionuclides in these trench waters.

5.2.6.1 Gross Alpha/Gross Beta

An aliquot of acidified filtrate (2-mL to 5-mL) is heated to dryness in a 50 mm planchette and counted with a Canberra model 2200 low-level alpha/beta gas flow proportional counter. Each sample is counted at two instrument settings corresponding to the plutonium-239 alpha plateau and the strontium-90/yttriium-90 beta plateau. This measurement is not made for the particulate fraction. Gross counting should be regarded as a rapid, semi-quantitative measure of sample activity.

5.2.6.2 Tritium

An aliquot of tritiated water, distilled by conventional methods at atmospheric pressure, is emulsified with Packard Insta-Gel liquid scintillation reagent and counted in a Searle Analytic-92 liquid scintillation counter.

5.2.6.3 Strontium-90

Strontium-90 is determined by radiochemically separating strontium from the trench water sample and counting the in-growth of yttrium-90 with a low-level beta counter.

5.2.6.4 Plutonium-238,239,240

Plutonium isotopes are radiochemically separated from other alpha emitting radionuclides by anion exchange chromatography and electroplated onto a counting disc. Plutonium isotopes on the disc are measured by alpha spectroscopy with a surface barrier silicon detector.

5.2.6.5 Gamma-Ray Emitters

Gamma-ray emitting radionuclides are measured by counting 15-mL- or 250-mL aliquots of the filtered trench water for 1000 minutes with a 2 keV resolution Ge(Li) detector. Gamma spectra are collected with a Tracor Northern

TN 1700 multichannel analyzer and analyzed by the computer code INTRAL (courtesy of J. Cumming, Chemistry Department, BNL). Radionuclide identifications are made on the basis of measured gamma ray energies and relative peak heights of nuclides emitting more than one gamma.

5.3 Results of Analyses

The analytical results of (i) field, (ii) inorganic, (iii) organic, and (iv) radiochemical measurements are presented in this section. The results are grouped according to disposal site.

The number of constituents that are analyzed has increased as the program developed. Consequently, there are missing entries in some tables.

5.3.1 Maxey Flats, Kentucky, Disposal Site

5.3.1.1 Field Measurements

In-situ measurements made at Maxey Flats for collections made September 1976, July 1977, and May 1978 are shown in Table 5.1. The sampling locations correspond to trenches indicated in Figure 4.1.

Table 5.1

Field Measurements of Water Samples Taken From Maxey Flats, Kentucky, Disposal Site[a]

Sampling Location	Date	Apparent Color	pH	Eh (mV,NHE)[b]	Dissolved Oxygen (mg/L)	Specific Conductance (μmho/cm)	Temperature (°C)
Trench 2	9/76	gray	6.7	c	c	3400	20.
	7/77	yellow	7.4	90	d	3200	15.
Trench 7	9/76	clear	6.9	c	c	2530	22.5
Trench 18	9/76	light brown	7.0	c	c	3450	21.5
Trench 19S	9/76	light green	6.6	c	c	2340	21.0
	5/78	light green	6.9	25	0.2	2310[e]	12.4
Trench 26	9/76	black	6.8	c	c	2910	21.0
	7/77	gray	7.3	130	d	2680	20.8
Trench 27	9/76	yellow-green	6.0	c	c	12 000	20.0
	5/78	light green	6.6	17	0.05	9370[e]	17.6
Trench 32	9/76	green-black	7.3	c	c	5750	20.0
	7/77	gray	7.9	10	d	5650	17.2
Trench 33L-4	9/76	yellow	12.3	c	c	7600	20.0
	5/78	light yellow-green	12.1	-7	4.1[f]	5580[e]	12.0
Trench 33L-9	9/76	light yellow	5.6	c	c	6150	22.0
Trench 33L-18	5/78	pale green	2.4	520	0.25	9390[e]	10.7
Trench 37	9/76	light green	5.1	c	c	6900	20.0
Well UB1-A	5/78	white cloudy	6.6	274	0.2	2310[e]	12.4

[a] In September 1976, the field measurements were made on separate aliquots of trench water within 30 minutes of the time of collection. On subsequent samplings, these measurements were made with probes inserted directly into the water flowing through the collection apparatus.

[b] Field measurements of redox potentials (Eh) are reported relative to the normal hydrogen electrode (NHE).

[c] Redox potential (Eh) and dissolved oxygen not measured in September 1976.

[d] Dissolved oxygen not measured in July 1977.

[e] Measurements made by USGS personnel in the field immediately after collecting the sample.

[f] Result of low water level; air in lines.

The high and low pH's in the "L" trenches (33L-4, 33L-9, and 33L-18) are related to the past practices of pouring liquid wastes into trenches and solidifying them either with cement or urea formaldehyde.

The Eh's of the trench waters are low (reducing) compared to well UB1-A, a test well not located in a trench. The Eh of water in 33L-18 is the highest, probably caused by the low pH, which may affect microbial activity.

5.3.1.2 Inorganic

Results of inorganic analyses for the collection dates shown are given in Tables 5.2 and 5.3.

5.3.1.2.1 Maxey Flats - 1976

Nitrogen as NO_3^- + NO_2^- is derived from only NO_3^- since NO_2^- was not detected in any of the samples. A preliminary analysis was made for nitrogen as ammonia in three randomly selected trench water samples, viz. trench 7, trench 19S, and trench 33L-4, since most of the trenches showed little or no nitrate + nitrite. Each of these trench waters contains more than 10 mg/L of nitrogen as ammonia. Ammonia analysis was added to the list of analyses for the trench water samples subsequently collected.

5.3.1.2.2 Maxey Flats - July 1977

Alkalinity titrations with standard acid were performed to pH 4.5 end point. Calculation of bicarbonate concentration from a total alkalinity measurement is not possible in a buffered trench water system and is not reported here.

Water collected anoxically from trench 32 was filtered anoxically within 24 hours after collection and analyzed for ammonia with a gas sensing probe. The measured concentration of nitrogen as ammonia was 112 mg/L. The same filtered sample (in a sealed bottle) re-analyzed three months later by the same method contained 114 mg/L nitrogen as ammonia.

The ammonia value reported in Table 5.2 (117 mg/L nitrogen as ammonia) was determined from the sample that was anoxically filtered in the laboratory and from which the other reported constituents were determined. At that time ammonia analyses were performed by both the probe and the Berthelot-colorimetric methods on freshly filtered samples from trenches 2, 26, and 32, which had been kept in the anoxic collection bottles for three months the results illustrated in Figure 5.5 indicate that the sample was not affected by storage, and that the two analytical methods are comparable. The open circles in Figure 5.5 correspond to samples filtered in the laboratory. The triangle is from the one sample measured by probe at Maxey Flats.

5.3.1.2.3 Maxey Flats - May 1978

Acid-base alkalinity titration curves for trenches 19S, 27, 33L-4 and 33L-18, and for well UB1-A are shown in Figure 5.6. The titration curve of water from well UB1-A resembles a typical simple groundwater. The shapes of the trench water samples indicate complex water systems.

Table 5.2

Concentration of Dissolved Non-Metals in Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site
(mg/L)

Dissolved Component	Date	Trench 2	Trench 7	Trench 18A	Trench 19S	Trench 26	Trench 27
Total	9/76	1560	1090	2050	980	1320	432
Alkalinity	7/77	1370	--[a]	--	--	860	--
(as $CaCO_3$)	5/78	--	--	--	910	--	330
Inorganic	9/76	270	210	440	78	150	<2
Carbon	7/77	330	--	--	--	100	--
	5/78	--	--	--	70	--	<2
DOC	9/76	210	250	500	620	950	730
	7/77	90	--	--	--	770	--
	5/78	--	--	--	500	--	540
Hardness (Ca+Mg)	9/76	400	630	670	680	590	3300
(as $CaCO_3$)	7/77	170	--	--	--	360	--
	5/78	--	--	--	810		1900
Residue (180°C)	9/76	2160	1410	2240	1670	1580	7620
	7/77	2740	--	--	--	1150	--
	5/78	--	--	--	2100	--	8400
Chloride	9/76	310	220	310	150	290	4200
	7/77	230	--	--	--	210	--
	5/78	--	--	--	140	--	3900
Nitrogen (N)	9/76	--	--	--	--	--	--
(NH_3 probe)	7/77	36	--	--	--	115	--
	5/78	--	--		4.1	--	80
Nitrogen (N)	9/76	--	--	--	--	--	--
(NH_4^+ Color)	7/77	39	--	--	--	99	--
	5/78	--	--	--	--	--	--
Nitrogen (N)	9/76	<0.5	<0.0	<0.05	<0.05	<0.05	1.6
(NO_2^- + NO_3^-)	7/77	0.08	--	--	--	<0.04	--
	5/78	--	--		<0.1	--	<0.1
Fluoride	9/76	--	--	--	--	--	--
Direct	7/77	--	--	--	--	--	--
Reading	5/78				0.8		0.4
Fluoride	9/76	--	--	--	--	--	--
Standard	7/77	--	--	--	--		--
Addition	5/78	--	--	--	1.0	--	0.9
Phosphate	9/76	--	--	--	--	--	--
	7/77	<0.5	--	--	--	1.0	--
	5/78	--	--	--	<2	--	17
Silica	9/76	14	12	13	9.0	9.0	14
	7/77	12	--	--	--	6.5	--
	5/78	--	--	--	9.0	--	5
Sulfate	9/76	11	<10	18	<10	<10	69
	7/77	<5	--	--	--	<1	--
	5/78	--	--	--	<5	--	<5
Total Anions	9/76	40	28	50	24	34	130
(meq/L)	7/77	34	--	--	--	28	--
	5/78	--	--	--	22	--	120

[a] -- Indicate no sample was collected.

Table 5.2, continued

Concentration of Dissolved Non-Metals in Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site
(mg/L)

Dissolved Component	Date	Trench 32	Trench 33L-4	Trench 33L-9	Trench 33L-18	Trench 37	Well UB1-A
Total	9/76	2720	1810	358	--[a]	125	--
Alkalinity	7/77	2600		--	--	--	--
(as $CaCO_3$)	5/78	--	1600	--	b	--	50
Inorganic	9/76	510	<2	180	--	23	--
Carbon	7/77	380	--	--	--	--	--
	5/78	--	9.3	--	98	--	74
DOC	9/76	790	1900	4500	--	3300	--
	7/77	990	--	--	--	--	--
	5/78	--	1071	--	5557	--	7.3
Hardness (Ca+Mg)	9/76	1200	3600	5700	--	3600	--
(as $CaCO_3$)	7/77	1300	--	--	--	--	--
	5/78	--	1600	--	120	--	1300
Residue (180°C)	9/76	3810	4870	9560	--	11200	--
	7/77	3590	--	--	--	--	--
	5/78	--	4960	--	5600	--	3360
Chloride	9/76	370	320	90	--	180	--
	7/77	580	--	--	--	--	--
	5/78	--	168	--	144	--	300
Nitrogen (N)	9/76	--	--	--	--	--	--
(NH_3 probe)	7/77	117	--	--	--	--	--
	5/78	--	18	--	<1		<1
Nitrogen (N)	9/76	--	--	--	--	--	--
(NH_4^+ Color)	7/77	99	--	--	--	--	--
	5/78	--	--	--	--	--	--
Nitrogen (N)	9/76	<0.05	21	900	--	13	--
(NO_2^- + NO_3^-)	7/77	<0.04	--	--	--	--	--
	5/78	--	10.6	--	2000	--	<0.1
Flouride	9/76	--	--	--	--	--	--
Direct	7/77	--	--	--	--	--	--
Reading	5/78	--	<0.1	--	<1.0	--	--
Fluoride	9/76	--	--	--	--	--	--
Standard	7/77	--	--	--	--	--	--
Addition	5/78	--	0.2	--	--	--	0.7
Phosphate	9/76	--	--	--	--	--	--
	7/77	24	--	--	--	--	--
	5/78	--	<2	--	<2	--	<3
Silica	9/76	14	1.7	9.0	--	35	--
	7/77	10	--	--	--	--	--
	5/78	--	1	--	132	--	14
Sulfate	9/76	11	<10	390	--	8000	--
	7/77	<1	--	--	--	--	--
	5/78	--	<5	--	1000	--	1200
Total Anions	9/76	65	47	32	--	140	--
(meq/L)	7/77	68	--	--	--	--	--
	5/78	--	38	--	170	--	35

[a] -- Indicate no sample was collected.

[b] Initial pH of 1.9 for the water sample from trench 33L-18 does not allow an alkalinity tritiation.

Table 5.3

Concentration of Dissolved Metals in Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site
(mg/L)

Metal	Date	Trench 2	Trench 7	Trench 18	Trench 19S	Trench 26	Trench 27
Calcium	9/76	29	130	14	58	31	600
	7/77	20	--[a]	--	--	45	--
	5/73	--	--	--	50	--	240
Cesium	9/76	--	--	--	--	--	--
	7/77	<0.1	--	--	--	0.2	--
	5/78	--	--	--	0.1	--	<0.05
Iron	9/76	40	61	33	150	65	1200
	7/77	28	--	--	--	110	--
	5/78	--	--	--	115	--	1150
Lithium	9/76	0.99	0.56	18		0.34	1.9
	7/77	1.3	--	--	-	0.15	--
	5/78	--	--	--	.38	--	1.85
Magnesium	9/76	79	73	160	130	130	430
	7/77	41	--	--	--	87	--
	5/78	--	--	--	124	--	255
Manganese	9/76	0.75	0.50	0.03	0.76	0.74	70
	7/77	--	--	--	--	--	--
	5/78	--	--	--	0.42	--	88
Potassium	9/76	66	140	50	25	39	120
	7/77	35	--	--	--	27	--
	5/78	--	--	--	12	--	36
Sodium	9/76	700	240	540	100	240	670
	7/77	1300	--	--	--	270	--
	5/78	--	--	--	650	--	450
Strontium	9/76	--	--	--	--	--	--
	7/77	--	--	--	--	--	--
	5/78	--	--	--	0.53	--	3.8
Total Cations (meq/L)	9/76	42	28	42	24	26	140
	7/77	66	--	--	--	34	--
	5/78	--	--	--	45	--	100

[a] -- Indicate no sample was collected.

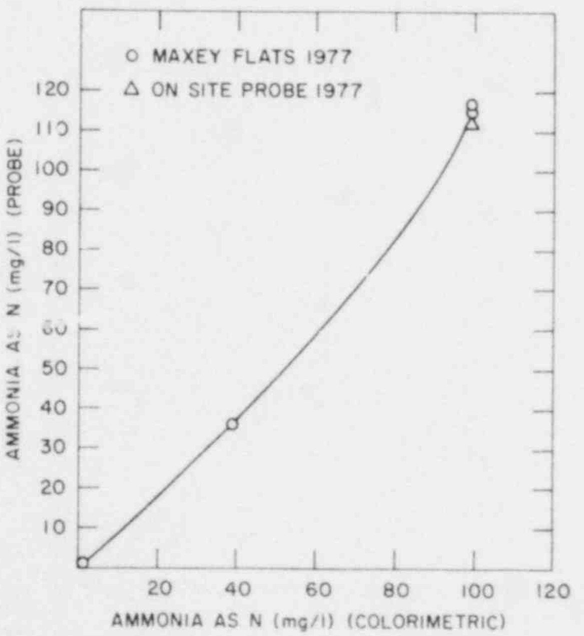

Figure 5.5 Comparison of ammonia analyses by gas sensing probe and Berthelot-colorimetric methods.

Table 5.3, continued

Concentration of Dissolved Metals in Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site
(mg/L)

Metal	Date	Trench 32	Trench 33L-4	Trench 33L-9	Trench 33L-18	Trench 37	Well UB1-A
Calcium	9/76	75	1400	2000	--[a]	250	--
	7/77	65	--	--	--	--	--
	5/78		650	650	44	--	160
Cesium	9/76	--	--	--	--	--	--
	7/77	<0.1	--	--	--	--	--
	5/78	--	<0.05	--	0.1	--	<0.05
Iron	9/76	16	<0.01	34	--	1100	--
	7/77	32	--	--	--	--	--
	5/78	--	0.3	--	194	--	<0.01
Lithium	9/76	0.15	0.23	0.08	--	0.30	--
	7/77	0.23	--	--	--	--	--
	5/78	--	0.16	--	0.50	--	0.44
Magnesium	9/76	230	0.03	190	--	730	--
	7/77	320	--	--	--	--	--
	5/78	--	0.08	--	18.4	--	224
Manganese	9/76	1.2	<0.01	20	--	42	--
	7/77	--	--	--	--	--	--
	5/78	--	<0.05	--	26	--	0.14
Potassium	9/76	210	160	13	--	20	--
	7/77	280	--	--	--	--	--
	5/78	--	30	--	14	--	4
Sodium	9/76	700	160	110	--	680	--
	7/77	1900	--	--	--	--	--
	5/78	--	180	--	185	--	500
Strontium	9/76	--	--	--	--	--	--
	7/77	--	--	--	--	--	--
	5/78	--	7.0	--	<0.1	--	2.5
Total Cations (meq/L)	9/76	59	83	121	--	180	--
	7/77	130	--	--	--	--	--
	5/78	--	41	--	21	--	49

[a] -- Indicate no sample was collected.

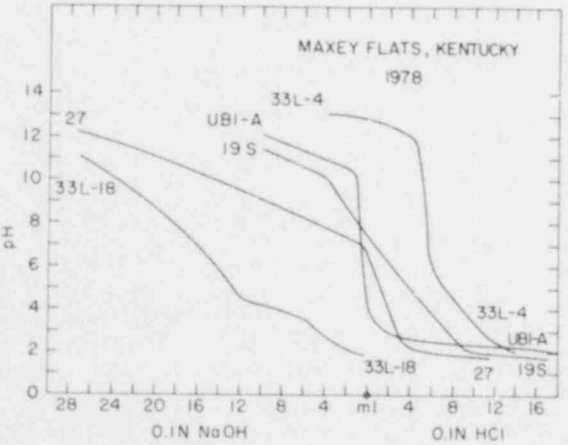

Figure 5.6. Acid-base titration curves of water samples from Maxey Flats, Kentucky, disposal site, May 1978.

Because the initial pH of the water sample from trench 33L-18 is 1.9, an alkalinity titration to pH 4.5 is not applicable (Table 5.2).

The probe method of analyzing for fluoride is sensitive to the presence of complexing agents which can combine with the F^- and consequently reduce the measured F^- values. When the fluoride concentration, as measured by standard addition, is higher than by direct reading, there is reason to suspect the presence of complexing substance.

The 2000 mg/L of nitrogen ($NO_2^- + NO_3^-$) measured in trench 33L-18 is predominantly in the NO_3^- form with 4 mg/L present as NO_2^-. It is presumed that liquid waste was solidified with urea formaldehyde in situ in trench 33L-18. This polymerization is acid catalyzed which is probably the source of the low pH measured in the trench water. The concentrations of chloride and phosphate are not high in the trench water, whereas sulfate is present at a concentration of 1000 mg/L. Sulfuric acid is commonly used as the catalyst with urea formaldehyde. Although nitric acid is not generally used to catalyze the polymerization, if it had been used, it could be the source of the high NO_3^- concentration found. This does not exclude the possibility that nitrates were in the buried waste.

It is presumed that liquid waste was solidified with cement in situ in trench 33L-4, which is the reason for the high pH measured in the trench water. Consequently the concentration of dissolved calcium is high, and cations such as iron and magnesium are low (Table 5.3).

A semi-quantitative search for mercury in trench water samples by conventional atomic absorption analysis indicated the presence of mercury in trench 27. A cold-vapor flameless atomic absorption procedure was used to determine the mercury with greater accuracy. Volatile organic compounds in the water, which interfered with the analyses, were decomposed by oxidative digestion using potassium permanganate and potassium persulfate. Using the method of standard additions, 7.5 mg/L of mercury was measured in trench 27 water sample.

5.3.1.3 Organic Analyses (A.J. Francis, B. Nine, C.R. Iden, and C. Chang)

Water samples collected from wells UB1 and UB1-A and from trenches 2, 7, 18, 19S, 26, 27, 32, 33L-4, 33L-9, 33L-18 and 37 at Maxey Flats were analyzed for dissolved organic carbon (DOC) and for various dissolved organic constituents.

The concentrations of dissolved inorganic and organic carbon in these water samples are shown in Table 5.4. The DOC concentrations in the trenches ranged from 90 mg/L to 5600 mg/L. The DOC in well UB1 (210 mg/L) is significantly higher than the 8 mg/L measured in well UB1-A, a level that is normally encountered in many unpolluted or slightly polluted well waters.

Results of the GC/MS analyses of the water samples are presented in Figures 5.7 through 5.14 and Tables 5.5 through 5.13. Each figure shows the gas chromatograms for the acidic, neutral, and basic organic fractions obtained by methylene chloride extraction from a single trench or well sample. The "X64" and "X4" designations on the abscissa refer to the degree of attenuation of the

Table 5.4

Concentration of Carbon in Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site

Sampling[a] Location	Collection Date	Total Carbon (mg/L)	Inorganic Carbon (mg/L)	Organic Carbon (mg/L)
Trench 2	9/76	480	270	210
	7/77	420	330	90
Trench 7	9/76	460	210	250
Trench 18	9/76	940	440	500
Trench 19S	9/76	700	78	620
	5/78	570	70	500
Trench 26	9/76	1100	150	950
	7/77	870	100	770
Trench 27	9/76	730	<2	730
	5/78	540	<2	540
Trench 32	9/76	1300	510	790
	7/77	1400	380	990
Trench 33L-4	9/76	1900	<2	1900
	5/78	1100	10	1100
Trench 33L-9	9/76	4700	180	4500
Trench 33L-18	5/78	5700	100	5600
Trench 37	9/76	3300	20	3300
Well UB1	10/77	310	100	210
Well UB1-A	5/78	15	7	8

[a] Sampling locations correspond to positions indicated in Figure 4.1.

recorder, and that the relative heights of the peaks in these two regions are 16:1. Not all peaks seen in a set of chromatograms from a single sample were identified. The first peaks shown are associated with the solvent and the TMS reagent. Those which were identified are numbered, and their concentrations are listed in the tables.

The organic compounds reported are those found in the methylene chloride extracts of the original water samples and are reported as concentrations per liter of the water sample. The solvent extraction efficiency for each compound in these complex aqueous solutions was not determined. Methylene chloride extraction is not expected to remove all organics from the water samples, so that hydrophillic organics, such as EDTA, are presumed to remain in the water phase.

The organic compounds found in the trench waters consisted of several straight- and branched-chain aliphatic acids, aromatic acids, alcohols,

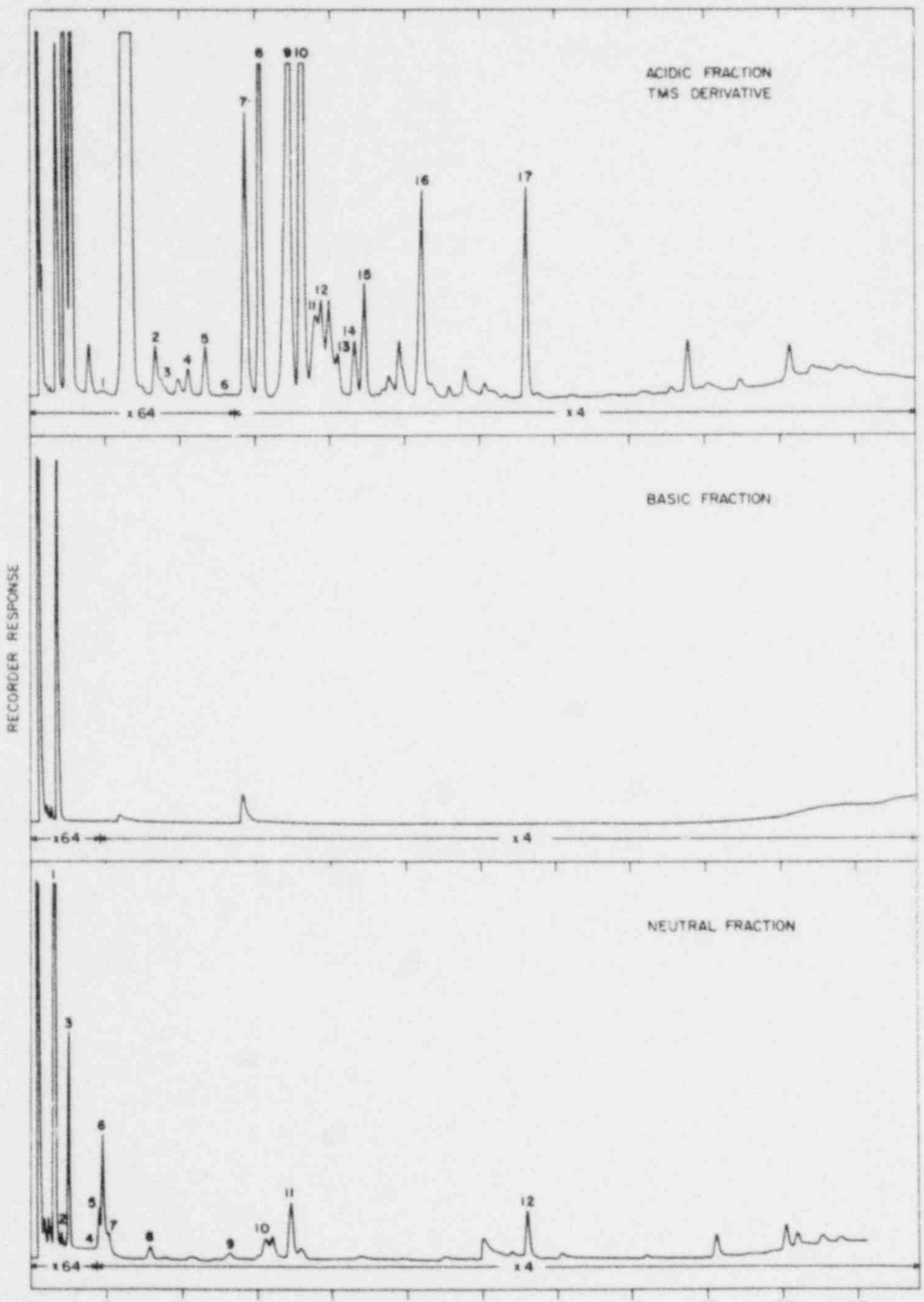

Figure 5.7. Gas chromatogram of methylene chloride extract of trench 19S water sample from Maxey Flats, Kentucky, disposal site.

Table 5.5

Concentration of Organic Compounds Identified in Trench 19S Water Sample From Maxey Flats, Kentucky, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	2-Methylpropionic acid	0.40
2	2-Methylbutanoic acid	4.6
3	3-Methylbutanoic acid	1.8
4	Valeric acid	2.0
5	3-Methylpentanoic acid	3.1
6	C_6 branched acid[b]	0.35
7	Hexanoic acid	1.5
8	2-Methylhexanoic acid	1.5
9	Cresol	2.9
10	2-Ethylhexanoic acid	5.6
11	C_8 branched acid[c]	0.72
12	C_8 branched acid[c]	0.68
13	Benzoic acid	0.22
14	Octanoic acid	0.36
15	Phenylacetic acid	0.56
16	Phenylpropionic acid	1.2
17	Phenylhexanoic acid	N.Q.[d]
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	Methyl isobutyl ketone	0.56
3	Toluene	2.9
4	Xylene (isomer)	N.Q.
5	Xylene (isomer)	N.Q.
6	Cyclohexanol	2.9
7	Xylene (isomer)	N.Q.
8	Dibutyl ketone	N.Q.
9	Fenchone	0.03
10	Triethyl phosphate	0.38
11	Naphthalene	0.12
12	Tributyl phosphate	0.16

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[a] Corresponds to numbers in Figure 5.7.

[b] Quantified using 3-Methylpentanoic acid standard.

[c] Quantified using 2-Ethylhexanoic acid standard.

[d] Not quantified.

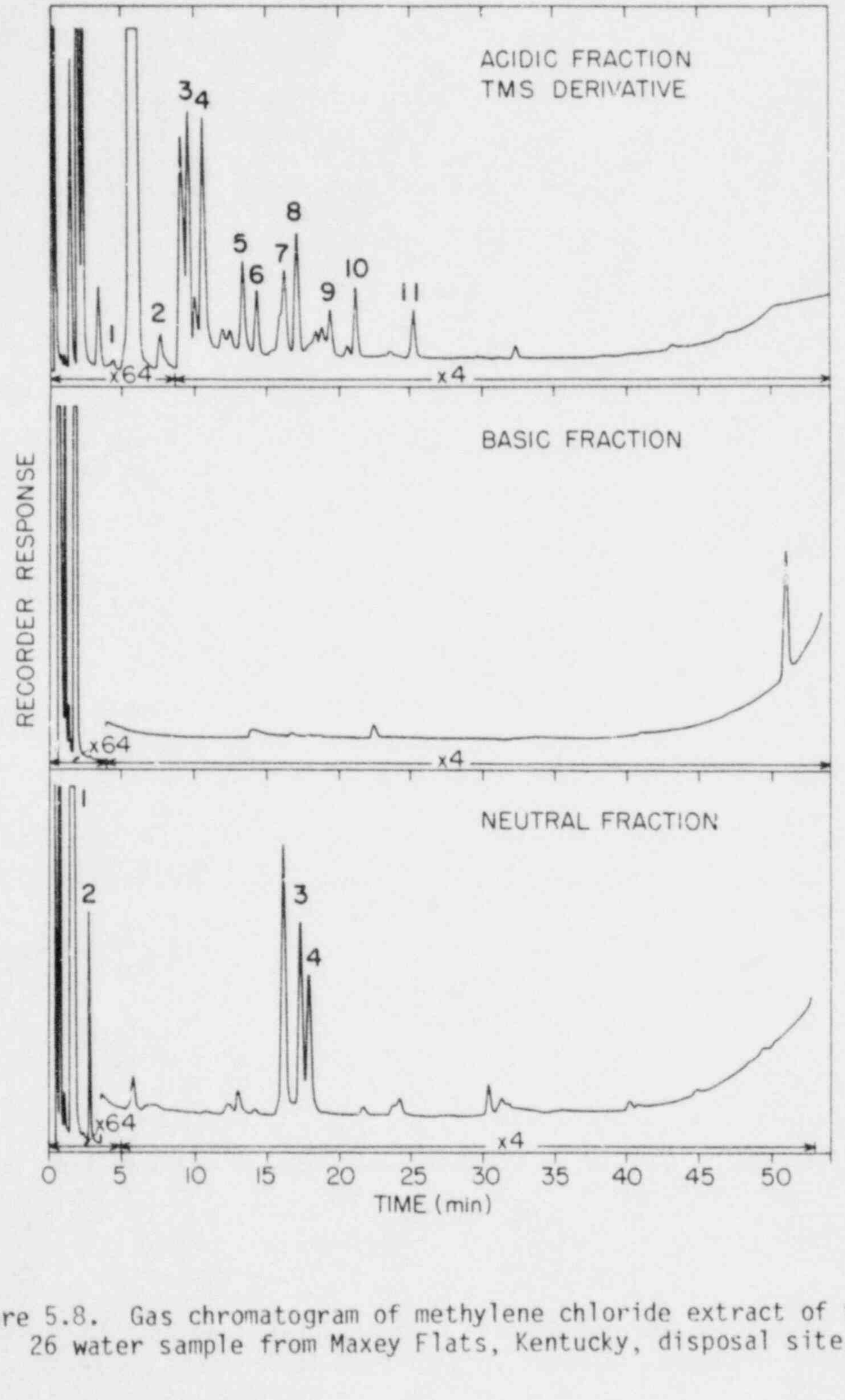

Figure 5.8. Gas chromatogram of methylene chloride extract of trench 26 water sample from Maxey Flats, Kentucky, disposal site.

Table 5.6

Concentration of Organic Compounds Identified in Trench 26 Water Sample From Maxey Flats, Kentucky, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	2-Methylpropionic acid	3.6
2	2-Methylbutanoic acid	19
3	Pentanoic acid	4.6
4	3-Methylpentanoic acid	4.2
5	Hexanoic acid	1.9
6	2-Methylhexanoic acid	1.2
7	Cresol (isomers)	2.0
8	2-Ethylhexanoic acid	3.4
9	Benzoic acid	1.2
10	Phenylacetic acid	1.5
11	Phenylpropionic acid	1.3
Neutral Fraction:		
1	p-Dioxane	N.Q.[b]
2	Toluene	3.5
3	Naphthalene	0.28
4	α-Terpineol	0.31

[a] Corresponds to numbers in Figure 5.8.

[b] Not quantified.

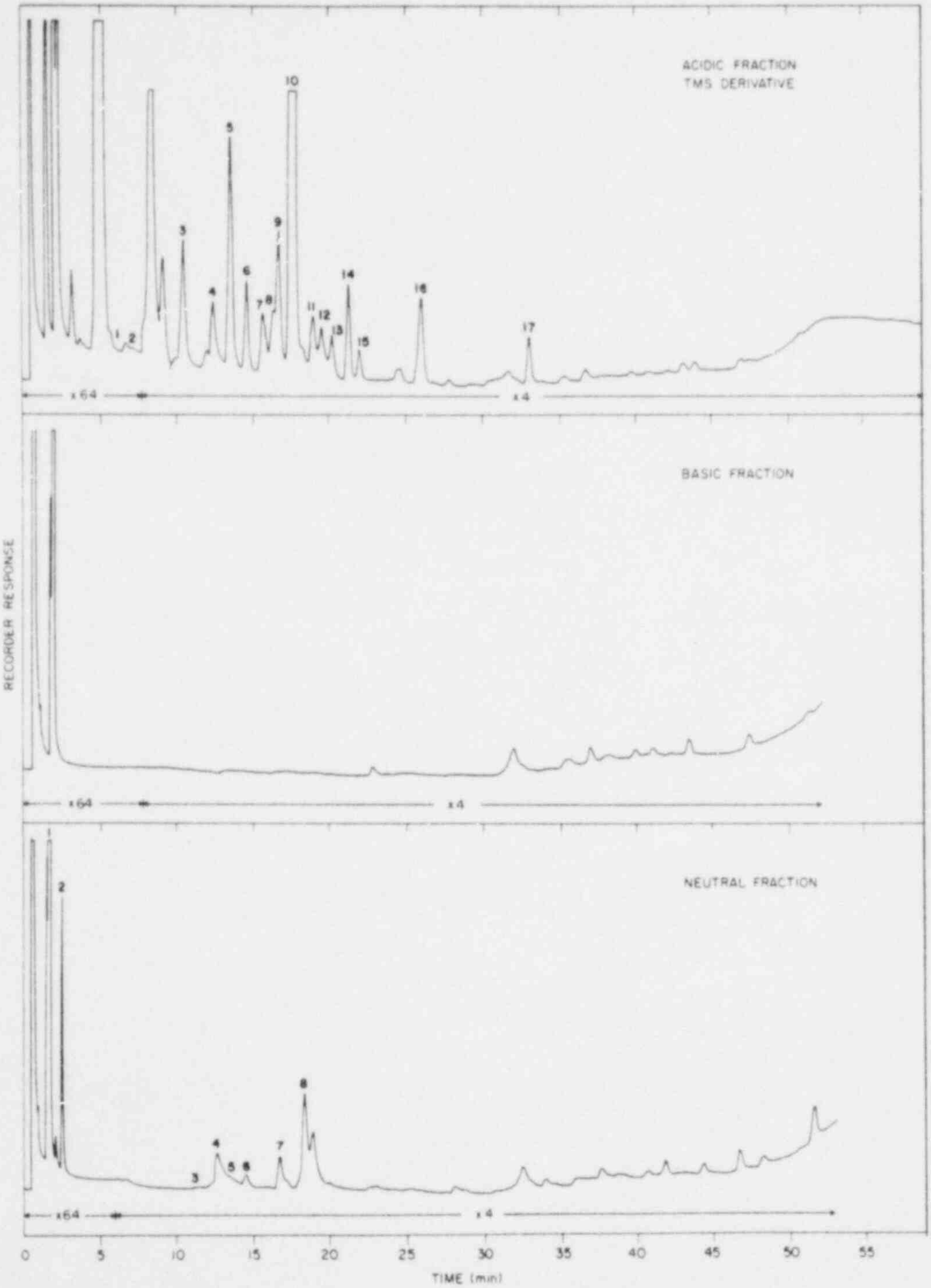

Figure 5.9. Gas chromatogram of methylene chloride extract of trench 27 water sample from Maxey Flats, Kentucky, disposal site.

Table 5.7

Concentration of Organic Compounds Identified in Trench 27 Water Sample From Maxey Flats, Kentucky, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	2-Methylbutanoic acid	0.98
2	3-Methylbutanoic acid	0.48
3	C_6 branched acid[b]	0.66
4	Phenol	0.40
5	Hexanoic acid	1.2
6	2-Methylhexanoic acid	0.40
7	C_8 acid	N.Q.
8,9	Cresol (isomers)	0.70
10	2-Ethylhexanoic acid	17
11	C_8 branched acid[c]	0.03
12	C_8 branched acid[c]	0.03
13	Benzoic acid	0.22
14	Octanoic acid	0.64
15	Phenylacetic acid	0.08
16	Phenylpropionic acid	0.56
17	Phenylhexanoic acid	N.Q.[d]
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	Toluene	3.4
3	Bis(2-ethoxyethyl) ether	N.Q.
4	2-Ethyl-1-hexanol	0.23
5	Fenchone	N.Q.
6	Triethyl phosphate	N.Q.
7	Camphor	N.Q.
8	Naphthalene	0.15

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[a] Corresponds to numbers in Figure 5.9.

[b] Quantified using 3-Methylpentanoic acid standard.

[c] Quantified using 2-Ethylhexanoic acid standard.

[d] Not quantified.

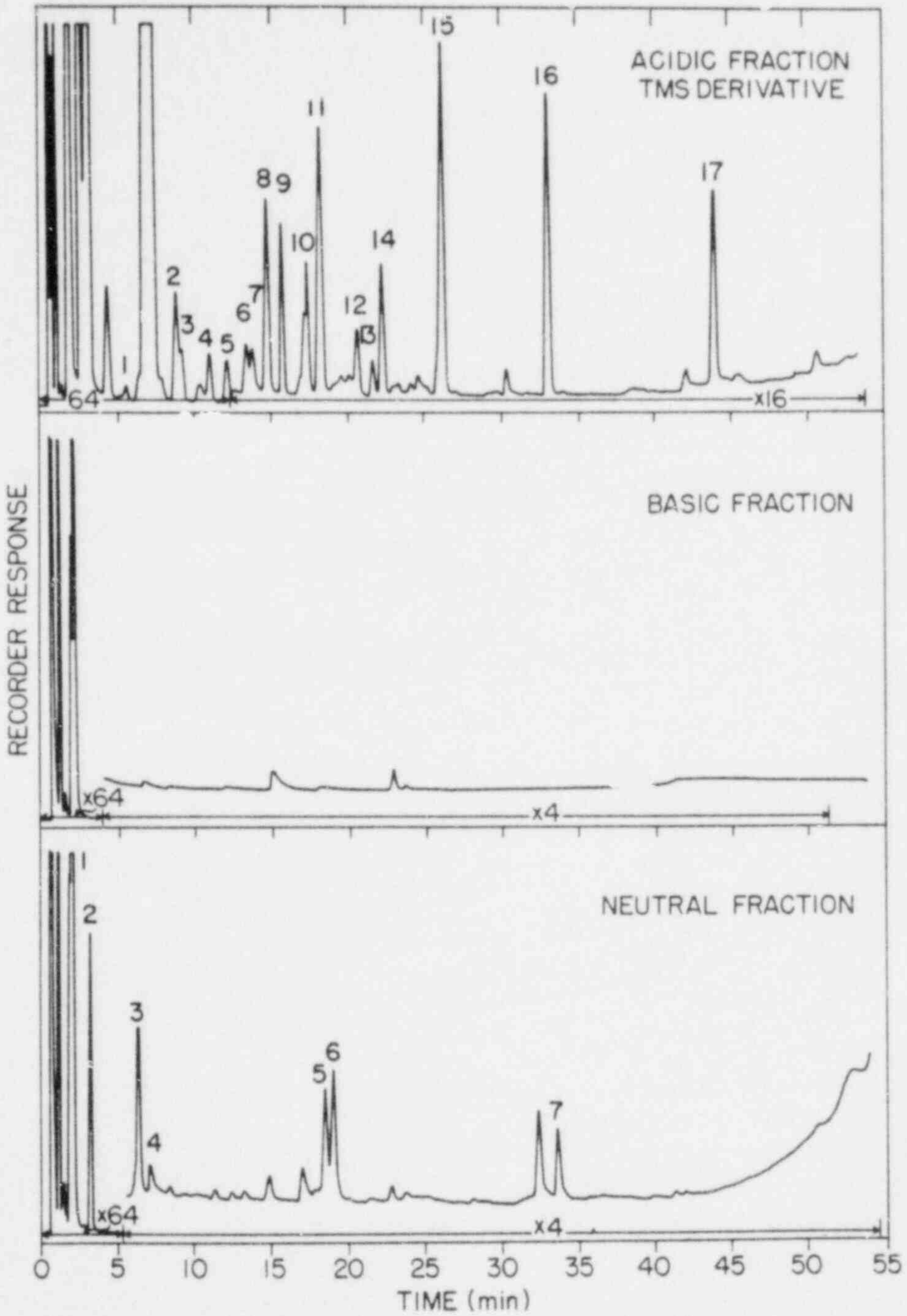

Figure 5.10. Gas chromatogram of methylene chloride extract of trench 32 water sample from Maxey Flats, Kentucky, disposal site.

Table 5.8

Concentration of Organic Compounds Identified in Trench 32
Water Sample From Maxey Flats, Kentucky, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	Isobutyric acid	2.0
2	2-Methylbutyric acid	13
3	3-Methylbutyric acid	5.8
4	Pentanoic acid	4.7
5	2-Methylpentanoic acid[b]	4.0
6	3-Methylpentanoic acid	1.4
7	Phenol	1.2
8	Hexanoic acid	4.7
9	2-Methylhexanoic acid	3.2
10	Cresol (isomers)	4.2
11	2-Ethylhexanoic acid	8.8
12	Benzoic acid	1.9
13	Octanoic acid	1.3
14	Phenylacetic acid	3.4
15	Phenylpropionic acid	9.8
16	Phenylhexanoic acid	N.Q.[c]
17	Phthalate	N.Q.
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	Toluene	7.0
3	Xylene	0.48
4	Cyclohexanol	0.24
5	Naphthalene	0.28
6	α-Terpineol	0.49
7	Tributyl phosphate	0.36

[a] Corresponds to numbers in Figure 5.10.

[b] Quantified using 3-Methylpentanoic acid standard.

[c] Not quantified.

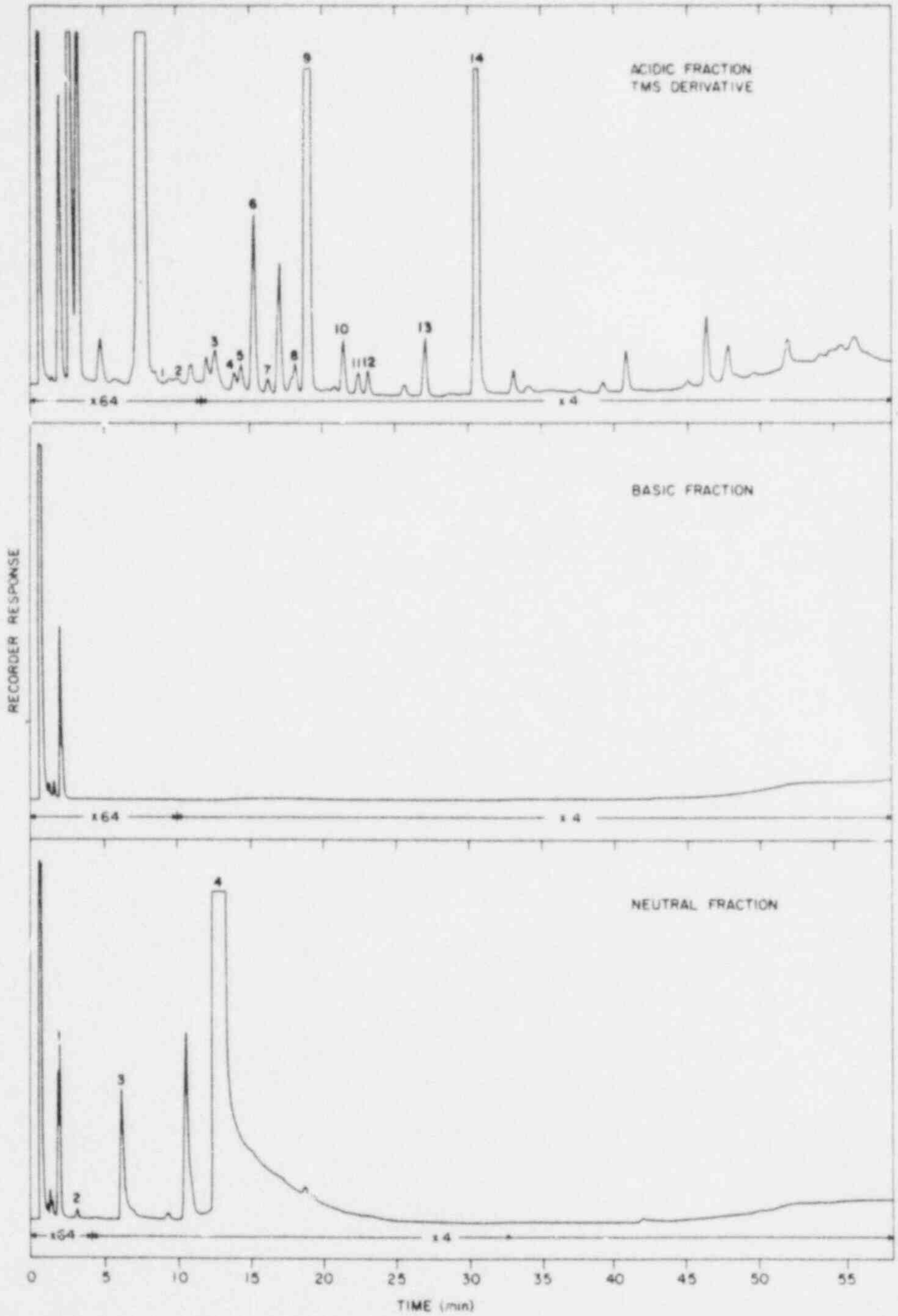

Figure 5.11. Gas chromatogram of methylene chloride extract of trench 33L-4 water sample from Maxey Flats, Kentucky, disposal site.

Table 5.9

Concentration of Organic Compounds Identified in Trench 33L-4 Water Sample From Maxey Flats, Kentucky, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
<u>Acidic Fraction:</u>		
1	3-Methylbutanoic acid	1.6
2	Valeric acid	1.3
3	C_6 branched acid[b]	0.74
4	C_6 branched acid[b]	0.41
5	Phenol	0.20
6	Hexanoic acid	2.0
7	2-Methylhexanoic acid	0.30
8	Cresol (isomers)	0.28
9	2-Ethylhexanoic acid	27
10	Benzoic acid	0.59
11	Octanoic acid	0.39
12	Phenylacetic acid	0.25
13	Phenylpropionic acid	0.70
14	Vanillin	8.6
<u>Neutral Fraction:</u>		
1	p-Dioxane	N.Q.[c]
2	Toluene	0.39
3	Cyclohexanol	1.1
4	2-Ethyl-1-hexanol	N.Q.

[a] Corresponds to numbers in Figure 5.11.

[b] Quantified using 3-Methylpentanoic acid standard.

[c] Not quantified.

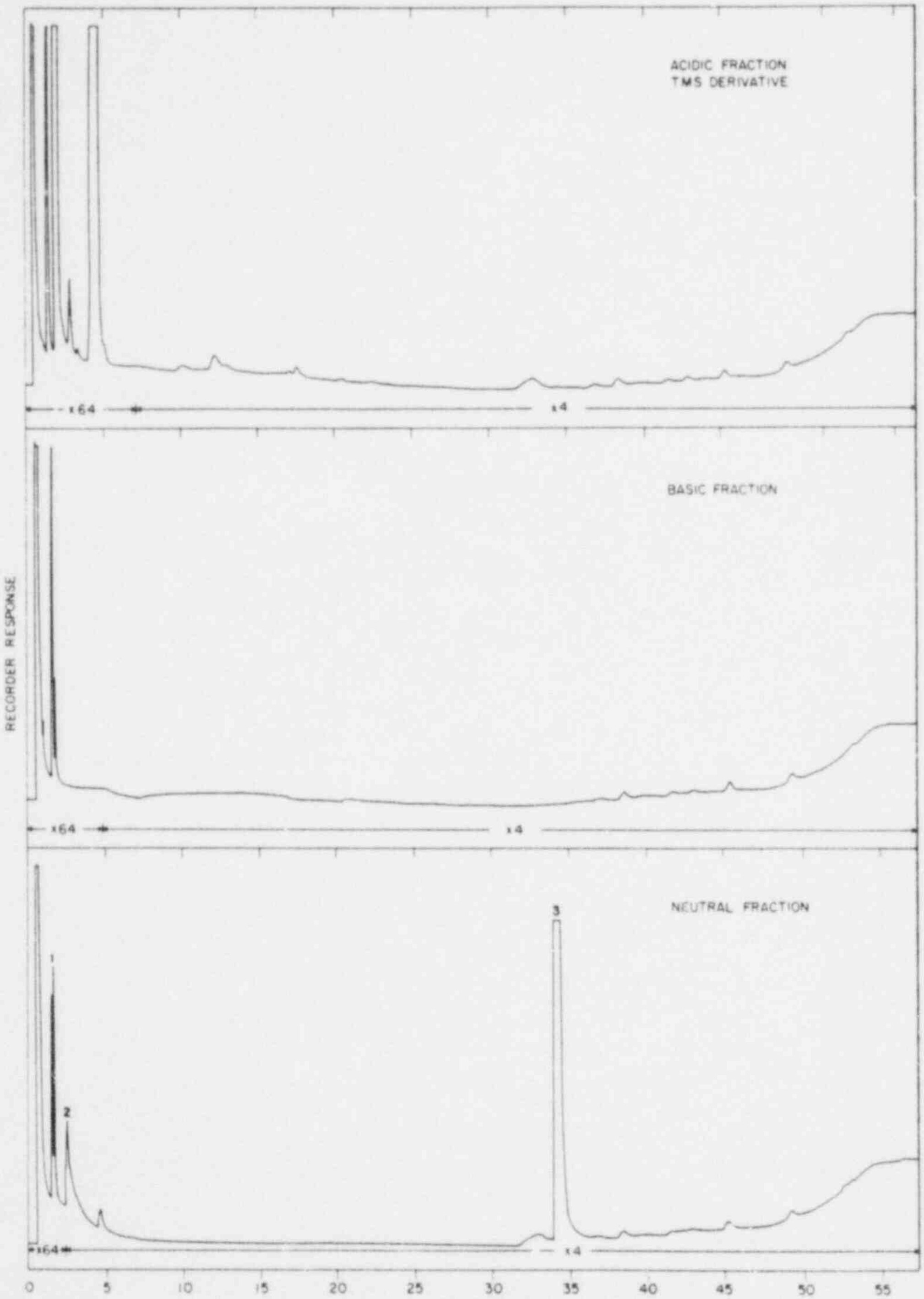

Figure 5.12. Gas chromatogram of methylene chloride extract of trench 33L-18 water sample from Maxey Flats, Kentucky, disposal site.

Table 5.10

Concentration of Organic Compounds Identified in Trench 33L-18 Water Sample From Maxey Flats, Kentucky, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Neutral Fraction:		
1	p-Dioxane	N.Q.[b]
2	Toluene	<0.12
3	Tributyl phosphate	N.Q.

[a] Corresponds to numbers in Figure 5.12.

[b] Not quantified.

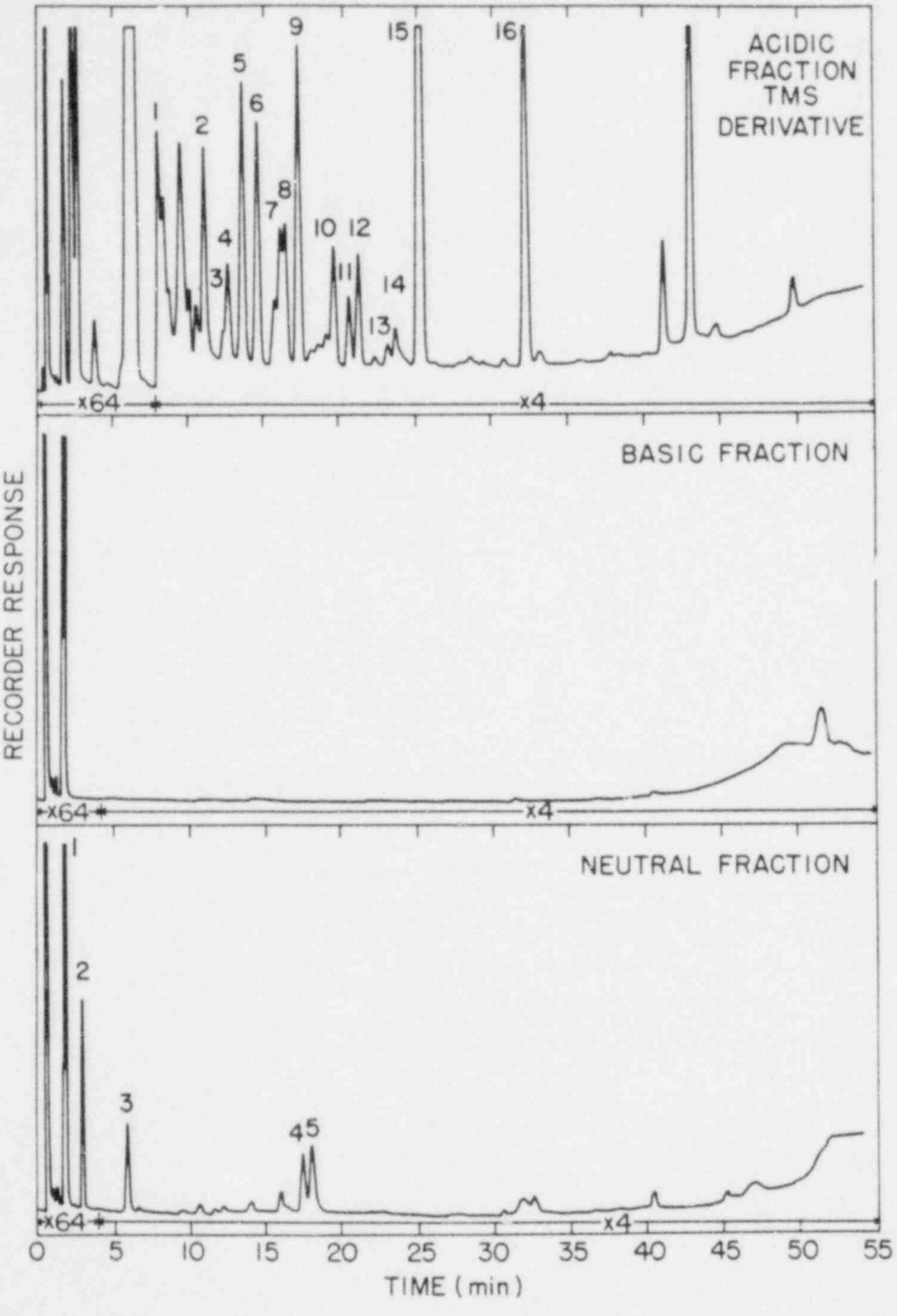

Figure 5.13. Gas chromatogram of methylene chloride extract of well UB1 water sample from Maxey Flats, Kentucky, disposal site.

Table 5.11

Concentration of Organic Compounds Identified in Well UB1 Water Sample From Maxey Flats, Kentucky, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	2-Methylbutyric acid[b]	0.84
2	2-Methylpentanoic acid[b]	0.73
3	3-Methylpentanoic acid	0.16
4	Phenol	0.31
5	Hexanoic acid	1.1
6	2-Methylhexanoic acid	0.74
7	Cresol (isomer)	0.39
8	Cresol (isomer)	0.38
9	2-Ethylhexanoic acid	1.6
10	Benzoic acid	0.40
11	Octanoic acid	0.38
12	Phenylacetic acid	0.44
13	Toluic acid (isomer)	0.13
14	Toluic acid (isomer)	0.28
15	Phenylpropionic acid	3.8
16	Phenylhexanoic acid	N.Q.[c]
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	Toluene	2.7
3	Xylene	0.12
4	Naphthalene	0.09
5	α-Terpineol	0.16

[a] Corresponds to numbers in Figure 5.13.

[b] Quantified using 3-Methylpentanoic acid standard.

[c] Not quantified.

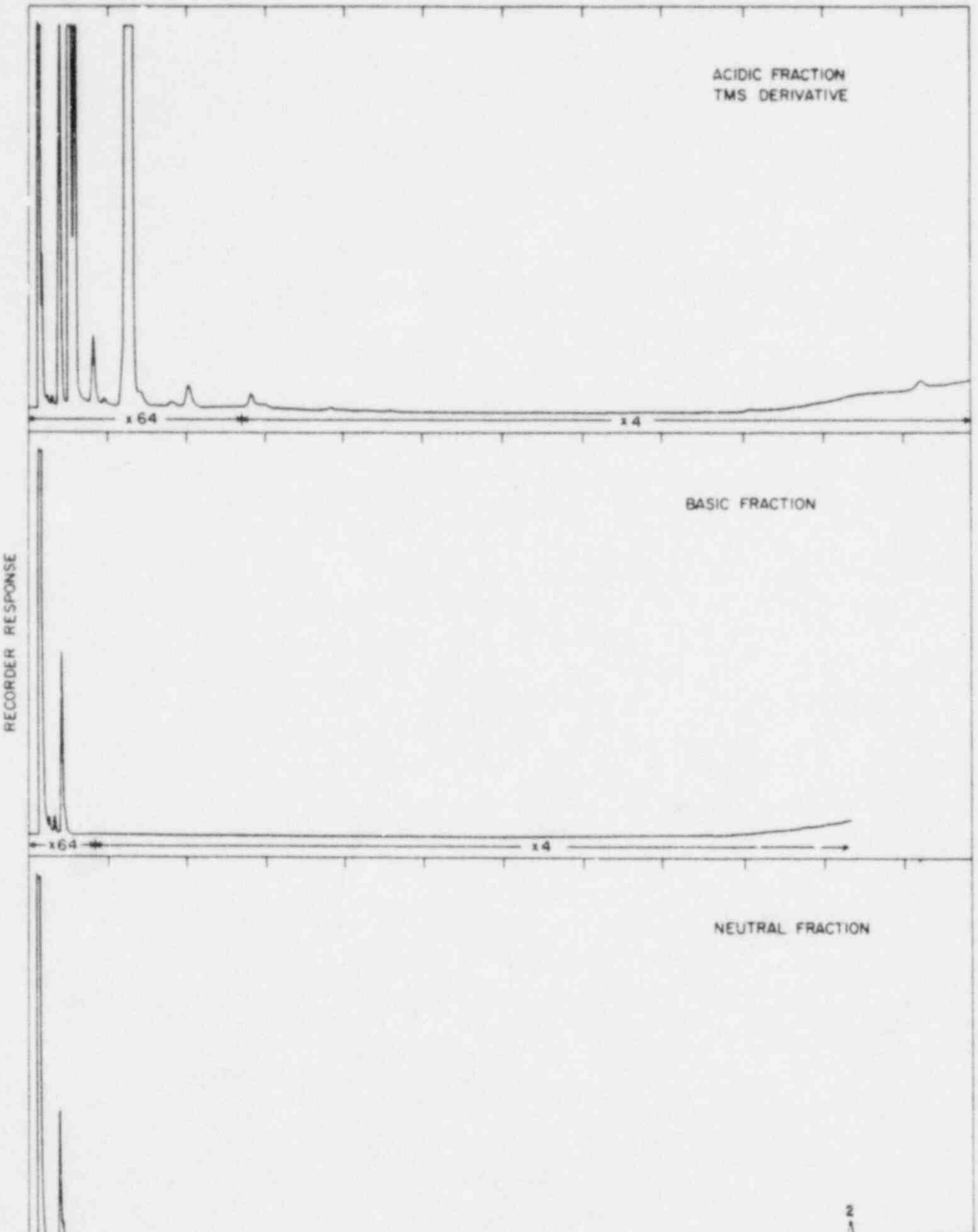

Figure 5.14. Gas chromatogram of methylene chloride extract of well UB1-A water sample from Maxey Flats, Kentucky, disposal site.

Table 5.12

Concentration of Organic Compounds Identified in Well UB1-A Water Sample From Maxey Flats, Kentucky, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Neutral Fraction:		
1	Dibutyl phthalate	0.02
2	Triphenyl phosphate	N.Q.[b]

[a] Corresponds to numbers in Figure 5.14.

[b] Not quantified.

Table 5.13

Organic Compounds Identified in Other Water Samples From Maxey Flats, Kentucky, Disposal Site[a]

Compound	Trench 2	7	18	33L-9	37
Aniline		+			
4-t-Butylphenol		+	+		
Benzoic acid					+
Bis(2-chloroethyl)ether	+	+			
Bis(2-chloroethoxy)ethane		+			
Bis(2-chloroethoxy)methane	+				
Cresol(isomers)		+			+
C_5 acid	+	+			
C_6 acid		+			+
C_8 acids		+	+		+
Cyclohexylamine			+		
Dicyclohexylamine			+		
Diethylphthalate			+		+
Dimethylnaphthalene			+		
p-Dioxane		+		+	
2-Ethylhexanol	+			+	+
Naphthalene					+
Octanoic acid					+
Phenol					+
2-Phenylcyclohexanol		+			
Phenylacetic acid		+			+
Phenylpropionic acid					+
(Propylene glycol)	+				
Tributyl phosphate[n]	+		+	+	
Triethyl phosphate			+		
Toluene	+				+
Xylene					+
Tripropylene glycol methyl ethyl			+		

[a] Organic compounds identified, but not quantified.

aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols. Typically, the acidic fraction contained several compounds, the neutral fraction contained fewer compounds, and the basic fraction, except in the case of one or two trench water samples, did not contain any detectable compounds. This may be due to the limitation of using a gas chromatographic column not specifically selected for the detection of basic compounds. It is interesting to note that in many cases two water samples from a trench taken a year apart contained the same or similar, types of major compounds, although quantitative variations between the two samples were generally observed.

A comparison of organics identified in well UB1 and trench 32 shows that every compound in well UB1, except tolulic acid, is present in trench 32, and a majority of these compounds are present in trench 19S. Other nearby trenches, which were not sampled, may also contain these compounds.

The types of organic compounds identified in the trench waters reflect both the nature of the buried waste and the products of biodegradation. Solvents or scintillation fluids, such as p-dioxane, toluene, and xylene are present. Tributyl phosphate may originate from the process of solvent extraction of metal ions from solutions of reactor products, and low molecular weight straight- and branched-chain aliphatic acids are due mainly to microbial degradation of complex natural and synthetic materials in the buried waste.

5.3.1.4 Radiochemical Results for Maxey Flats, Kentucky

5.3.1.4.1 Dissolved Radionuclides

The activities of dissolved radionuclides for trench waters collected September 1976, July 1977 and May 1978 are reported in Table 5.14. The most outstanding feature was the increase in ^{3}H and $^{239,240}Pu$ activity by one order of magnitude and the activity of ^{238}Pu by two orders of magnitude, in trench 32. Also, an order of magnitude increase in ^{238}Pu was noted for trench 26. The well water sample UB1-A contained the lowest radionuclide activities. Tritium (2.3 E9 pCi/L, trench 32) was the most abundant radionuclide found. ^{90}Sr (2.0 E6 pCi/L, trench 7) and ^{238}Pu (2.1 E5 pCi/L, trench 19S) were the next most abundant radionuclides found.

5.3.1.4.2 Well UB1

Contaminated water was encountered in five wells drilled by USGS. The water from well UB1 contained 4.8 E8 pCi/L tritium, 7.1 E4 pCi/L ^{90}Sr, 4.7 E3 pCi/L ^{60}Co, 3.3 E1 pCi/L ^{238}Pu, and 4.2 E-1 pCi/L $^{239,240}Pu$. The zone of contamination in four wells, including well UB1, was subsequently grouted with cement, but well UB1-A drilled nearby was left open to the contaminated zone (Figure 4.1). Water from well UB1-A is also contaminated, but at a lower activity level than UB1.

The presence of radioisotopes above background in wells UB1 and UB1-A shows that migration of radionuclides from trenches has occurred.

5.3.1.4.3 Radionuclides in Particulates

Radionuclides in suspended particulates filtered from trench and well waters collected at Maxey Flats, Kentucky, during May of 1978 are shown in Table 5.15 and Table 5.16. The particulates were obtained at the time the samples were anoxically filtered through 0.45 μm Millipore filters (Section 5.3).

Table 5.14

Concentration of Dissolved Radionuclides in Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site
pCi/L (±2σ%) [a]

Radionuclide	Date	Trench 2	Trench 7	Trench 18	Trench 19S[b]	Trench 26	Trench 27
Gross Alpha	9/76	1.2 E4 (4.3)	2.7 E3 (5.3)	1.5 E4 (4.3)	2.3 E5 (<1)	4.1 E4 (2.7)	4.8 E4 (2.3)
	7/77	6.7 E3 (8.5)	---[c]	---	---	2.7 E4 (4.0)	---
	5/78	---	---	---	1.7 E5 (1.7)	---	4.9 E3 (11)
Gross Beta	9/76	2.8 E4 (3.6)	5.3 E6 (<1)	1.5 E5 (1.4)	7.5 E5 (<1)	1.3 E5 (1.6)	7.2 E5 (<1)
	7/77	2.4 E4 (5.5)	---	---	---	1.2 E5 (1.2)	---
	5/78	---	---	---	6.4 E5 (2.0)	---	4.0 E5 (2.6)
Tritium	9/76	2.5 E7 (<1)	4.4 E8 (<1)	4.5 E8 (<1)	6.9 E7 (<1)	2.0 E8 (<1)	3.1 E8 (<1)
	7/77	2.1 E7 (<1)	---	---	---	1.3 E8 (<1)	---
	5/78	---	---	---	6.8 E7 (<1)	---	5.9 E8 (<1)
^{90}Sr[d]	9/76	6.8 E3 (<1)	2.0 E6 (<1)	4.7 E4 (<1)	2.6 E5 (<1)	3.5 E4 (<1)	2.0 E5 (<1)
	7/77	3.6 E3 (10)	---	---	---	3.0 E4 (10)	---
	5/78	---	---	---	2.9 E5 (10)	---	2.1 E5 (10)
^{238}Pu[d]	9/76	3.8 E3 (2.7)	5.0 E0 (20)	5.9 E2 (5.9)	1.7 E5 (7.6)	3.1 E4 (6.8)	1.3 E4 (3.1)
	7/77	9.4 E3 (10)	---	---	---	1.3 E5 (10)	---
	5/78	---	---	---	2.1 E5 (10)	---	4.1 E3 (10)
^{239,240}Pu[d]	9/76	4.1 E2 (8.6)	<1	5.1 E1 (26)	2.1 E4 (24)	2.7 E3 (2.2)	1.7 E3 (13)
	7/77	2.8 E2 (10)	---	---	---	3.5 E3 (10)	---
	5/78	---	---	---	8.4 E2 (10)	---	6.7 E2 (10)
^{241}Am	9/76	4.3 E3 (3.9)	<20	<20	7.7 E2 (7.0)	1.0 E3 (5.7)	1.5 E4 (3.8)
	7/77	2.9 E3 (8.9)	---	---	---	N.D.[e]	---
	5/78	---	---	---	1.5 E3 (17)	---	1.4 E3 (17)
^{60}Co	9/76	1.4 E4 (1.9)	2.5 E3 (5.1)	2.2 E4 (1.5)	1.3 E3 (23)	1.3 E3 (6.6)	2.0 E4 (3.2)
	7/77	1.0 E4 (4.5)	---	---	---	1.4 E3 (14)	---
	5/78	---	---	---	2.5 E3 (11)	---	1.3 E3 (21)
^{134}Cs	9/76	<100	<100	<100	<100	3.1 E2 (18)	<100
	7/77	N.D.	---	---	---	N.D.	---
	5/78	---	---	---	N.D.	---	N.D.
^{137}Cs	9/76	<100	4.6 E[illegible] ([illegible].9)	4.9 E3 (3.0)	3.2 E3 (9.8)	7.5 E3 (2.0)	2.3 E4 (2.4)
	7/77	N.D.	---	---	---	5.3 E3 (5.7)	---
	5/78	---	---	---	1.0 E4 (3.8)	---	8.0 E3 (4.6)

[a] Number in ( ) = 2σ percent counting uncertainty.
[b] Trench 19S sample collected 9/76 contained 2.3 E1 (11) pCi/L ^{22}Na in addition to radionuclide listed in table.
[c] --- indicates sample was not collected from trench on indicated date.
[d] Analyses of 7/77 and 5/78 series performed by LFE Laboratories, Richmond, California.
[e] N.D. = not detected.

The most abundant radionuclide sorbed on the particulates was ^{238}Pu (1.4 E4 pCi/L in trench 19S). The next most abundant elements sorbed on suspended particulates were ^{90}Sr, ^{239,240}Pu, ^{241}Am and ^{60}Co. Well water from UB1-A was found to contain ^{238}Pu in both the aqueous and solid phase.

The distributions of radionuclides between suspended particulates and the aqueous phases of the water samples are given in Table 5.17 and Table 5.18. These distribution ratios <u>do</u> <u>not</u> represent the total retardation capability of the soil since they are not the sorption coefficients for the bulk sediment.

Table 5.14, continued

Concentration of Dissolved Radionuclides in Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site
pCi/L (±2σ%)[a]

Radionuclide	Date	Trench 32	Trench 33L-4[f]	Trench 33L-9	Trench 33L-18	Trench 37[g]	Well UB1-A
Gross Alpha	9/76	8.6 E4 (1.4)	7.6 E3 (5.2)	2.2 E4 (3.2)	---	3.2 E4 (2.8)	---
	7/77	3.1 E4 (3.9)	---	---	---	---	---
	5/78	---	4.9 E3 (11)	---	5.9 E5 (3.0)	---	<10
Gross Beta	9/76	1.2 E6 (<1)	7.0 E4 (1.9)	4.2 E4 (2.6)	---	1.1 E5 (1.9)	---
	7/77	1.8 E6 (<1)	---	---	---	---	---
	5/78	---	3.7 E4 (8.8)	---	2.3 E5 (3.5)	---	3.1 E2 (30)
Tritium	9/76	2.1 E8 (<1)	6.2 E7 (<1)	6.2 E7 (<1)	---	1.1 E7 (<1)	---
	7/77	2.3 E9 (<1)	---	---	---	---	---
	5/78	---	2.9 E7 (<1)	---	4.6 E7 (<1)	---	5.8 E6 (<1)
^{90}Sr	9/76	3.8 E5 (<1)	2.4 E4 (<1)	1.1 E4 (<1)	---	1.9 E3 (<1)	---
	7/77	5.4 E5 (<10)	---	---	---	---	---
	5/78	---	1.7 E4 (10)	---	3.4 E4 (10)	---	6.3 E1 (10)
^{238}Pu	9/76	3.6 E3 (4.2)	9.9 E3 (4.4)	---	---	1.8 E4 (1.0)	---
	7/77	1.1 E5 (10)	---	---	---	---	---
	5/78	---	4.2 E2 (10)	---	8.0 E3 (12)	---	1.4 E1 (16)
^{239,240}Pu	9/76	1.1 E2 (25)	8.4 E2 (40)	---	---	3.1 E2 (2.6)	---
	7/77	2.9 E3 (10)	---	---	---	---	---
	5/78	---	6.6 E3 (10)	---	2.4 E3 (20)	---	5.4 E-1 (110)
^{241}Am	9/76	<40	<20	<40	---	2.8 E4 (1.0)	---
	7/77	N.D.	---	---	---	---	---
	5/78	---	N.D.	---	3.9 E3 (5.8)	---	N.D.
^{60}Co	9/76	6.0 E3 (5.6)	<300	3.2 E3 (9.0)	---	5.0 E4 (1.0)	---
	7/77	3.5 E3 (8.1)	---	---	---	---	---
	5/78	---	3.6 E1 (64)	---	5.5 E3 (6.6)	---	2.5 E2 (13)
^{134}Cs	9/76	4.2 E2 (24)	<100	<100	---	1.7 E3 (4.3)	---
	7/77	N.D.	---	---	---	---	---
	5/78	---	N.D.	---	1.2 E3 (14)	---	N.D.
^{137}Cs	9/76	6.0 E3 (4.6)	<100	4.8 E3 (5.3)	---	9.8 E3 (2.1)	---
	7/77	4.8 E3 (5.5)	---	---	---	---	---
	5/78	---	2.1 E2 (66)	---	2.2 E4 (2.4)	---	N.D.

[f] Trench 33L-4 sample collected 5/78 contained [illegible] E0 (22) pCi/L ^{22}Na.
[g] Trench 37 sample collected 9/76 contained 3.7 E3 (6.5) pCi/L ^{54}Mn and 2.7 E3 (16) pCi/L ^{65}Zn.

These distribution ratios of the suspended particulates do, however, reflect the potential for radionuclide mobility of plutonium as a sorbed species relative to dissolved plutonium. Similar radionuclide sorption was observed for suspended particulates in trench waters collected at the West Valley, New York, disposal site. The most strongly sorbed species are ^{241}Am and ^{238,239,240}Pu. In addition, ^{90}Sr, ^{60}Co and ^{137}Cs were sorbed on the suspended particulates.

See section 5.3.2.4.2 for further comments relative to geohydrological considerations.

Table 5.15

Radionuclides in Particulates Filtered From Water Samples Taken From Maxey Flats, Kentucky, Disposal Site, May 1978[a]

[pCi/mg ($\pm$ 2σ%)]

Radionuclide	Trench 19S	Trench 27	Trench 33L-4	Trench 33L-18	Well UB1-A
^{90}Sr[b]	5.0 E1 (10)	1.4 E 1 (10)	2.4 E 0 (10)	1.6 E 0 (30)	N.D.[c]
^{238}Pu[b]	1.5 E3 (10)	6.9 E 1 (12)	7.1 E-1 (10)	2.5 E 0 (10)	2.3 E-1 (12)
^{239,240}Pu[b]	2.7 E1 (10)	1.4 E 1 (16)	1.2 E 0 (10)	7.6 E-1 (14)	N.D.
^{241}Am	1.9 E1 (2)	7.0 E 0 (3)	N.D.	2.8 E-1 (20)	N.D.
^{60}Co	2.4 E0 (15)	4.1 E-1 (30)	N.D.	4.4 E-1 (20)	N.D.
^{134}Cs	N.D.	1.1 E-1 (66)	N.D.	8.0 E-2 (49)	N.D.
^{137}Cs	3.3 E0 (10)	1.0 E 0 (13)	N.D.	1.4 E 0 (7)	N.D.

[a] Water samples were filtered through 0.45 μm Millipore filter.
[b] Analyses performed by LFE Laboratories, Richmond, California.
[c] N.D. = not detected.

Table 5.16

Radionuclides in Particulates Filtered From Water Samples Taken From Maxey Flats, Kentucky, Disposal Site, May 1978[a]

$$\left[\frac{\text{picocuries}}{\text{liter of water filtered } (\pm 2\sigma\%)}\right]$$

Radionuclide	Trench 19S	Trench 27	Trench 33L-4	Trench 33L-18	Well UB1-A
^{90}Sr[b]	4.8 E2 (10)	3.3 E2 (10)	3.9 E1 (10)	6.3 E1 (30)	N.D.[c]
^{238}Pu[b]	1.4 E4 (10)	1.6 E3 (12)	1.2 E1 (10)	9.9 E1 (10)	3.1 E0 (12)
^{239,240}Pu[b]	2.6 E2 (10)	3.2 E2 (16)	1.9 E1 (10)	3.0 E1 (14)	N.D.
^{241}Am	1.8 E2 (2.4)	1.6 E2 (2.8)	N.D.	1.1 E1 (20)	N.D.
^{60}Co	2.2 E1 (15)	9.6 E0 (30)	N.D.	1.7 E1 (20)	N.D.
^{134}Cs	N.D.	2.5 E0 (66)	N.D.	3.2 E0 (49)	N.D.
^{137}Cs	3.2 E1 (10)	2.3 E1 (13)	N.D.	5.4 E1 (6.8)	N.D.

[a] Water samples filtered through 0.45 μm Millipore filter.
[b] Analyses performed by LFE Laboratories, Richmond, California.
[c] N.D. = not detected.

Table 5.17

Distribution of Radionuclides Between Suspended Particulates and Aqueous Phase in Water Samples Taken From Maxey Flats, Kentucky, Disposal Site, May 1978[a]

[mL/g (± 2σ%)]

Radionuclide	Trench 19S	Trench 27	Trench 33L-4	Trench 33L-18	Well UB1-A
^{90}Sr	1.7 E2 (14)	6.7 E1 (14)	1.4 E2 (14)	4.7 E1 (32)	d
^{238}Pu	6.8 E3 (14)	1.7 E4 (16)	1.7 E3 (14)	3.1 E2 (16)	1.6 E4 (20)
$^{239,240}Pu$	3.2 E4 (14)	2.1 E4 (19)	1.8 E2 (14)	3.2 E2 (24)	d
^{241}Am	1.2 E4 (17)	5.0 E3 (17)	c	7.2 E1 (21)	c
^{60}Co	9.3 E2 (19)	3.1 E2 (27)	d	8.0 E1 (21)	d
^{134}Cs	c	b	c	6.5 E1 (51)	c
^{137}Cs	3.2 E2 (11)	1.2 E2 (14)	d	6.2 E1 (7)	c

$$^{a}\text{Ratio} = \frac{\text{Activity in suspended particulates (pCi/g)}}{\text{Activity in aqueous phase (pCi/mL)}} .$$

[b] Activity found only in the particulate fraction.
[c] No activity found in either fraction.
[d] Activity found only in the dissolved fraction.

Table 5.18

Comparison of Radionuclide Activity in the Dissolved Fraction Relative to That in the Suspended Particulate Fraction in Water Samples Taken From Maxey Flats, Kentucky, Disposal Site, May 1978

[Ratio[a] (± 2σ%)]

Radionuclide	Trench 19S	Trench 27	Trench 33L-4	Trench 33L-18	Well UB1-A
^{90}Sr	6.1 E2 (14)	6.4 E2 (14)	4.4 E2 (14)	5.4 E2 (32)	d
^{238}Pu	1.5 E1 (14)	2.6 E0 (16)	3.5 E1 (14)	8.1 E1 (16)	4.6 E0 (20)
$^{239,240}Pu$	3.3 E0 (14)	2.1 E0 (19)	3.4 E2 (14)	7.9 E1 (24)	d
^{241}Am	8.5 E0 (17)	8.6 E0 (17)	c	3.5 E2 (21)	c
^{60}Co	1.1 E2 (19)	1.4 E2 (37)	d	3.2 E2 (21)	d
^{134}Cs	c	b	c	3.8 E2 (51)	c
^{137}Cs	3.2 E2 (11)	3.4 E2 (14)	d	4.0 E2 (7)	c

$$^{a}\text{Ratio} = \frac{\text{Concentration of dissolved radionuclides (pCi/L)}}{\text{Activity in suspended particulates expressed as picocuries per liter of water filtered}}$$

[b] Activity found only in the particulate fraction.
[c] No activity found in either fraction.
[d] Activity found only in the dissolved fraction.

5.3.2 West Valley, New York, Disposal Site

5.3.2.1 Field Measurement

In-situ measurements made at West valley for collection periods, November 1977 and October 1978, are shown in Table 5.19. The sampling locations correspond to positions indicated in Figure 4.4. The pH range is not as wide as observed in Maxey Flats trench waters.

The field measured Eh potential for each West Valley, New York, trench water was more negative at the second sampling, approximately a year later. The decrease in Eh values ranged from 36 mv for trench 1 to 227 mv for trench 3. The same electrode system and calculation methods were used. It appears that a more progressively reducing environment was being produced, possibly by continuing anaerobic microbial activity or chemical changes due to leaching of the buried wastes. Although changes in the inorganic species were noted in Section 5.3.2.2, no specific reason for the decreases in Eh was identified. However, new trench caps were placed over the north trenches between August 1978 and September 1978, which may have reduced air movement into the trenches, and the north trenches (3,4,5) showed larger Eh decreases than the south trenches (8,9).

Table 5.19

Field Measurements of Water Samples Taken From West Valley, New York, Disposal Site[a]

Sampling Location	Date	Apparent Color	pH	Eh (mV,NHE)[a]	Dissolved Oxygen (mg/L)	Specific Conductance (μmho/cm)	Temperature (°C)
Trench 2	11/77	black	7.7	47	b	6700	11.7
Trench 3	11/77	dark gray	7.5	240	b	8750	10.2
	10/78	black tint	7.3	-3.4	0.1	7600	10.5
Trench 4	11/77	light yellow	7.2	210	b	8100	13.3
	10/78	light green	6.5	54	0.1	14 200	13.5
Trench 5	11/77	yellow-gray	7.1	240	b	7200	10.8
	10/78	dark green	6.7	40	0.2	6750	10.5
Trench 8	11/77	light yellow	6.7	93	b	7900	11.1
	10/78	light yellow	6.9	-6.3	0.05	5900	12.5
Trench 9	11/77	light grey	7.3	71	b	3850	13.6
	10/78	yellow-green	6.7	18	0.15	3400	13.5

[a] Field measurements of redox potentials (Eh) are reported relative to the normal hydrogen electrode (NHE).

[b] Dissolved oxygen not measured in November 1977.

5.3.2.2 Inorganic

Results of inorganic analyses for the two sampling periods are given in Tables 5.20 and 5.21.

The shape of an acid-base titration curve can yield some generalized characterizations of the chemical system. As such, comparisons between titration curves of the same trenches sampled on two different occasions are shown in Figures 5.15-5.19. Standard 0.1 N HCl and 0.1 N NaOH were added to 25-ml aliquots of trench water immediately after filtration.

Trenches 3, 8, and 9 demonstrated little variation over a year, whereas trenches 4 and 5 appear to have changed, demonstrating the non-static composition of these burial sites leachates.

Shown in Figure 5.20 is a titration curve of Ehmke well water, which is representative of a natural ground water one mile south of the West Valley, burial site. A sharp inflection point at pH ∿7 and large changes of pH following small additions of acid and base are typical with simple ground water. The long plateaus and bumps in the trench water titration curves indicate complex water systems. Alkalinity values given in parenthesis are obtained by determining the inflection point of the corresponding pH vs. mL of titrant graph. The conventional method of titrating to pH 4.5 ascribes the entire alkalinity to bicarbonate, carbonate and hydroxide. This is not possible in the buffered trench water systems reported here. As graphically illustrated, the pH 4.5 end point is on the plateau of the curve.

Nitrogen in an oxidized state was found in small quantities (less than 3 mg/L). Nitrogen as ammonia was found more abundantly in all the trenches and this is presumed to be a consequence of the reducing environment present in the trenches.

The probe method of analyzing for fluoride is sensitive to the presence of complexing agents which can combine with the F^- and results in lower measured F^- values. The standard additions method for measuring F^- by probe is a convenient check on the direct reading method. When the fluoride concentration, as measured by standard addition, is higher than by direct reading, there is reason to suspect the presence of complexing agents. All trenches sampled in 1977, except trench 3, show higher F^- concentrations by standard addition; hence all trenches sampled in 1978 were analyzed by standard addition.

The presence of large amounts of dissolved barium is probably the reason for the absence of dissolved sulfate in trenches 4, 5, and 8, since the solubility product of barium sulfate is $\sim 1 \times 10^{-10}$. However, the presence of both barium and sulfate in trench 3 may be reasonable if the barium is tied up with a chelate, and as such is not available for reaction with dissolved sulfate.

The barium concentration in trench 4 increased in 1978 with no corresponding increase in the anion concentration.

Table 5.20

Concentration of Dissolved Non-Metals in Water Samples Taken From West Valley, New York, Disposal Site (mg/L)

Dissolved Component	Date	Trench 2	Trench 3	Trench 4	Trench 5	Trench 8	Trench 9
Total Alkalinity (as $CaCO_3$)	11/77	3120	1600	1800	1000 (1200)[a]	2040 (3200)[a]	1480
	10/78	--[b]	1730	800	2300	2000	1600
Inorganic Carbon	11/77	670	90	130	50	100	140
	10/78	--	95	130	10	70	120
DOC	11/77	200	1600	350	3600	2700	1400
	10/78	--	1700	630	2900	2900	1700
Hardness (Ca+Mg) (as $CaCO_3$)	11/77	1100	1100	1400	1400	1600	870
	10/78	--	1100	1500	1700	1400	930
Residue (180°C)	11/77	3070	3850	5030	4170	5380	2700
	10/78	--	5140	1240	5310	5600	3850
Chloride	11/77	470	1300	2100	840	850	230
	10/78	--	1300	2100	820	870	82
Nitrogen (N) (NH_3 probe)	11/77	230	240	68	17	140	53
	10/78	--	300	130	180	290	84
Nitrogen (N) (NH_4^+ color)	11/77	230	230	65	16	120	49
	10/78	--	--	--	--	--	--
Nitrogen (N) ($NO_2^- + NO_3^-$)	11/77	<0.05	<0.05	<0.05	2.9[c]	<0.1	<0.05
	10/78	--	1.6	0.87	1.1	<0.02	<0.02
Fluoride Direct Reading	11/77	2.6	1.6	0.6	1.5	0.5	1.6
	10/78	--	--	--	--	--	--
Fluoride Standard Addition	11/77	4.1	1.6	0.9	2.5	2.3	2.3
	10/78	--	1.8	0.4	2.0	0.6	1.8
Phosphate	11/77	<1	7.0	2.9	7.4	<1	<1
	10/78	--	2.9	8.0	3.4	5.8	12
Silica	11/77	15	6.8	13	26	12	10
	10/78	--	2.0	13	9.2	10	14
Sulfate	11/77	<5	24	<5	<5	<5	20
	10/78	--	26	<5	<5	<5	<5
Total Anions (meq/L)	11/77	76	68	95	44	65	36
	10/78	--	90	79	87	81	45

[a] End point taken from titration curve (Figure 5.18).

[b] -- Indicate no sample was collected.

[c] Present as NO_2^-.

Table 5.21

Concentration of Dissolved Metals in Water Samples Taken From West Valley, New York, Disposal Site (mg/L)

Metal	Date	Trench 2	Trench 3	Trench 4	Trench 5	Trench 8	Trench 9
Barium	11/77	<1	62	700	86	560	<1
	10/78	--[a]	70	2900	100	570	<1
Calcium	11/77	72	150	180	300	200	130
	10/78	--	150	250	--	--	--
Cesium	11/77	<0.1	<0.1	<0.1	<0.5	<0.1	<0.1
	10/78	--	<0.1	<0.1	<0.1	<0.1	<0.1
Iron	11/77	13	86	82	260	130	72
	10/78	--	56	150	540	130	57
Lithium	11/77	0.87	2.5	0.62	0.62	0.21	1.1
	10/78	--	2.0	0.39	0.98	0.16	1.3
Magnesium	11/77	220	170	160	140	220	130
	10/78	--	180	190	200	240	150
Manganese	11/77	<0.1	0.6	0.5	1.5	0.6	0.3
	10/78	--	0.34	1.5	2.3	0.5	0.2
Potassium	11/77	330	320	330	340	330	120
	10/78	--	320	820	270	300	91
Sodium	11/77	900	880	970	800	1600	500
	10/78	--	1000	1100	690	1700	430
Strontium	11/77	0.9	3.6	8.3	3.3	5.7	1.0
	10/78	--	0.2	7.7	0.5	1.6	0.5
Total	11/77	86	90	91	82	130	49
Cations[b] (meq/L)	10/78	--	100	150	100	140	47

[a] Trench 2 not sampled in October 1978.
[b] Nitrogen as NH_4^+ from Table 5.20 is included in the total cations.

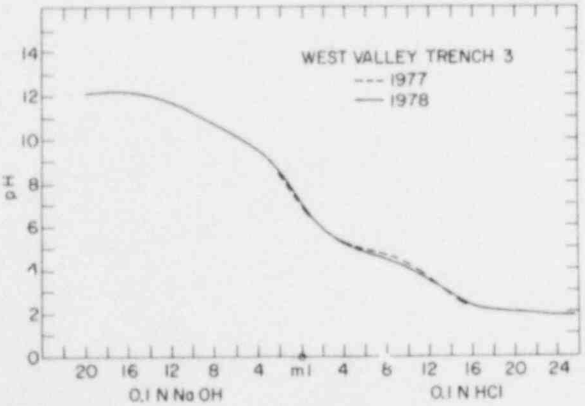

Figure 5.15. Comparison of acid-base titration curves of trench 3 water from West Valley, New York, disposal site.

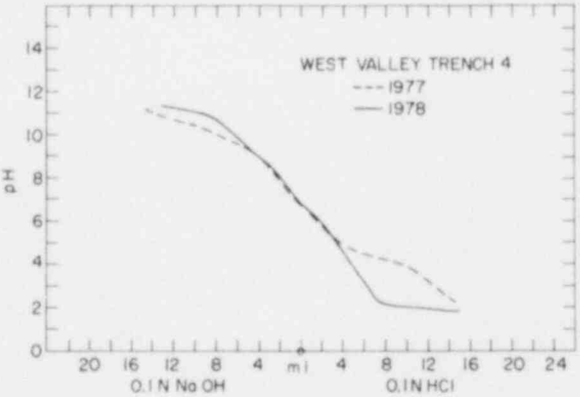

Figure 5.16. Comparison of acid-base titration curves of trench 4 water from West Valley, New York, disposal site.

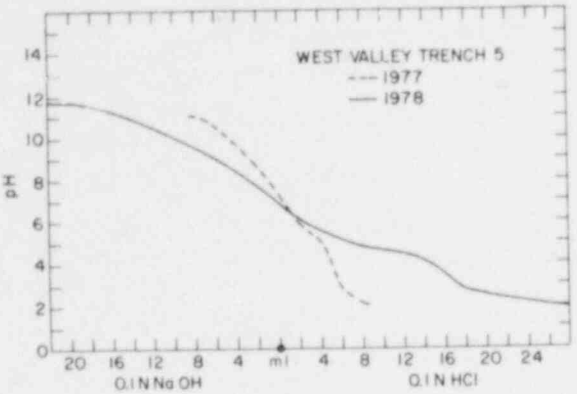

Figure 5.17. Comparison of acid-base titration curves of trench 5 water from West Valley, New York, disposal site.

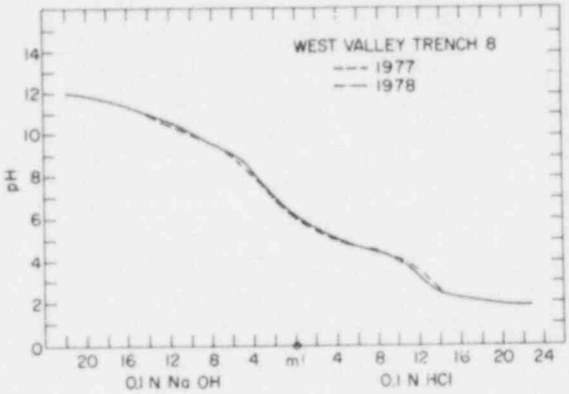

Figure 5.18. Comparison of acid-base titration curves of trench 8 water from West Valley, New York, disposal site.

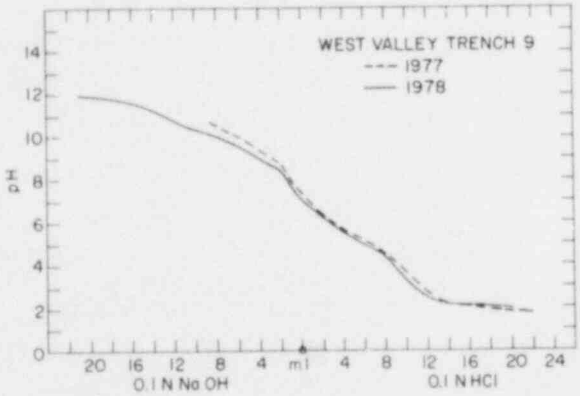

Figure 5.19. Comparison of acid-base titration curves of trench 9 water from West Valley, New York, disposal site.

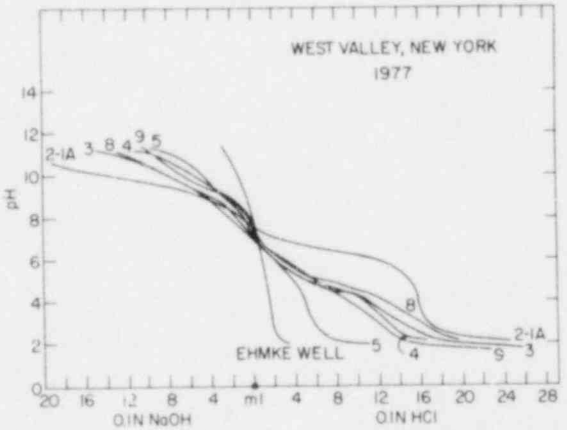

Figure 5.20. Acid-base titration curves of trench waters from West Valley, New York, disposal site, November 1977.

In the calculation of total dissolved cations (meq/L), the iron was considered to have been as Fe^{+2}. Nitrogen as ammonium ion may have been present in the waste when buried and/or may have been produced by microbial conversion of NO_2^- and NO_3^- in the waste. Regardless, nitrogen as NH_4^+ from Table 5.20 is included in the total cations shown in Table 5.21. There is no explanation given at this time for the imbalance between total cations and total anions. It would seem that not all of the constituents in the water are being measured.

5.3.2.3 Organic Results

The concentrations of dissolved inorganic and organic carbon in the trench water samples from West Valley are shown in Table 5.22. The DOC content ranged from 200 to 3600 mg/L.

Table 5.22

Concentration of Carbon in Water Samples
Taken From West Valley, New York, Disposal Site

Sampling[a] Location	Collection Date	Total Carbon (mg/L)	Inorganic Carbon (mg/L)	Organic Carbon (mg/L)
Trench 2	11/77	870	670	200
Trench 3	11/77	1700	90	1600
	10/78	1800	95	1700
Trench 4	11/77	480	130	350
	10/78	760	130	630
Trench 5	11/77	3700	50	3600
	10/78	2900	10	2900
Trench 8	11/77	2800	100	2700
	10/78	3000	70	2900
Trench 9	11/77	1500	140	1400
	10/78	1800	120	1700

[a] Sampling locations correspond to positions indicated in Figure 4.4.

Organic compounds identified in the trench water samples collected November 1977 are shown in Figures 5.21-5.26. Concentrations of identified compounds in acidic, basic, and neutral fractions are given in Tables 5.23-5.29. Table 5.29 gives the concentration in the same trenches collected October 1978. Several straight and branched chain aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, plasticizers, ethers and phenols were identified. These compounds in general represent the synthetic and natural organic wastes buried in the trenches, such as contaminated cellulosic materials, scintillation liquids, solvents, and decontamination fluids and their biological decomposition products. Some qualitative differences of the organic constituents identified between the trenches were normally observed.

The concentrations of organic compounds reported are those present in the methylene chloride extract and are not corrected for the solvent extraction efficiency and possible matrix effects in such complex solutions, as discussed in Section 5.3.1.3.

The same types of organic compounds identified in the water samples from the West Valley are seen in the water samples from Maxey Flats. However, differences were observed in the organic constituents among the trenches and between the two disposal sites.

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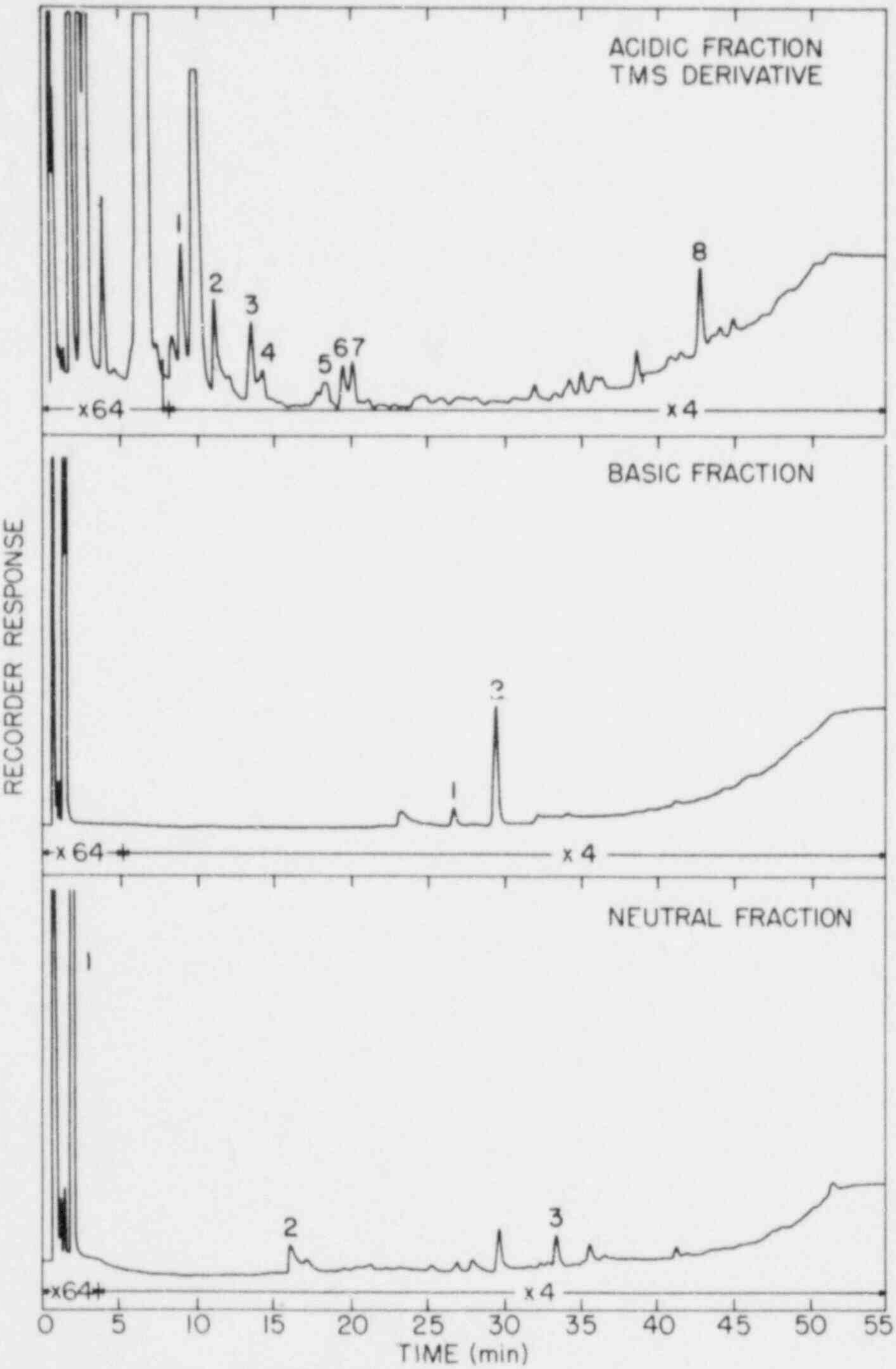

Figure 5.21. Gas chromatogram of methylene chloride extract of trench 2 water sample from West Valley, New York, disposal site.

Table 5.23

Concentration of Organic Compounds Identified in Trench 2 Water Sample From West Valley, New York, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction		
1	2-Methylbutyric acid	0.21
2	Pentanoic acid	0.11
3	C_6 branched acid	N.Q.[b]
4	Phenol	0.04
5	Cresol (isomers)	0.08
6	2-Ethylhexanoic acid	0.06
7	C_8 branched acid	N.Q.
8	Unknown phthalate	N.Q.
Basic Fraction		
1	Dicyclohexylamine	N.Q.
2	Methyldicyclohexylamine	N.Q.
Neutral Fraction		
1	p-Dioxane	N.Q.
2	Triethyl phosphate	N.Q.
3	Tributyl phosphate	0.04

[a] Corresponds to numbers in Figure 5.21.

[b] Not quantified.

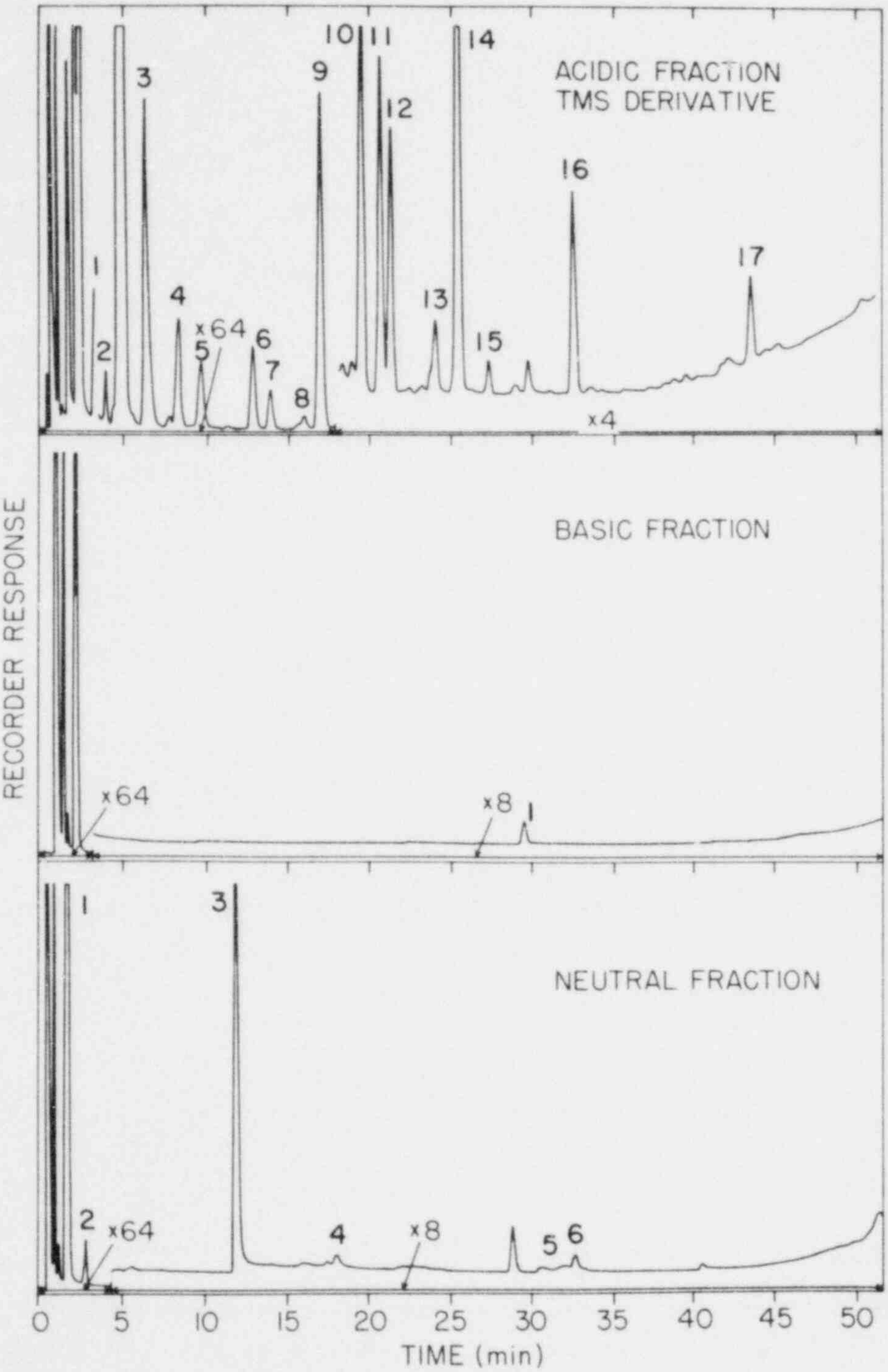

Figure 5.22. Gas chromatogram of methylene chloride extract of trench 3 water sample from West Valley, New York, disposal site.

Table 5.24

Concentration of Organic Compounds Identified in Trench 3 Water Sample From West Valley, New York, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	Propionic acid + ?	N.Q.[b]
2	2-Methylpropionic acid	12
3	2-Methylbutyric acid	88
4	Pentanoic acid	30
5	2-Methylpentanoic acid	14
6	Hexanoic acid	22
7	2-Methylhexanoic acid	7.5
8	Cresol (isomers)	3.4
9	2-Ethylhexanoic acid	11
10	Benzoic acid	5.8
11	Octanoic acid	6.4
12	Phenylactic acid	3.8
13	Nonanoic acid	2.0
14	Phenylpropionic acid	9.4
15	Decanoic acid	0.[illegible]7
16	Phenylhexanoic acid	N.Q.
17	Butyl phthalate	N.Q.
Basic Fraction:		
1	Methyldicyclohexylamine	N.Q.
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	Toluene	1.9
3	2-Ethyl-1-hexanol	8.0
4	Tripropylene glycol methyl ether	N.Q.
5	Octyl phenol (isomer)	N.Q.
6	Tributyl phosphate	0.35

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[a] Corresponds to numbers in Figure 5.22.

[b] Not quantified.

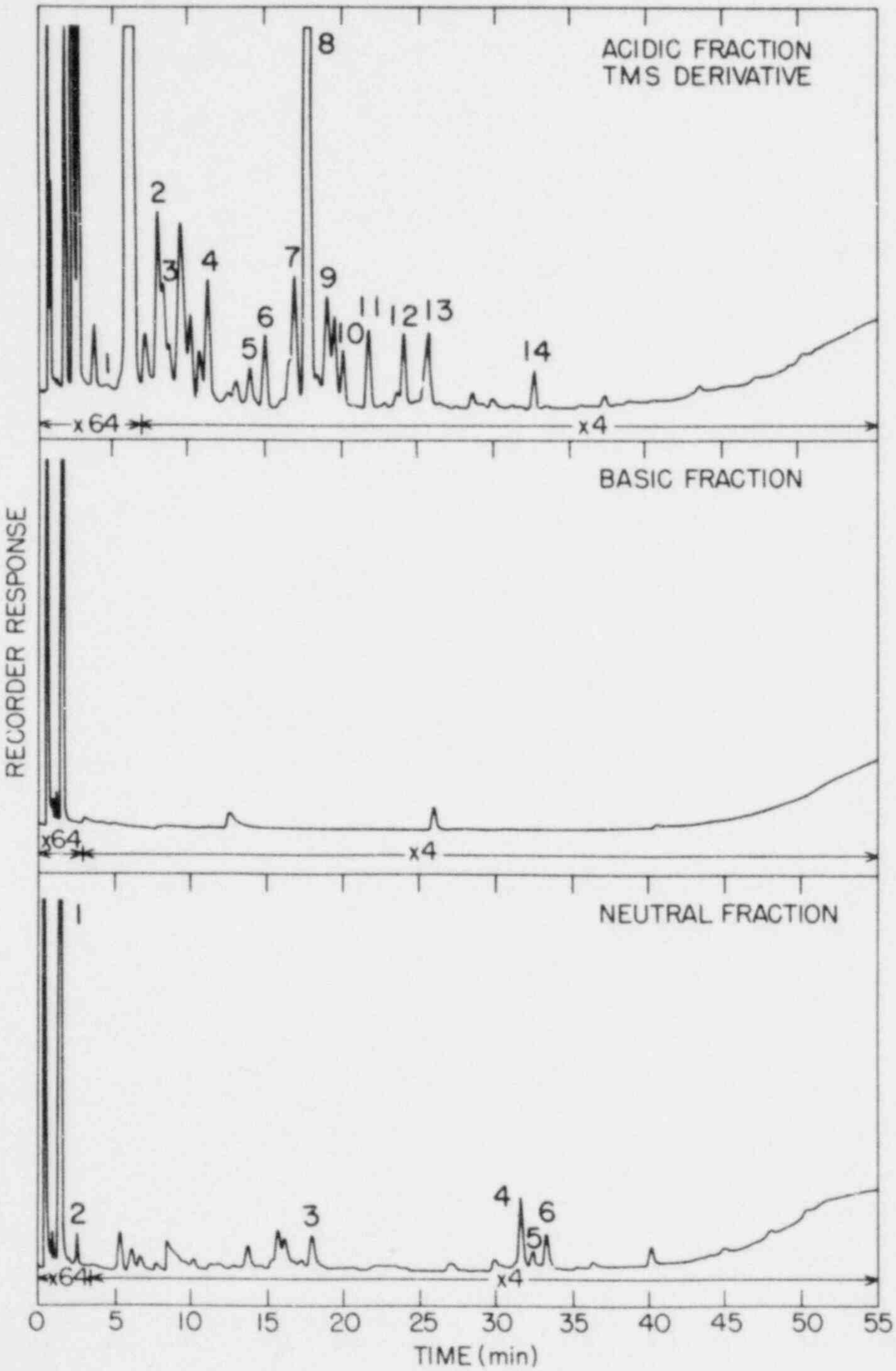

Figure 5.23. Gas chromatogram of methylene chloride extract of trench 4 water sample from West Valley, New York, disposal site.

Table 5.25

Concentration of Organic Compounds Identified in Trench 4 Water Sample From West Valley, New York, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	2-Methylpropionic acid	0.28
2	2-Methylbutanoic acid	1.0
3	Methylbutanoic acid	0.57
4	3-Methylpentanoic acid	0.60
5	Hexanoic acid	0.20
6	2-Methylhexanoic acid	0.33
7	Cresol	0.56
8	2-Ethylhexanoic acid	12
9	C_8 acid	N.Q.[b]
10	Benzoic acid	0.28
11	Phenylacetic acid	0.41
12	Toluic acid	0.59
13	Phenylpropionic acid	0.56
14	Phenylhexanoic acid	N.Q.
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	Toluene	0.31
3	Tripropylene glycol methyl ether	N.Q.
4	N-Ethyl tolyl sulphonamide (isomer)[c]	N.Q.
5	Tributyl phosphate	0.04
6	N-Ethyl tolyl sulphonamide (isomer)[c]	N.Q.

[a] Corresponds to numbers in Figure 5.23.

[b] Not quantified.

[c] Tentative identification.

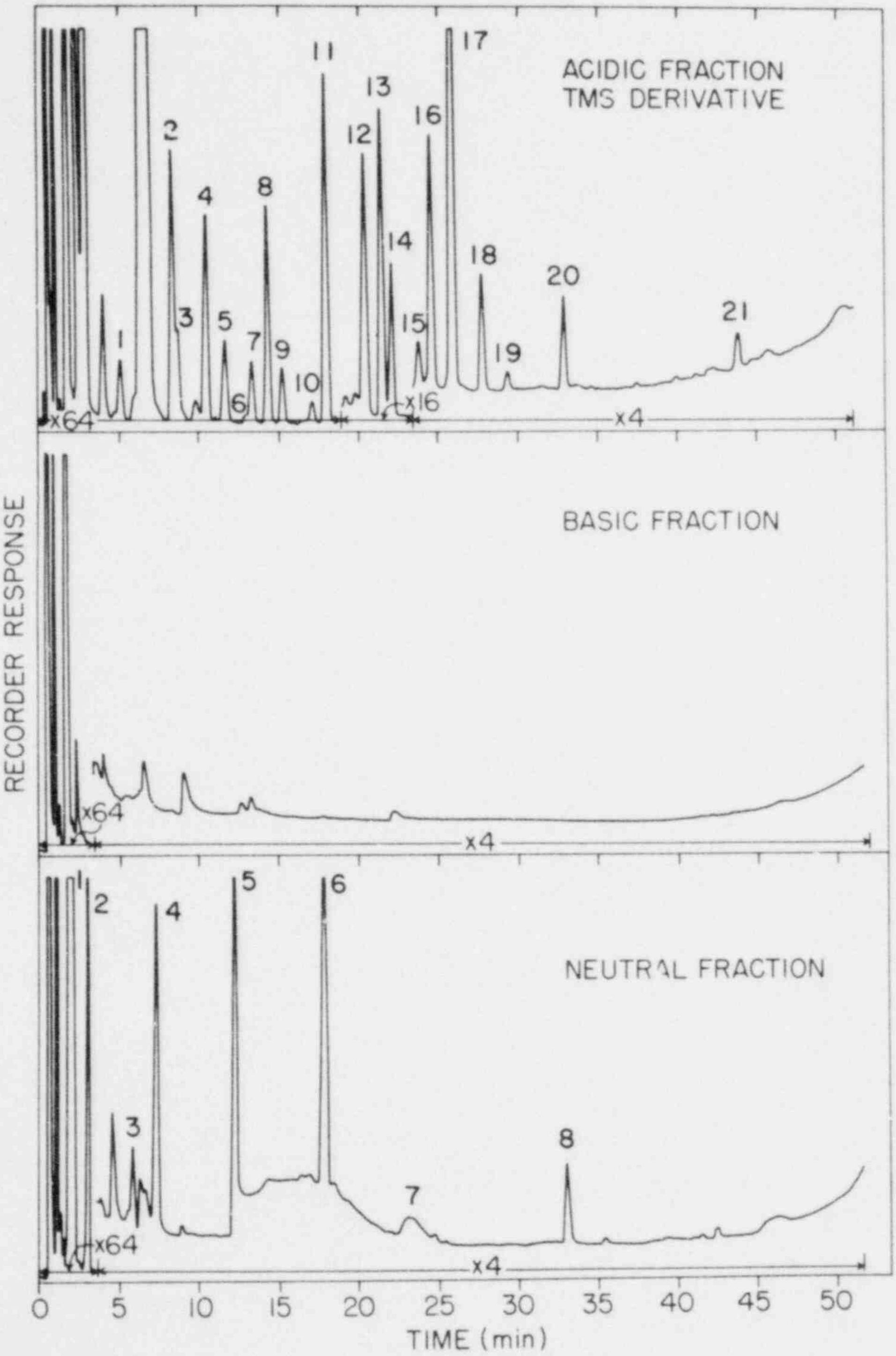

Figure 5.24. Gas chromatogram of methylene chloride extract of trench 5 water sample from West Valley, New York, disposal site.

Table 5.26

Concentration of Organic Compounds Identified in Trench 5 Water Sample From West Valley, New York, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	Isobutyric acid	15
2	2-Methylbutyric acid	60
3	3-Methylbutyric acid	17
4	Pentanoic acid	40
5	2-Methylpentanoic acid[b]	12
6	3-Methylpenanoic acid	1.6
7	Phenol	9.5
8	Hexanoic acid	43
9	2-Methylhexanoic acid	15
10	Cresol (isomer)	3.4
11	2-Ethylhexanoic acid	89
12	Benzoic acid	13
13	Octanoic acid	19
14	Phenylacetic acid	7.5
15	Toluic acid	0.78
16	Nonanoic acid	5.0
17	Phenylpropionic acid	8.6
18	Decanoic acid	2.6
19	Hydroxybenzoic acid	N.Q.[c]
20	Phenylhexanoic acid	N.Q.
21	Unknown phthalate	N.Q.
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	Toluene	18
3	Cyclohexanol	0.59
4	Anisole	2.7
5	2-Ethyl-1-hexanol	3.6
6	Naphthalene	1.7
7	Tripropylene glycol methyl ether	N.Q.
8	Tributyl phosphate	0.76

[a] Corresponds to numbers in Figure 5.24.

[b] Quantified using 3-Methylpentanoic acid.

[c] Not quantified.

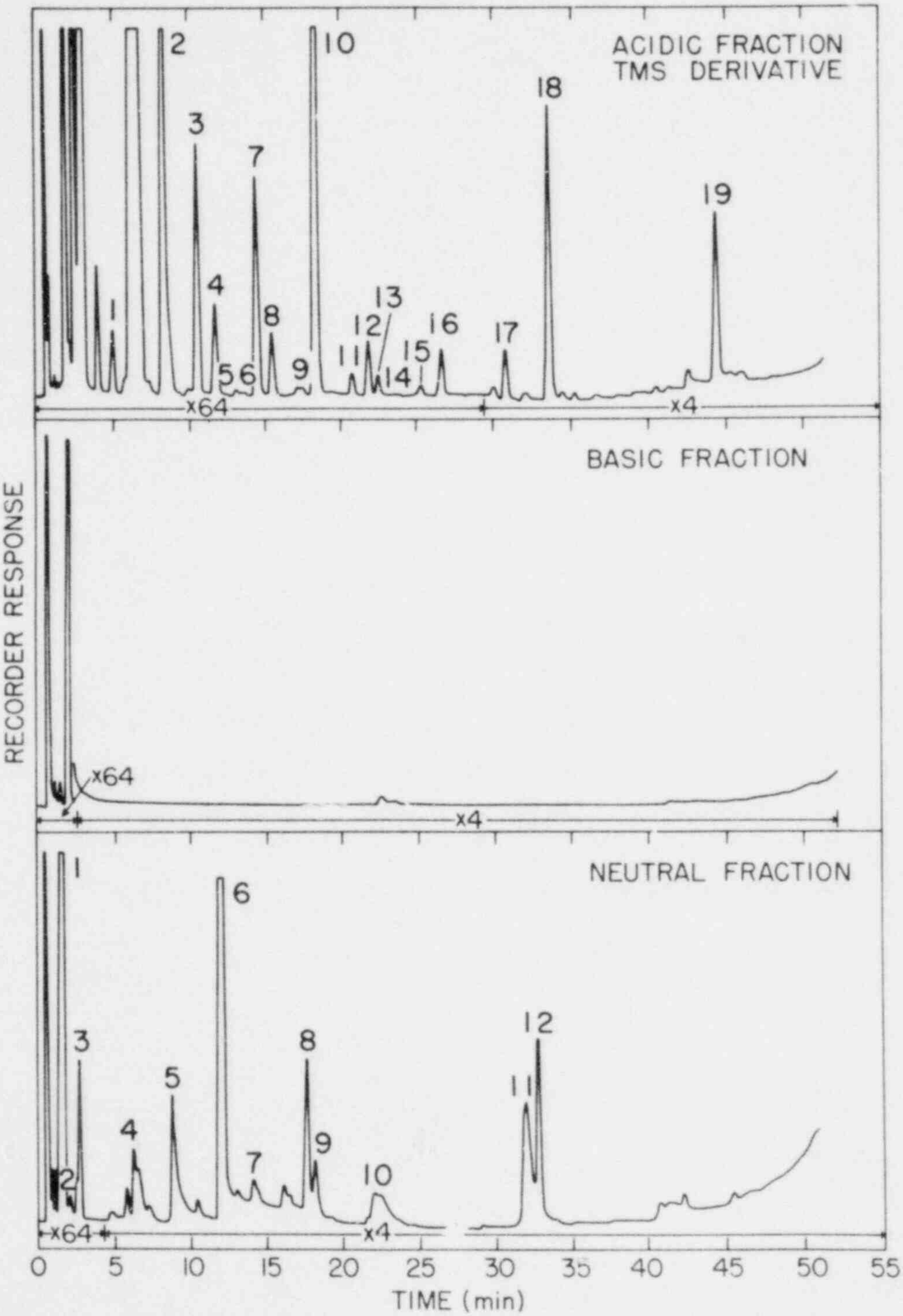

Figure 5.25. Gas chromatogram of methylene chloride extract of trench 8 water sample from West Valley, New York, disposal site.

Table 5.27

Concentration of Organic Compounds Identified in Trench 8 Water Sample From West Valley, New York, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	Isobutyric acid	21
2	2-Methylbutyric acid + 3-Methylbutyric acid	190
3	Pentanoic acid	73
4	2-Methylpentanoic acid[c]	20
5	3-Methylpentanoic acid	2.1
6	Phenol	0.88
7	Hexonoic acid	65
8	2-Methylhexanoic acid	14
9	Cresol (isomer)	4.2
10	2-Ethylhexanoic acid	220
11	Benzoic acid	6.7
12	Octanoic acid	20
13	Phenylacetic acid	6.0
14	Toluic acid	0.63
15	Nonanoic acid	6.4
16	Phenylpropionic acid	14
17	Decanoic acid	1.1
18	Phenylhexanoic acid	N.Q.[b]
19	Unknown phthalate	N.Q.
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	2-Hexanol	N.Q.
3	Toluene	4.8
4	Cyclohexanol	0.44
5	Bis(2-methoxyethyl) ether	N.Q.
6	2-Ethyl-1-hexanol	5.7
7	Fenchone	0.14
8	Naphthalene	0.46
9	α-Terpineol	0.26
10	Tripropylene glycol methyl ether	N.Q.
11	Octyl phenol (isomer)	N.Q.
12	Tributyl phosphate	0.85

[a] Corresponds to numbers in Figure 5.25.

[b] Not quantified.

[c] Quantified using 3-Methylpentanoic acid.

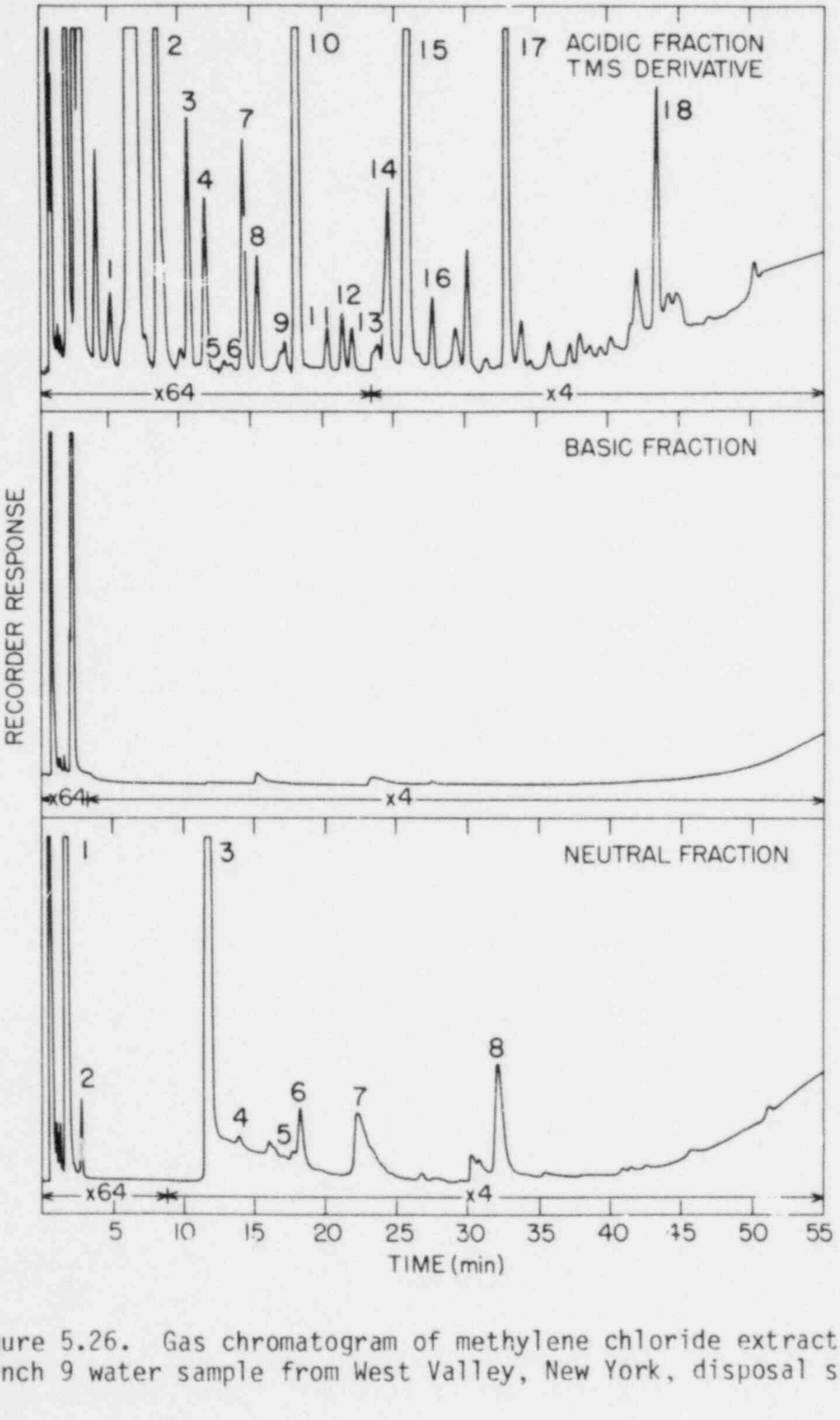

Figure 5.26. Gas chromatogram of methylene chloride extract of trench 9 water sample from West Valley, New York, disposal site.

Table 5.28

Concentration of Organic Compounds Identified in Trench 9 Water Sample From West Valley, New York, Disposal Site

Peak Number[a]	Compound	Concentration (mg/L)
Acidic Fraction:		
1	Isobutyric acid	5.2
2	2-Methylbutyric acid + 3-Methylbutyric acid	48
3	Pentanoic acid	16
4	2-Methylpentanoic acid[c]	7.9
5	3-Methylpentanoic acid	0.74
6	Phenol	0.38
7	Hexanoic acid	15
8	2-Methylhexanoic acid	5.2
9	Cresol (isomer)	2.6
10	2-Ethylhexanoic acid	110
11	Benzoic acid	2.5
12	Octanoic acid	4.6
13	Phenylacetic acid	2.6
14	Nonanoic acid	1.5
15	Phenylpropionic acid	6.9
16	Decanoic acid	0.51
17	Phenylhexanoic acid	N.Q.[b]
18	Unknown Phthalate	N.Q.
Neutral Fraction:		
1	p-Dioxane	N.Q.
2	Toluene	1.1
3	2-Ethyl-1-hexanol	6.8
4	Fenchone	0.03
5	Biphenyl	N.Q.
6	α-Terpineol	0.15
7	Tripropylene glycol methyl ether	N.Q.
8	Octyl phenol (isomer)	N.Q.

[a] Corresponds to numbers in Figure 5.26.

[b] Not quantified.

[c] Quantified using 3-Methylpentanoic acid.

Table 5.29

Concentration of Organic Compounds Identified in Water Samples Taken From West Valley, New York, Disposal Site, October 1978 (mg/L)

Compound	Trench				
	3	4	5	8	9
Acids					
Benzoic acid	7.6	1.0	14	7.5	2.7
Decanoic acid	0.7	N.D.[a]	1.9	1.7	0.68
2-Ethylhexanoic acid	71	5.6	78	170	100
Hexanoic acid	28	5.8	90	66	16
2-Methylbutyric acid	69	5.8	120	160	51
3-Methylbutyric acid	16	3.7	40	+[b]	8.4
2-Methylhexanoic acid	11	1.0	17	14	6.8
C_6 branched acid[c]	1.4	0.59	2.7	2.3	0.95
3-Methylpentanoic acid	23	2.1	23	22	10
2-Methylpropionic acid	10	1.5	33	20	6.0
Nonanoic acid	3.5	N.D.	5.8	6.3	2.9
Octanic acid	6.9	0.76	30	21	4.9
Pentanoic acid	40	6.2	87	76	18
Phenylacetic acid	5.2	1.9	11	4.5	2.6
Phenylhexanoic acid	+	+	+	+	+
Phenylpropionic acid	11	1.6	8.8	12	6.4
Propionic acid	+	+	+	+	+
Toluic acid	N.D.	0.52	1.9	N.D.	N.D.
Others					
Benzene	N.D.	N.D.	+	N.D.	N.D.
Biphenyl	+	N.D.	N.D.	N.D.	N.D.
Bis(2-methoxyethyl)ether	+	N.D.	N.D.	N.D.	N.D.
Camphor	+	N.D.	N.D.	N.D.	N.D.
1,8-Cineole	+	N.D.	N.D.	N.D.	N.D.
Cresol (isomers)	7.5	1.5	5.4	5.9	2.6
Cyclohexanol	N.D.	N.D.	2.1	N.D.	N.D.
1,2-Dimethoxyethane	N.D.	+	N.D.	N.D.	N.D.
p-Dioxane	+	+	+	+	+
2-Ethyl-1-hexanol	N.D.	N.D.	18	3.8	30
Fenchone	0.34	N.D.	N.D.	N.D.	N.D.
2-Hexanol	+	N.D.	N.D.	N.D.	N.D.
Methyl butyl ketone	N.D.	N.D.	+	N.D.	N.D.
Naphthalene	N.D.	N.D.	1.1	N.D.	N.D.
Phenol	0.3	0.1	6.1	0.64	0.2
α-Terpineol	0.95	N.D.	N.D.	N.D.	N.D.
Tetrahydrofuran	N.D.	N.D.	+	N.D.	N.D.
Tetramethyl butyl phenol (isomer)	N.D.	N.D.	N.D.	N.D.	+
Toluene	5.0	1.5	25	8.3	3.1
Tributyl phosphate	0.89	0.12	0.7	0.77	N.D.
Tripropylene glycol methyl ether	N.D.	N.D.	+	+	+

[a] N.D. = Not detected.

[b] + = Compound present but not quantified.

[c] = Quantified using 3-Methylpentanoic acid.

5.3.2.4 Radiochemical Results for West Valley, New York

5.3.2.4.1 Dissolved Radionuclides

The activities of dissolved radionuclides for trench waters collected in November 1977 and October 1978 are reported in Table 5.30. Significant increases in radionuclide activities were observed for gross alpha in trench 8, ^{3}H in trench 5, and ^{137}Cs in trench 3 for samples from the two periods. Tritium was the most abundant radionuclide (3.7 E9 pCi/L) in trench 8. The next most abundant radionuclides were ^{90}Sr (8.6 E6 pCi/L, trench 4), ^{137}Cs (1.0 E6 pCi/L, trench 3) and ^{238}Pu (1.6 E5 pCi/L, trench 8) as of the October 1978 collection.

Table 5.30

Concentrations of Dissolved Radionuclides in Water Samples
Taken From West Valley, New York, Disposal Site
[pCi/L (±2σ%)][a]

Radionuclide	Date	Trench 2[b]	Trench 3	Trench 4	Trench 5	Trench 8	Trench 9
Gross Alpha	11/77	1.6 E2 (1.2)	4.1 E2 (7.1)	6.3 E2 (5.6)	4.9 E2 (6.4)	6.9 E4 (1.6)	1.8 E2 (12)
	10/78	---[b]	7.3 E2 (14)	1.4 E3 (11)	8.9 E2 (11)	1.3 E5 (1.5)	2.7 E2 (15)
Gross Beta	11/77	8.0 E4 (2.1)	1.9 E6 (<1)	3.8 E7 (<1)	1.4 E6 (<1)	4.2 E5 (1.6)	1.2 E5 (1.7)
	10/78	---	2.9 E6 (<1)	1.7 E7 (<1)	4.7 E5 (<1)	4.7 E5 (1.7)	1.2 E5 (3.4)
Tritium	11/77	8.9 E7 (<1)	3.7 E8 (<1)	3.0 E8 (<1)	9.5 E8 (<1)	2.9 E9 (<1)	4.4 E8 (<1)
	10/78	---	4.8 E8 (<1)	3.0 E8 (<1)	2.3 E9 (<1)	3.7 E9 (<1)	4.6 E8 (<1)
^{90}Sr[c]	11/77	3.4 E4 (10)	9.7 E5 (10)	2.4 E7 (10)	6.1 E5 (10)	1.5 E5 (10)	4.8 E4 (10)
	10/78	---	8.5 E5 (10)	8.6 E6 (10)	1.5 E5 (10)	1.4 E5 (10)	3.8 E4 (10)
^{238}Pu[c]	11/77	3.3 E1 (24)	6.6 E1 (10)	2.8 E1 (22)	3.9 E2 (10)	1.5 E5 (10)	2.4 E2 (10)
	10/78	---	7.6 E1 (14)	9.8 E0 (40)	1.3 E2 (10)	1.6 E5 (10)	2.8 E2 (10)
^{239,240}Pu[c]	11/77	1.9 E2 (10)	9.2 E1 (10)	7.1 E1 (10)	3.3 E1 (10)	3.1 E2 (10)	2.4 E0 (24)
	10/78	---	8.1 E1 (12)	1.5 E1 (32)	8.1 E1 (12)	3.4 E2 (20)	3.0 E0 (100)
^{241}Am	11/77	N.D.[d]	N.D.	N.D.	N.D.	3.6 E2 (36)	N.D.
	10/78	---	N.D.	N.D.	N.D.	2.0 E2 (57)	N.D.
^{22}Na	11/77	N.D.	2.3 E2 (25)	2.6 E2 (18)	5.5 E2 (9.2)	3.3 E2 (11)	4.7 E2 (9)
	10/78	---	1.5 E2 (40)	1.3 E2 (21)	4.3 E2 (8.2)	2.7 E2 (11)	3.9 E2 (9)
^{40}K	11/77	4.7 E2 (35)	N.D.	5.6 E2 (55)	N.D.	3.0 E2 (65)	N.D.
	10/78	---	4.5 E2 (72)	1.5 E3 (20)	N.D.	3.9 E2 (53)	3.1 E2 (62)
^{60}Co	11/77	3.3 E2 (12)	2.6 E4 (1)	1.1 E3 (6.4)	1.8 E3 (4.3)	2.0 E2 (19)	1.1 E3 (5.9)
	10/78	---	7.0 E4 (<1)	9.9 E2 (6.0)	3.9 E2 (10)	2.0 E2 (18)	9.7 E2 (5.8)
^{133}Ba	11/77	N.D.	N.D.	N.D.	6.8 E2 (24)	3.6 E2 (25)	1.4 E2 (43)
	10/78	---	N.D.	9.3 E1 (65)	2.7 E2 (57)	4.5 E2 (23)	8.0 E1 (52)
^{134}Cs	11/77	N.D.	N.D.	1.3 E2 (54)	5.0 E3 (3.2)	1.5 E3 (6.2)	1.9 E3 (4.2)
	10/78	---	N.D.	6.4 E1 (49)	1.7 E3 (3.6)	9.4 E2 (6.6)	9.6 E2 (5.4)
^{137}Cs	11/77	2.7 E4 (<1)	2.9 E5 (<1)	1.1 E4 (1.4)	2.7 E5 (<1)	1.4 E5 (<1)	3.4 E4 (<1)
	10/78	---	1.0 E6 (<1)	1.1 E4 (1.2)	3.3 E4 (<1)	1.4 E5 (<1)	2.6 E4 (<1)

[a] Number in ( ) = 2σ percent counting uncertainty.
[b] Not sampled in October, 1978.
[c] Analyses performed by LFE Laboratories, Richmond, California.
[d] N.D. = not detected.

5.3.2.4.2 Radionuclides in Particulates

Radionuclides in particulates filtered from trench waters collected at the West Valley, New York, disposal site during November of 1977 and October of 1978 are given in Table 5.31 and Table 5.32. The particulates were obtained at the time the samples were anoxically filtered through 0.45 μm Millipore filters (Section 5.3).

Several radionuclides, ^{40}K, ^{125}Sb and ^{133}Ba, were found on the particulates but were not as dissolved species in the corresponding trench waters. The radionuclide of the highest concentration on the particulates was ^{238}Pu (1.0 E5 pCi/L, trench 8), but in the particulates from all other trench water samples ^{90}Sr was the most abundant radionuclide. Other nuclides strongly sorbed by the particulates were ^{60}Co and ^{137}Cs.

Table 5.31

Radionuclides in Particulates Filtered From Water Samples
Taken From West Valley, New York, Disposal Site[a]
[pCi/mg (±2σ%)]

Radionuclide	Date	Trench 2[b]	Trench 3	Trench 4	Trench 5	Trench 8	Trench 9
^{90}Sr[c]	11/77	7.8 E 0 (10)	1.1 E 2 (10)	2.2 E 3 (10)	5.3 E 1 (10)	2.2 E 0 (120)	1.3 E 1 (10)
	10/78	---	8.2 E 1 (10)	3.4 E 2 (10)	1.7 E 1 (10)	1.5 E 1 (12)	6.1 E 0 (10)
^{238}Pu[c]	11/78	3.7 E 1 (10)	1.5 E 0 (10)	1.2 E 0 (10)	7.1 E 1 (10)	4.2 E 3 (10)	2.0 E 1 (10)
	10/78	---	4.6 E-1 (10)	4.5 E-1 (10)	2.4 E 0 (10)	5.1 E 3 (10)	1.8 E 1 (10)
^{239,240}Pu[c]	11/77	7.9 E 1 (10)	5.0 E 0 (10)	2.5 E 0 (10)	7.9 E-1 (10)	7.7 E 0 (10)	1.7 E-1 (10)
	10/78	---	3.6 E 0 (10)	7.9 E-1 (10)	1.3 E 0 (10)	1.3 E 1 (10)	1.6 E-1 (10)
^{241}Am	11/77	3.1 E-1 (18)	3.2 E 0 (6.6)	1.5 E 0 (16)	5.7 E-1 (10)	9.1 E 0 (2)	1.7 E 0 (4.4)
	10/78	---	8.6 E-1 (13)	3.6 E-1 (24)	7.6 E-1 (8)	6.3 E 0 (2)	9.5 E-1 (5)
^{40}K	11/77	1.3 E 0 (55)	7.1 E-1 (66)	1.5 E 0 (57)	1.1 E-1 (44)	1.4 E-1 (68)	1.0 E 0 (46)
	10/78	---	7.2 E-1 (103)	9.2 E-1 (44)	8.7 E-1 (49)	6.4 E-1 (51)	7.5 E-1 (60)
^{57}Co	11/77	N.D.[d]	1.2 E-1 (67)	N.D.	N.D.	N.D.	8.2 E-2 (48)
	10/78	----	1.6 E-1 (62)	1.3 E-1 (45)	N.D.	N.D.	7.3 E-2 (53)
^{60}Co	11/77	2.7 E-1 (25)	1.9 E 1 (2)	1.0 E 0 (12)	8.7 E-1 (8.4)	1.1 E 0 (11)	2.4 E 0 (5.6)
	10/78	---	1.3 E 2 (<1)	2.4 E 0 (5)	3.2 E-1 (16)	6.7 E-1 (9)	4.4 E 0 (3.4)
^{125}Sb	11/77	N.D.	N.D.	N.D.	N.D.	2.7 E-1 (57)	1.7 E-1 (61)
	10/78	---	N.D.	1.3 E-1 (77)	1.8 E-1 (52)	2.4 E-1 (47)	2.7 E-1 (54)
^{133}Ba	11/77	N.D.	N.D.	N.D.	2.0 E-1 (39)	N.D.	1.7 E-1 (33)
	10/78	---	N.D.	N.D.	5.2 E-2 (63)	7.7 E-2 (48)	4.4 E-2 (43)
^{134}Cs	11/77	N.D.	N.D.	N.D.	1.3 E 0 (5.2)	1.1 E-1 (41)	1.4 E-1 (33)
	10/78	---	N.D.	N.D.	1.6 E-1 (24)	7.4 E-2 (32)	1.1 E-1 (38)
^{137}Cs	11/77	3.9 E 0 (3)	2.3 E 1 (1.6)	1.0 E 0 (10)	4.8 E 1 (0.6)	8.2 E 0 (2.6)	2.8 E 0 (4.4)
	10/78	---	1.1 E 2 (<1)	6.5 E-1 (10)	3.4 E 0 (3)	9.2 E 0 (2)	3.7 E 0 (3.3)

[a] Water samples were filtered through 0.45 μm Millipore filter.
[b] Not sampled in October 1978.
[c] Analyses performed by LFE Laboratories, Richmond, California.
[d] N.D. = not detected.

Table 5.32

Radionuclides in Particulates Filtered From Water Samples Taken From West Valley, New York, Disposal Site[a]

$$\left[\frac{\text{picocuries}}{\text{liter of water filtered}}\ (\pm 2\sigma\%)\right]$$

Radionuclide	Date	Trench 2[b]	Trench 3	Trench 4	Trench 5	Trench 8	Trench 9
^{90}Sr[c]	11/77	2.2 E2 (10)	4.6 E3 (10)	4.9 E4 (10)	2.0 E3 (10)	4.1 E1 (120)	3.3 E2 (10)
	10/78	---[b]	7.5 E3 (10)	1.2 E4 (10)	1.1 E3 (10)	3.0 E2 (10)	1.4 E2 (10)
^{238}Pu[c]	11/77	1.0 E1 (10)	6.3 E1 (10)	2.7 E1 (10)	2.7 E1 (10)	7.9 E4 (10)	5.2 E2 (10)
	10/78	---	4.1 E1 (10)	1.6 E1 (10)	1.6 E2 (10)	1.0 E5 (10)	4.1 E2 (10)
$^{239,240}Pu$[c]	11/77	2.3 E1 (10)	2.1 E2 (10)	5.7 E1 (10)	3.0 E1 (10)	1.9 E2 (10)	4.5 E0 (10)
	10/78	---	3.3 E2 (10)	2.9 E1 (10)	8.9 E1 (10)	2.7 E2 (10)	3.8 E0 (10)
^{241}Am	11/77	8.8 E0 (18)	1.3 E2 (7)	3.3 E1 (16)	2.2 E1 (10)	1.7 E2 (2)	4.4 E1 (4)
	10/78	---	7.8 E1 (13)	1.3 E1 (24)	5.2 E1 (8)	1.3 E2 (2)	2.2 E1 (5)
^{40}K	11/77	3.7 E1 (55)	2.9 E1 (66)	3.3 E1 (57)	4.2 E0 (44)	2.6 E0 (68)	2.6 E1 (46)
	10/78	---	6.5 E1 (103)	3.4 E1 (44)	5.9 E1 (49)	1.3 E1 (51)	1.8 E1 (60)
^{57}Co	11/77	N.D.[d]	4.8 E0 (57)	N.D.	N.D.	N.D.	2.1 E0 (48)
	10/78	---	1.4 E1 (62)	4.6 E0 (45)	N.D.	N.D.	1.7 E0 (53)
^{60}Co	11/77	7.8 E0 (25)	7.9 E2 (1)	2.5 E1 (8)	3.1 E1 (8.4)	2.1 E1 (11)	6.4 E1 (6)
	10/78	---	1.2 E4 (<1)	8.8 E1 (5)	2.1 E1 (16)	1.4 E1 (9)	1.0 E2 (3)
^{125}Sb	11/77	N.D.	N.D.	N.D.	N.D.	5.1 E0 (57)	4.3 E0 (61)
	10/78	---	N.D.	4.6 E0 (77)	1.2 E1 (52)	4.8 E0 (47)	6.4 E0 (54)
^{133}Ba	11/78	N.D.	N.D.	N.D.	7.4 E0 (39)	N.D.	4.5 E0 (33)
	10/78	---	N.D.	N.D.	3.5 E0 (63)	1.5 E0 (48)	1.0 E0 (43)
^{134}Cs	11/77	N.D.	N.D.	N.D.	4.8 E1 (5)	2.0 E0 (41)	4.0 E0 (33)
	10/78	---	N.D.	N.D.	1.4 E1 (19)	1.5 E0 (32)	2.6 E0 (38)
^{137}Cs	11/77	1.1 E2 (3)	9.4 E2 (2)	2.3 E1 (10)	1.8 E3 (<1)	1.5 E2 (3)	7.4 E1 (4)
	10/78	---	1.0 E4 (<1)	2.4 E1 (10)	2.3 E2 (3)	1.8 E2 (3)	8.7 E1 (3)

[a] Water samples filtered through 0.45 μm Millipore filter.
[b] Not sampled in October, 1978.
[c] Analyses performed by LFE Laboratories, Richmond, California.
[d] N.D. = not detected.

Considerable variation in radionuclide concentration on the particulates was observed for the same trench, from waters collected at the two sampling times. The variation could be due to the particle size and clay mineral composition of the particulates which may have different sorption capabilities for radionuclides. The particulates filtered from the solution probably only represent the finest clay fraction of the sediment and amorphous materials. Mineral characterization of these particulates would be essential to an understanding of radionuclide mobilization on these suspended particulates. The distribution of radionuclides between suspended particulates and the aqueous phase of the trench waters are given in Table 5.33 and Table 5.34. These distribution ratios are <u>not</u> sorption coefficients for the bulk sediment and <u>do not</u> represent the total retardation capability of the soil. However, the distribution ratios do represent the sorption capabilities of suspended (colloidal?) particulates and reflect the potential for radionuclide mobility on these particles vs. transport or dissolved species. The most strongly sorbed species, without exception, are ^{238}Pu, $^{239/240}$Pu and ^{241}Am.

Table 5.33

Distribution of Radionuclides Between Suspended Particulates and Aqueous Phase in Water Samples Taken From West Valley, New York, Disposal Site[a]
[(mL/g)(± 2σ Percent)]

Radionuclide	Date	Trench 2	Trench 3	Trench 4	Trench 5	Trench 8	Trench 9
^{90}Sr	11/77	2.3 E2 (14)	1.1 E2 (14)	9.2 E1 (14)	8.7 E1 (14)	1.5 E1 (120)	2.6 E2 (14)
	10/78	---[b]	9.6 E1 (14)	3.9 E1 (14)	1.1 E2 (14)	1.1 E2 (16)	1.6 E2 (14)
^{238}Pu	11/77	1.1 E4 (26)	2.3 E4 (14)	4.3 E4 (24)	1.8 E3 (14)	2.9 E4 (37)	8.4 E4 (14)
	10/78	---	6.0 E3 (17)	4.6 E4 (41)	1.8 E4 (14)	3.3 E4 (14)	6.3 E4 (14)
^{239,240}Pu	11/77	4.2 E3 (14)	5.5 E4 (14)	3.6 E4 (14)	2.4 E4 (14)	3.2 E4 (14)	7.2 E4 (26)
	10/78	---	4.4 E4 (16)	5.2 E4 (34)	1.6 E4 (16)	4.0 E4 (22)	5.5 E4 (100)
^{241}Am	11/77	c	c	c	c	2.5 E4 (36)	c
	10/78	---	c	c	c	3.2 E4 (57)	c
^{22}Na	11/77	d	e	e	e	e	e
	10/78	---	e	e	e	e	e
^{40}K	11/77	2.8 E3 (65)	c	2.7 E3 (79)	c	4.8 E2 (94)	c
	10/78	---	1.6 E3 (126)	6.3 E2 (48)	c	1.6 E3 (74)	2.4 E3 (86)
^{57}Co	11/77	d	c	d	d	d	c
	10/78	---	c	c	d	d	c
^{60}Co	11/77	8.4 E2 (28)	7.3 E2 (2.6)	9.0 E2 (14)	4.8 E2 (9.4)	5.6 E3 (22)	2.3 E3 (8.1)
	10/78	---	1.9 E3 (<1)	2.4 E3 (7.5)	8.1 E2 (19)	3.3 E3 (20)	4.5 E3 (6.7)
^{125}Sb	11/77	d	d	d	d	c	c
	10/78	---	d	c	c	c	c
^{133}Ba	11/77	d	d	d	2.9 E2 (46)	e	1.3 E3 (55)
	10/78	---	d	e	1.9 E2 (85)	1.7 E2 (53)	5.5 E2 (68)
^{134}Cs	11/77	d	d	e	2.6 E2 (6.1)	7.2 E1 (42)	7.3 E1 (34)
	10/78	---	d	e	9.5 E1 (24)	7.9 E1 (33)	1.2 E2 (38)
^{137}Cs	11/77	1.4 E2 (4.0)	7.7 E1 (1.6)	8.9 E1 (10)	1.8 E2 (0.6)	5.9 E1 (2.6)	8.3 E1 (4.4)
	10/78	---	1.1 E2 (<1)	5.8 E1 (9.7)	1.0 E2 (3.2)	6.5 E1 (1.6)	1.4 E2 (3.4)

[a] $\text{Ratio} = \dfrac{\text{Activity in suspended particulates (pCi/g)}}{\text{Activity in aqueous phase (pCi/mL)}}$

[b] Trench 2 not sampled in October 1978.

[c] Activity found only in particulate fraction.

[d] No activity found in either fraction.

[e] Activity found only in the dissolved fraction.

Table 5.34

Comparison of Radionuclide Activity in the Dissolved Fraction Relative to That in the Suspended Particulate Fraction in Water Samples Taken From West Valley, New York, Disposal Site [Ratio[a] (± 2σ Percent)]

Radionuclide	Date	Trench 2	Trench 3	Trench 4	Trench 5	Trench 8	Trench 9
^{90}Sr	11/77	1.5 E2 (14)	2.1 E 2 (14)	4.9 E 2 (14)	3.0 E 2 (14)	3.7 E3 (120)	1.4 E 2 (14)
	10/78	---[b]	1.1 E 2 (14)	7.0 E 2 (14)	1.3 E 2 (14)	4.6 E2 (14)	2.6 E 2 (14)
^{238}Pu	11/77	3.2 E0 (26)	1.1 E 0 (24)	1.1 E 0 (24)	1.5 E 1 (14)	1.9 E0 (37)	4.6 E-1 (14)
	10/78	---	1.8 E-0 (17)	6.0 E-1 (41)	8.1 E-1 (14)	1.5 E0 (14)	6.7 E-1 (14)
$^{239,240}Pu$	11/77	8.3 E0 (14)	4.4 E-1 (14)	1.3 E 0 (14)	1.1 E 0 (14)	1.7 E0 (14)	5.3 E-1 (26)
	10/78	---	2.5 E-1 (16)	5.2 E-1 (34)	9.0 E-1 (16)	1.3 E0 (22)	7.7 E-1 (100)
^{241}Am	11/77	c	c	c	c	2.1 E0 (36)	c
	10/78	---	c	c	c	1.5 E0 (57)	c
^{32}Na	11/77	d	e	e	e	e	e
	10/78	---	e	e	e	e	e
^{40}K	11/77	1.3 E1 (65)	c	1.7 E 1 (79)	c	1.2 E2 (94)	c
	10/78	---	6.9 E 0 (126)	4.3 E 1 (48)	c	3.1 E1 (74)	1.7 E 1 (86)
^{57}Co	11/77	d	c	d	d	d	c
	10/78	---	c	c	d	d	c
^{60}Co	11/77	4.2 E1 (28)	3.3 E 1 (2.6)	4.4 E 1 (6.5)	5.8 E 1 (9.4)	9.5 E0 (22)	1.7 E 1 (8.1)
	10/78	---	5.8 E 0 (<1)	1.1 E 1 (7.5)	1.8 E 1 (19)	1.5 E1 (20)	9.4 E 0 (6.7)
^{125}Sb	11/77	d	d	d	d	c	c
	10/78	---	d	c	c	c	c
^{133}Ba	11/77	d	d	d	9.2 E 1 (46)	e	3.0 E 1 (55)
	10/78	---	d	e	7.7 E 1 (85)	2.9 E2 (53)	7.7 E 1 (68)
^{134}Cs	11/77	d	d	e	1.1 E 2 (6.1)	7.5 E2 (42)	4.6 E 2 (33)
	10/78	---	d	e	1.6 E 2 (24)	6.4 E2 (33)	3.7 E 2 (38)
^{137}Cs	11/77	2.5 E2 (4.0)	3.1 E 2 (1.6)	5.0 E 2 (10)	1.5 E 2 (<1)	9.0 E2 (2.6)	4.6 E 2 (4.4)
	10/78	---	1.0 E 2 (<1)	4.7 E 2 (9.7)	1.4 E 2 (3.2)	7.8 E2 (1.6)	2.9 E 2 (3.4)

[a] $\text{Ratio} = \dfrac{\text{Concentration of dissolved radionuclide (pCi/L)}}{\text{Activity in suspended particulates expressed as picocuries per liter of water filtered}}$

[b] Trench 2 not sampled in October 1978.

[c] Activity found only in the suspended particulates.

[d] No activity found in either fraction.

[e] Activity found only in the dissolved fraction.

Such fine grained suspended material may be transported through the geological media at rates equal to that of ground water flow. In hydrologic regimes, where flow-rates are controlled by intergranular flow, some of this suspended material may be retained via filtration by the solid media. Where fracture flow controls ground water movement, radionuclides held on suspended particles can be transported in greater amounts and greater distances than predicted by transport modeling, using K_d numbers from laboratory experiments (see Chapter 7).

More attention needs to be focused on the nature of the suspended material and its role in migration.

5.3.3 Sheffield, Illinois, Disposal Site

5.3.3.1 Field Measurements

In situ measurements made at Sheffield, April 1979, are shown in Table 5.35. The Eh in the two trenches that were sampled are more positive than the trenches at Maxey Flats and West Valley.

The trenches at Sheffield do not have large amounts of water for long periods of time compared to the other sites.

Water samples for organic analysis were obtained by bailing from wells 536, 513, and 523 (Figure 4.6), and kept cold in amber bottles.

Table 5.35

Field Measurements of Water Samples Taken From Sheffield, Illinois, Disposal Site, April 1979

Sampling Location	pH	Eh (mV,NHE)[a]	Dissolved Oxygen (mg/L)	Specific Conductance (μmho/cm)	Temperature (°C)
Trench 14	5.0	143	0.3	600	8.5
Trench 18A	6.8	181	0.1	1600	10.0
Well 525	7.5	1.9	2.2	510	10.0

[a] Field measurements of redox potentials (Eh) are reported relative to the normal hydrogen electrode (NHE).

5.3.3.2 Inorganic

Tables 5.36 and 5.37 summarize the inorganic constituents measured in the samples from the Sheffield site.

Ammonia analysis was done colorimetrically in both the presence and absence of air. Figure 5.27 demonstrates the direct correlation between the "air poor" and "conventional" colorimetric ammonia analysis methods for Sheffield, Illinois waters. The waters at these sites have much lower cation concentrations and can be readily analyzed by conventional colorimetric methods.

Ferrous/ferric iron ratio was measured in order to more completely study the chemical systems of these trench waters. Trench 14A was anoxic while well 525 appeared to be more oxic in nature.

The alkalinity titration curve, Figure 5.28, indicates that trench 18 was a buffered system.

Table 5.36

Concentration of Dissolved Non-Metals in Water Samples Taken From Sheffield, Illinois, Disposal Site, April 1979 (mg/L)

Dissolved Component	Trench 14A	Trench 18	Well 525
Total Alkalinity (as $CaCO_3$)	200	850	320
Inorganic Carbon	40	190	70
DOC	100	50	3
Hardness (Ca+Mg) (as $CaCO_3$)	200	870	330
Residue (180°C)	395	1050	300
Chloride	20	28	13
Nitrogen (N) (ammonia)	5.1	9.0	<0.1
Nitrogen (N) (NO_2^- + NO_3^-)	0.04	0.38	<0.04
Phosphate	<0.5	<0.5	<0.5
Silica	7.4	7.0	14
Sulfate	78	190	47
Sulfide	<1	<1	<1
Total Anions (meq/L)	6.4	22	7.4

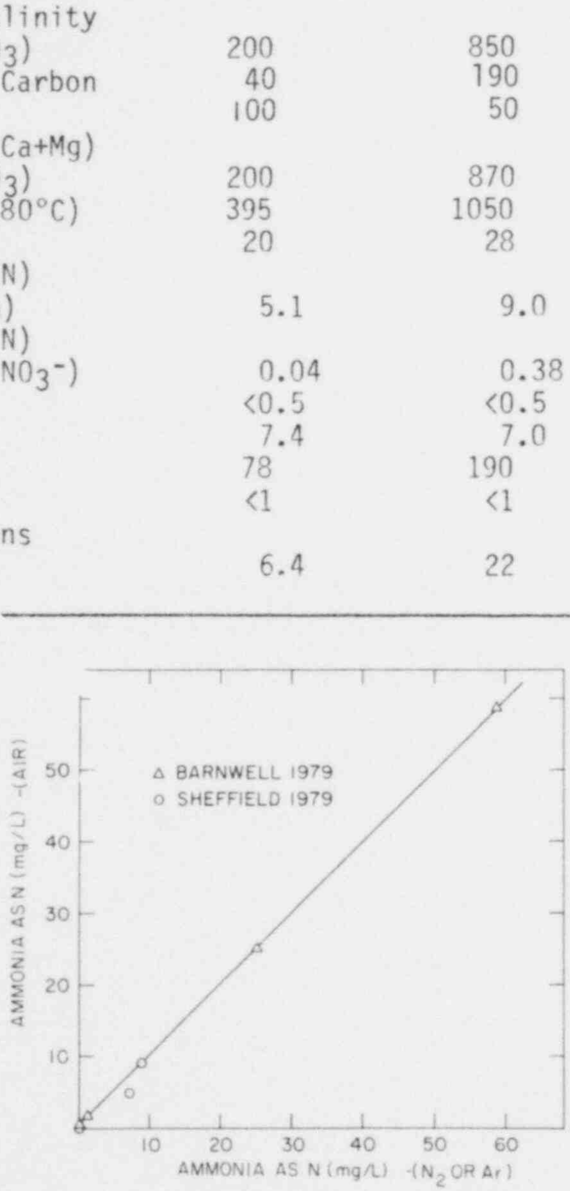

Figure 5.27. Correlation between ammonia concentrations determined in both the presence and absence of air.

Table 5.37

Concentration of Dissolved Metals in Water Samples Taken From Sheffield, Illinois, Disposal Site, April 1979 (mg/L)

Metal	Trench 14A	Trench 18	Well 525
Barium	<1	<1	<1
Calcium	52	190	74
Cesium	<0.1	<0.1	<0.1
Iron			
Fe^{2+}	7.5	0.4[a]	2
Fe^{3+}	3.4		8
Lithium	<0.1	<0.1	<0.1
Magnesium	17	94	34
Manganese	1.6	1.1	0.15
Potassium	13	72	0.7
Sodium	50	67	35
Strontium	<0.1	0.6	<0.1
Total Cations (meq/L)[b]	7.3	22	8.3

[a] Total iron.

[b] Includes nitrogen as NH_4^+.

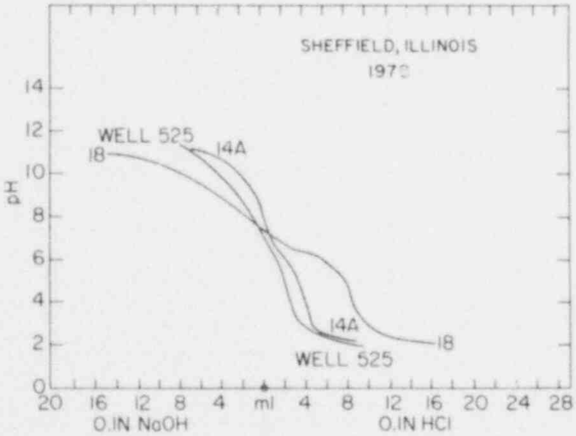

Figure 5.28. Acid-base titration curves of water samples from Sheffield, Illinois, disposal site, April 1979.

5.3.3.3 Organic Analysis

Carbon analysis of the Sheffield samples collected April 1979 are shown in Table 5.38. Wells 536, 513, and 523 were not sampled by the anoxic procedure, but were bailed. The DOC concentration in trench 14A is somewhat above background levels, but considerably less than the levels found in trenches at Maxey Flats and West Valley.

Table 5.38

Concentration of Carbon in Water Samples
Taken From Sheffield, Illinois, Disposal Site

Sampling[a] Location	Collection Date	Total Carbon (mg/L)	Inorganic Carbon (mg/L)	Organic Carbon (mg/L)
Trench 14A	4/79	140	40	100
Trench 18	4/79	240	190	50
Well 525	4/79	73	70	3
Well 536	4/79	110	90	20
Well 513	4/79	66	51	15
Well 523	4/79	260	220	40

[a] Sampling locations correspond to positions indicated in Figure 4.6.

The methylene chloride extract of trench 14A water sample did not show any significant peaks in the GC/MS analysis.

A two orders of magnitude decrease in DOC is observed in water samples from wells 513, 523, 525, and 535 compared to the values reported in the 1977 survey study (Table 4.14). The DOC levels found in 1977 were higher than expected for groundwater. A possible explanation is that the wells were contaminated with oil that normally coats the surface of new pipes, and that the original contamination was washed out of the well.

5.3.3.4 Radiochemical Results for Sheffield, Illinois

5.3.3.4.1 Dissolved Radionuclides

The activities of dissolved radionuclides in water samples collected at Sheffield, Illinois, in April of 1979 are given in Table 5.39. Tritium was the most abundant radionuclide found in the trench waters (6.2 E5 pCi/L, trench 14A). No radionuclides were found in the water from well 525, and very little activity was detected in trench 18.

Table 5.39

Concentration of Dissolved Radionuclides in Water Samples Taken From Sheffield, Illinois, Disposal Site, April 1979[a]
pCi/L (±2σ%)

Radionuclide	Trench 14A	Trench 18	Well 525
Gross Alpha	8.6 E2 (4.3)	<9	<14
Gross Beta	5.6 E4 (<1)	4.5 E2 (7.9)	<28
Tritium	6.2 E5 (<1)	2.0 E5 (1)	<6.2 E2
^{238}Pu	1.4 E0 (48)	1.4 E0 (58)	b
^{239,240}Pu	2.3 E-1 (200)	2.2 E-1 (120)	b
^{90}Sr	2.2 E3 (10)	1.3 E2 (10)	b
^{22}Na	1.1 E3 (6.4)	N.D.[c]	N.D.
^{40}K	N.D.	N.D.	N.D.
^{54}Mn	2.3 E3 (4.8)	N.D.	N.D.
^{60}Co	2.3 E4 (1.0)	4.1 E2 (8.8)	N.D.
^{134}Cs	1.4 E4 (1.2)	N.D.	N.D.
^{137}Cs	3.0 E4 (<1)	N.D.	N.D.

[a] Samples filtered through 0.45 μm Millipore filter.

[b] Not analyzed.

[c] N.D. = not detected.

5.3.3.4.2 Suspended Radionuclides

Analyses not yet completed.

5.3.4 Barnwell, South Carolina, Disposal Site

5.3.4.1 Field Measurements

In situ measurements made at Barnwell, March 1979, are shown in Table 5.40. The Eh's measured in these samples are in an oxidizing range for groundwaters. Groundwater does not remain in the trenches very long at Barnwell because of the high soil porosity precluding anaerobic microbial activity.

Table 5.40

Field Measurements of Water Samples Taken From
Barnwell, South Carolina, Disposal Site, March 1979

Sampling Location	pH	Eh (mV,NHE)[a]	Dissolved Oxygen (mg/L)	Specific Conductance (μmho/cm)	Temperature (°C)
Trench 3D1[b]	5.8	225	0.1	210	13.0
Trench 5D2[b]	6.6	148	0.8	600	19.0
Trench 6D1	5.9	358	1.3	370	19.5
Trench 8D2[b]	c	308[d]	1.5	1400	19.0[d]
Trench 25/21D1	5.9	538	1.0	550	18.5

[a] Field measurements of redox potentials (Eh) are reported relative to the normal hydrogen electrode (NHE).

[b] Measurements made prior to loss of suction due to presence of insufficient recoverable water in the trench.

[c] No measurement due to equipment malfunction.

[d] Redox potential (Eh) calculated using an assumed water temperature of 19 °C.

5.3.4.2 Inorganic

The results of the inorganic analysis are summarized in Tables 5.41 and 5.42.

Sulfide frequently controls some metal concentrations, due to sulfide precipitation. Analysis for sulfide by electrochemical probes indicated concentrations of less than 1 mg/L. Since the waters are oxic there is no reason to expect sulfide in the water.

Alkalinity titration curves of the trench water samples taken from Barnwell are shown in Figure 5.29.

Table 5.41

Concentration of Dissolved Non-Metals in Water Samples Taken From Barnwell, South Carolina, Disposal Site, March 1979 (mg/L)

Dissolved Component	Trench 8D2	Trench 6D1	Trench 25/21-D1	Trench 3D1	Trench 5D2
Total Alkalinity (as $CaCO_3$)	600	40	80	100	200
Inorganic Carbon					
DOC					
Hardness (Ca+Mg) (as $CaCO_3$)	160	44	66	20	81
Residue (180°C)	650	330	185	80	385[a]
Chloride	85	90	42	7	10
Nitrogen (N) (ammonia)	59	1.4	25	0.3	--[b]
Nitrogen (N) ($NO_2^- + NO_3^-$)	8.0	23	15	<0.04	<0.1
Phosphate	<0.5	<0.5	<0.5	<0.5	<0.5
Silica	6.0	5.8	5.0	4.3	7.6
Sulfate	34	18	56	<5	7
Sulfide	<1	<1	<1	<1	<1
Total Anions (meq/L)	16	4	5.7	2.3	4.4

[a] Filtered acidified sample.
[b] Insufficient sample for analysis.

Table 5.42

Concentration of Dissolved Metals in Water Samples Taken From Barnwell, South Carolina, Disposal Site, March 1979 (mg/L)

Metal	Trench 8D2	Trench 6D1	Trench 25/21-D1	Trench 3D1	Trench 5D2
Barium	<1	<1	<1	<1	<1
Calcium	34	16	21	4.0	3.2
Cesium	<0.1	<0.1	<0.1	<0.1	<0.1
Iron	1.2	0.4	0.2	0.15	1.5
Lithium	<0.1	<0.1	<0.1	<0.1	<0.1
Magnesium	18	1.0	3.3	2.5	3.3
Manganese	0.72	0.45	0.32	0.24	0.34
Potassium	12	1.4	3.5	1.0	4.6
Sodium	87	29	37	2.3	20
Strontium	<0.1	<0.1	<0.1	<0.1	<0.1
Total Cations[a] (meq/L)	12	2.3	4.8	0.55	2.9

[a] Includes nitrogen as NH_4^+.

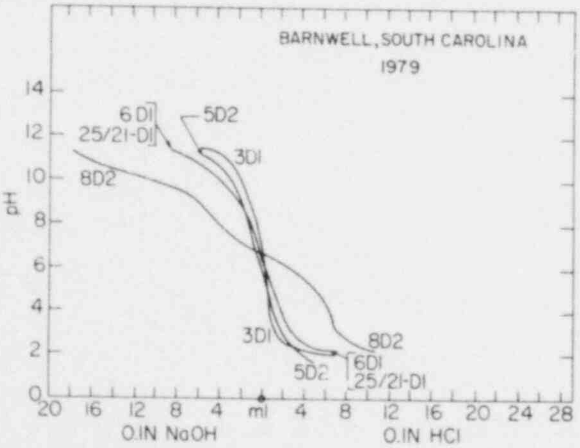

Figure 5.29. Acid-base titration curves of water samples from Barnwell, South Carolina, disposal site, March 1979.

The end points of the alkalinity titration curve are sharp for all the trenches except trench 8D2, which appears to be a more buffered system. This is also related to the short residence time of ground water in the trenches.

5.3.4.3 Organic Analysis

Carbon analysis for the Barnwell samples collected March 1979 are shown in Table 5.43. Only trench water 8D2 had any significant amount of DOC.

Table 5.43

Concentration of Carbon in Water Samples Taken From Barnwell, South Carolina, Disposal Site

Sampling[a] Location	Collection Date	Total Carbon (mg/L)	Inorganic Carbon (mg/L)	Organic Carbon (mg/L)
Trench 8D2	3/79	300	130	170
Trench 6D1	3/79	13	11	2
Trench 25/21D1	3/79	50	38	12
Trench 3D1	3/79	31	24	7

[a] Sampling locations correspond to positions indicated in Figure 4.7.

5.3.4.4 Radiochemical Results for Barnwell, South Carolina

5.3.4.4.1 Dissolved Radionuclides

The activities of dissolved radionuclides in water samples collected from the Barnwell site in March 1979 are given in Table 5.44. Trenches 5D2 and 8D2 have detectable amounts of beta and gamma emitting radionuclides. Tritium is the most abundant radionuclide (4.8 E8 pCi/L, trench 8D2) and is present in all trench waters.

5.3.4.4.2 Suspended Radionuclides

Analyses not yet completed.

Table 5.44

Concentration of Dissolved Radionuclides in Water Samples Taken From Barnwell, South Carolina, Disposal Site, March 1979[a] pCi/L (±2σ%)

Radionuclide	Trench 3D1	Trench 5D2	Trench 6D1	Trench 8D2	Trench 25/21-D1
Gross Alpha	<14	<14	1.6 E1 (65)	<9	<14
Gross Beta	<28	4.1 E2 (8.3)	<28	7.9 E2 (6.6	1.0 E2 (27)
Tritium	1.2 E4 (6.5)	9.6 E6 (<1)	5.7 E5 (<1)	4.8 E8 (<1)	3.7 E5 (<1)
^{238}Pu	b	1.4 E0 (56)	b	1.9 E0 (40)	4.6 E0 (18)
$^{239,240}Pu$	b	1.9 E-1 (200)	b	4.6 E-1 (110)	1.9 E-1 (200)
^{90}Sr	b	4.2 E1 (10)	b	3.7 E1 (18)	9.3 E0 (78)
^{54}Mn	N.D.[c]	3.5 E1 (58)	N.D.	N.D.	N.D.
^{60}Co	N.D.	1.3 E2 (18)	N.D.	2.6 E1 (69)	N.D.
^{137}Cs	N.D.	1.6 E2 (14)	N.D.	N.D.	N.D.

[a] Samples were filtered through a 0.45 μm Millipore filter.
[b] Not analyzed.
[c] N.D. = not detected.

5.4 Summary and Conclusions

5.4.1 Objectives of the Analytical Effort

The analytical effort described in this chapter was designed to gather information pertinent to the following objectives:

- Determine concentrations of radionuclides and other chemical species to assess the magnitude and temporal stability of source term input used in modeling efforts.
- Describe the nature of the water systems in the disposal trenches.
- Evaluate the potential for radionuclide migration from the disposal trenches studied.

5.4.2 Interim Conclusions

- No overall systematic changes in the Maxey Flats and West Valley disposal sites were observed during the brief sampling interval. However, changes in some radionuclide and cation concentrations were observed in several trenches. This may be the result of random breaking of drums and other buried containers.

- To date only one sampling has been performed at the Barnwell, and Sheffield, disposal sites, whereas, the Maxey Flats and West Valley facilities were sampled more extensively over the duration of the program. The water regimes at these sites are oxic relative to the Maxey Flats and West Valley facilities. More detailed conclusions must await the results of further sampling and analysis.

- Tritium was the most abundant of the radionuclides and was found in all the trench waters. Chemically bound as HTO, tritium would be the most mobile radionuclide.

- ^{90}Sr, $^{238,239,240}Pu$ and ^{137}Cs were found as dissolved species in all trench waters and sorbed on suspended particulates at Maxey Flats and West Valley.

- Trench waters are complex anoxic chemical systems which require more extensive investigation to assess their role in radionuclide retention and mobilization.

- Numerous organic compounds were identified in the trench waters at Maxey Flats and West Valley, some of which have the potential for chelation with radionuclides (e.g., Tributyl phosphate, Methyl Isobutyl ketone, phthalates, aniline, cyclohexylamine, etc.).

- The presence of radionuclides above background in wells UB1 and UB1-A together with organic compounds that are also found in nearby trenches indicates communication between the wells and trench water leachates, and that migration of radionuclides from trenches has occurred.

- The two orders of magnitude decrease in DOC in well waters from Sheffield between 1977 and 1979 indicates that the previously suspected contamination from the chemical disposal site adjacent to the radioactive disposal site may not be a problem.

5.4.3 Comparison With 10CFR20, Appendix B, Table II

Radionuclides measured as dissolved species in trench waters may be compared to the standard in 10CRF20, Appendix B, Table II. However, it is understood that the waters in the trenches are not releases and that the standards apply only to releases to an unrestricted area. In this context, Table 5.45 lists in a general way trenches at the disposal sites whose measured concentrations of radionuclides exceed the limits for unrestricted release.

Table 5.45

Trenches Containing Dissolved Radionuclides Exceeding the Standard in 10CFR20, Appendix B, Table II

	Disposal Site			
Radionuclide	Maxey Flats[a]	West Valley[b]	Sheffield[c]	Barnwell[d]
Tritium	All	All	None	5D2, 8D2
^{241}Am	37	None	None	None
^{134}Cs	None	None	None	None
^{137}Cs	None	2, 3, 5, 8, 9	14A	None
^{60}Co	None	3	None	None
^{90}Sr	All	All	14A	None
^{238}Pu	2, 19S, 26, 27, 32, 33L-18	8	None	None
^{239,240}Pu	19S	None	None	None

[a] Trenches at Maxey Flats in Talbe 5.14: 2, 7, 18, 19S, 26, 27, 32, 33L-4, 33L-9, 33L-18, 37.

[b] Trenches at West Valley in Table 5.30: 2, 3, 4, 5, 8, 9.

[c] Trenches at Sheffield in Table 5.39: 14A, 18.

[d] Trenches at Barnwell in Table 5.44: 3D1, 5D2, 6D1, 8D2, 25/21-D1.

6 MICROBIOLOGY

(A. J. Francis, S. Dobbs, B. Nine, and R. F. Doering)

6.1 Introduction

This chapter addresses the potential problem of movement of radionuclides out of the low-level trenches by microbial activity.

Low-level radioactive wastes buried in the commercially operated shallow land disposal sites contain solids and liquids generated from fuel-cycle and non-fuel cycle sources. In general, much of the wastes consist of organic materials such as contaminated paper, clothing, plastics, packing materials, cleanup solutions, and radioactive carcasses of experimental animals.

Microorganisms play an important role in the decomposition of natural and man-made organic materials and are responsible for the transformation of various elements in nature. However, there is very little information on the microbial activities of the low-level radioactive wastes in relation to long term storage, disposal, and possible release of radioactivity in the biosphere.

The objectives of this study are: (i) to enumerate the abundance and distribution of microorganisms active in the trench leachates, and (ii) to determine the effects of various microbial processes on the transformation and migration of the buried radionuclides from the trenches into the environment. This report describes the abundance, distribution, and growth of microorganisms in the waste leachates containing a variety of radionuclides and organics and preliminary data on the degradation of organic constituents of the leachates.

It was found that: (i) aerobic, and anaerobic bacteria, sulfate reducing, denitrifying, and methanogenic bacteria are present in the leachate samples, (ii) the bacteria identified are *Bacillus* sp., *Pseudomonas* sp., *Citrobacter* sp., and *Clostridium* sp., (iii) mixed bacterial cultures isolated from the trench leachates are able to grow anaerobically in trench leachates, which indicates that the radionuclides and organics present in leachates are not toxic to these bacteria, (iv) the organic compounds in the leachates are utilized by the bacteria as a carbon source for growth, (v) preliminary studies on the anaerobic degradation of organic compounds of the leachate sample indicate that several of the organic compounds are being both synthesized and destroyed by these bacteria, and (vi) methane bacteria present in the leachate samples produced appreciable amounts of tritiated and carbon-14 methane from the leachates.

Work was initiated on microbial generation of tritiated- and carbon-14 methane from trench leachates.

6.2 Enumeration of Bacteria in Trench Leachate Samples

Water leachate samples from trenches at Maxey Flats, Kentucky; West Valley, New York; Sheffield, Illinois; and Barnwell, South Carolina disposal sites were collected under anoxic conditions in sterile nitrogen-filled 100-mL serum bottles, packed in ice, and shipped to BNL. The bacterial populations were enumerated within 24 hours after sample collection.

Total aerobic and anaerobic bacterial populations were determined by the pour-plate technique using tripticase soy agar. Tenfold serial dilutions of trench water were made in 90-mL sterile distilled water blanks in stoppered serum bottles, previously flushed and filled with N_2. The dilution agar plates were incubated aerobically or anaerobically at 28°C for up to 2 weeks. Anaerobic incubation was achieved by using anaerobic jars with disposable gas generators and anaerobic indicators (BBL Gas-pak 150, anaerobic system, Bioquest, Cockeyville, Maryland).

Denitrifying bacteria were determined by the most-probable-number (MPN) technique using nitrate broth as described by Focht and Joseph.(1) The denitrifiers are responsible for the reduction of nitrate and nitrite in the presence of an adequate supply of available organic compounds under anaerobic conditions. The end products of biological denitrification are N_2O and N_2.

Sulfate-reducing bacteria were determined by the MPN technique using prereduced anaerobically sterilized (PRAS)(2) sulfate API broth (Difco, Detroit, Michigan) prepared in 9-mL volumes in 20-mL serum bottles. Inoculations and dilutions were carried out simultaneously as described in the Difco technical information supplement No. 0233. Vials were incubated at 28°C for 1 to 3 weeks and examined daily for blackening of the medium. Sulfate-reducing bacteria convert the sulfate to sulfide which reacts with ferrous ion and gives a black color. These bacteria are active in the corrosion of iron and aluminum alloys, desulfurization of oil, and deposition of mineral sulfides. An anaerobic environment with hydrogen or an adequate supply of organic materials is required for efficient reduction of sulfate.

Complex organic materials in soils can be degraded by microorganisms to simple organic acids, alcohols, aldehydes, ketones, esters, and gases such as H_2, H_2S, CO_2, and CH_4(3,4,5). In anaerobic environments, the methane-producing bacteria are the terminal organisms in the microbial food chain. Organic acids, alcohols, H_2, and possibly other simple organic compounds serve as energy sources for them. Methanogenic bacteria were determined by the MPN technique by measuring the production of methane in a PRAS modified medium.(6,7) The composition of the medium used in this study is given in Table 6.1. Inoculations and dilutions in 9 mL of media in aluminum sealed tubes (Bellco Glass Co., Vineland, New Jersey) fitted with butyl-rubber septum-lip stoppers(6) were carried out in the same manner as described for sulfate-reducing bacteria. The inoculated media was incubated at 28°C in an atmosphere of 80% H_2 and 20% CO_2. After 4 weeks incubation, the presence of methane in the head space was determined by gas chromatography. A Perkin-Elmer model 3920 gas chromatograph equipped with a flame ionization detector and fitted with 3.7-m x 3.2-mm i.d. stainless steel column, packed with Porapak R (80/100 mesh) was used. The operating temperatures of the injector, column and detector were 150°C, 60°C, and 250°C, respectively.

The population distribution of aerobic and anaerobic bacteria, denitrifiers, sulfate-reducers, and methanogens in the trench water and well water samples are given in Tables 6.2 and 6.3. The number of aerobic and anaerobic bacteria is expressed as colony forming units (CFU). The denitrifier populations are much higher than the sulfate-reducers and methanogens.

Table 6.1

Composition of Media for Culturing Methanogens

Component	Amount
KH_2PO_4	0.75 g
K_2HPO_4	1.45 g
NH_4Cl	0.9 g
$MgCl_2 \cdot 6H_2O$	0.2 g
Na_2CO_3	2.0 g
$Na_2S \cdot 9H_2O$	0.5 g
L-Cysteine hydrochloride	0.5 g
Trypticase peptone	2.0 g
Yeast extract	2.0 g
Sodium formate	2.0 g
Sodium acetate	2.0 g
Trace mineral solution[a]	9 mL
Resazurin solution (0.1%)	1 mL
Distilled H_2O	1,000 mL

[a] Composition of trace mineral solution per liter distilled water (adjusted to pH 7.0 with KOH): nitrilotriacetic acid, 4.5g; $FeCl_2 \cdot 4H_2O$, 0.4g; $MnCl_2 \cdot 4H_2O$, 0.1g; $CoCl_2 \cdot 6H_2O$, 0.17g; $ZnCl_2$, 0.1g; $CaCl_2$, 0.02g; H_3BO_3, 0.019g; and $Na_2MoO_4 \cdot 2H_2O$, 0.01g.

Table 6.2

Population of Bacteria in Leachate Samples
From Low-Level Radioactive Waste Disposal Sites

Sample	Collection Date	Aerobic CFU/mL	Anaerobic CFU/mL
Maxey Flats			
Trench 2	7/77	1.2×10^3	1.0×10^2
" 26	7/77	4.7×10^3	4.1×10^2
" 32[a]	7/77	4.8×10^4	1.2×10^4
" 19S	5/78	2.2×10^2	3.2×10^2
Well UB1-A	5/78	3.4×10^3	N.D.[b]
West Valley			
Trench 3	10/78	5.0×10^4	4.0×10^3
" 4	10/78	2.3×10^3	3.3×10^3
" 5	10/78	1.6×10^3	3.5×10^2
" 8	10/78	1.4×10^3	7.6×10^2
" 9	10/78	5.0×10^2	7.3×10^3
Barnwell			
Trench 8D2	3/79	2.0×10^8	1.0×10^4
" 6D1	3/79	3.3×10^3	1.3×10^2
"25/21-D1	3/79	3.5×10^4	2.2×10^3
" 3D1	3/79	1.5×10^5	1.2×10^3
Sheffield			
Trench 14A	4/79	1.7×10^5	4.4×10^4
" 18	4/79	7.1×10^2	6.9×10^1
Well 525	4/79	6.3×10^2	4.2×10^2

[a] Sample analyzed 7 days after collection.
[b] N.D.- Not detected.

Table 6.3

Population of Denitrifying, Sulfate Reducing, and Methanogenic Bacteria in Leachate Samples From Low-Level Radioactive Waste Disposal Sites

Sample	Collection Date	Denitrifiers MPN/mL	Sulfate-Reducers MPN/mL	Methanogens MPN/mL
Maxey Flats				
Trench 19S	5/78	3.3×10^1	4.0×10^0	4.9×10^0
Well UB1-A	5/78	4.6×10^2	N.D.[a]	1.0×10^0
West Valley				
Trench 3	10/78	1.3×10^4	7.0×10^1	2.3×10^1
" 4	10/78	2.3×10^3	4.9×10^2	1.7×10^0
" 5	10/78	3.3×10^2	1.1×10^1	N.D.
" 8	10/78	7.9×10^2	1.7×10^2	1.0×10^0
" 9	10/78	1.3×10^2	3.5×10^2	4.5×10^0
Barnwell				
Trench 8D2	3/79	2.3×10^5	1.1×10^0	0.8×10^0
" 6D1	3/79	1.1×10^3	N.D.	N.D.
"25/21-D1	3/79	1.3×10^4	1.3×10^2	0.2×10^0
" 3D1	3/79	5.4×10^4	N.D.	N.D.
Sheffield				
Trench 14A	4/79	2.4×10^5	N.D.	0.2×10^0
" 18	4/79	9.5×10^2	4.9×10^1	N.D.
Well 525	4/79	1.7×10^3	2.3×10^0	N.D.

[a] N.D.- Not detected.

6.3 Identification of Bacteria

On the basis of differences in colony morphology, several colonies of bacteria were isolated from the aerobic and anaerobic agar plates from Maxey Flats and West Valley samples. Tentative identification of some of the isolates was made with the aid of Bergey's Manual of Determinative Bacteriology,(8) (according to Willis,(9) Holdeman, and Moore(2)), descriptive keys included with the BBL-Minitek differentiation sets, and the Roche Oxi/ferm and Enterotubes The bacteria identified were Bacillus sp, Pseudomonas sp, Citrobacter sp, [illegible] Clostridium sp. Several aerobic gram negative isolates with different [illegible] properties were present but not identified. The radionuclides and the [illegible] compounds present in the trench leachate may be acting as mutagenic agents [illegible] these bacteria. The following isolates 26E1, 26E5, 32E2, and 32E3 were identified as Bacillus sp; 26E2, 26E3, 26E4, 32E6, 32E100, 2E1, 2E2, and 2E3 as Pseudomonas sp; and 32E101 as Citrobacter sp (Table 6.4). The strict anaerobes listed in Table 6.5 were identified as Clostridium sp.

Table 6.4

Characteristics of Bacteria Isolated From Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site

Characteristic	Isolate Number															
	Trench 26						Trench 32							Trench 2		
	26E1	26E2	26E3	26F4	26E5	26E6	32E1	32E2	32E3	32E5	32E6	32E100	32E101	2E1	2E2	2E3
Micromorphology:																
Gram stain	+	-	-	-	+	-	+	+	+	-	-	-	-	-	-	-
Cell morphology[a]	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
Spores	+	ND	ND	ND	+	ND	+	+	+	ND	ND	ND	ND	ND	ND	ND
Motility	-	+	-	-	-	-	-	+	+	-	+	+	+	-	+	-
Biochemical reactions:																
Oxidose	+	+	+	+	-	-	+	+	+	-	+	+	-	+	+	+
Citrate	+	-	+	+	-	-	+	+	-	-	+	+	+	+	+	+
Nitrates reduced[b]	den	den	den	den	-	-	den	den	den	-	-	+	+	+	+	+
Methyl red	+	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-
Dextrose	-	aer[c]	aer	aer	+	-	ND	-	-	-	-	+	+	aer	+	+
Maltose	-	-	+	+	+	-	+	-	-	-	-	+	ND	-	+	+
H_2S	-	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-
Indole	-	-	-	-	-	-	-	-	-	-	-	+	-	-	+	+
Amylase	+	+	+	+	+	-	+	-	-	-	+	+	-	-	+	+
Lysine decarboxylase	ND[d]	-	-	-	-	-	ND	ND	-	-	-	+	-	-	+	+
Gelatinase	-	-	-	-	+	-	+	-	-	-	-	+	-	-	+	+

[a] R, rods
[b] den, denitrified
[c] aer, aerobic degradation
[d] ND, not determined

Table 6.5

Biochemical Reactions of Strictly Anaerobic Bacteria Isolated
From Water Samples Taken From Maxey Flats, Kentucky and
West Valley, New York, Disposal Sites[a]

Test	Isolate Number													
	Maxey Flats, Kentucky							West Valley, New York						
	Trench 26		Trench 32		Trench 19S			Trench 3				Trench 8		
	26-5	26-9	32-3	32E7	19S-11	19S-13	19S-14	35-7	35E2	35-10	35E3	38-4	38-5	38-6
Dextrose	-	-	-	+	-	+	+	+	+	-	-	-	-	-
Maltose	-	-	-	-	-	+	+	+	-	-	-	-	-	-
Xylose	-	-	-	-	-	-	+	+	-	-	-	-	-	-
Lactose	-	-	-	-	-	-	-	+	-	-	-	-	-	-
Nitrates reduced	-	-	-	-	-	-	-	+	-	-	-	-	-	-
Esculin	-	-	+	-	-	-	-	+	-	-	-	-	-	-
Glycerol	-	-	-	-	-	-	-	+	-	-	-	-	-	-
Cooked meat media[b]	D,B	D	D	d	D	d,g	o	d	d	D,B	D	D,B	B	D

[a] All strains are spore forming rods; will not grow aerobically.
[b] Reactions on cooked meat media: D, digestion; d, slow digestion; g, gas; B, blackening; o, no reaction.

6.4 Growth of Bacteria in Trench Leachates

Although aerobic, anaerobic, and facultative organisms are present in the trench leachates, it is not known which of these organisms are actively growing in the trenches. To distinguish and isolate those organisms that are capable of growth in the trench leachate from those organisms that are dormant or not actively growing, 1 mL of the raw trench leachate sample from Maxey Flats trenches 26 and 32, and West Valley trenches 3 and 5 were added to 50 mL of the respective filter sterilized trench leachates. The inoculated samples were incubated anaerobically (BBL Gas-Pak anaerobic system) at 28°C. At periodic intervals, 1 mL aliquots were removed from the enrichment cultures and transferred to their respective filter sterilized trench leachates. After a few days, the inoculated trench leachate samples turned cloudy indicating bacterial growth. Several days after incubation, the leachates turned black indicating the possible formation of metal sulfides. Microbiological examination of the leachate samples revealed the presence of a mixed bacterial population in all of the leachate samples.

A detailed study was undertaken to determine the growth of bacteria in undiluted filter sterilized trench leachate and trench leachate supplemented with mineral salts. For this purpose, 0.5 mL of a 7-day old mixed culture from Maxey Flats trenches 26 and 32, and West Valley trenches 3 and 5 were used to inoculate 100 mL of the respective filter sterilized trench leachate with and without mineral salts. The composition of the mineral salts is given in Table 6.6. The inoculated samples were incubated at 28°C in anaerobic jars. At periodic intervals 1 mL aliquots were removed from each culture flask and the bacterial populations were enumerated by the serial dilution agar pour plate method. Triplicate plates of trypticase soy agar medium were used for each appropriate dilution series, and the plates were incubated anaerobically at 28°C for 3 days. The bacterial populations were enumerated after 3 days, and the results are expressed as colony forming units/mL (Figures 6.1 to 6.4). Addition of mineral salts to the leachates had some influence on the growth of bacteria, but not to the extent that it is a major growth limiting factor for the bacteria. On the basis of colony morphology, there appear to be three to five types of colonies. However, there may be more types of bacteria present that were not distinguishable by colony morphology alone.

These results indicate that: (i) microorganisms are present in the trench leachates, (ii) they are able to grow under anoxic conditions using the nutrients present in the leachates, (iii) the organic compounds present in the leachates are not toxic to these bacteria, and (iv) the radionuclides present in the leachates are not lethal to these bacteria.

6.5 Effect of Radionuclides on Trench Leachate Bacteria

The radioactivity of the waste in the trenches is several orders of magnitude higher than the levels of activity detected in the trench leachate. In addition to radionuclides, a variety of low molecular weight organic acids and alcohols are present in the leachates. The presence of these organic compounds is primarily due to the microbial decomposition of complex organic materials under anaerobic conditions. Although aerobic and anaerobic bacteria have been detected in the leachate samples and have been shown to be metabolically active, it is not known whether these bacteria can grow in the presence of higher levels

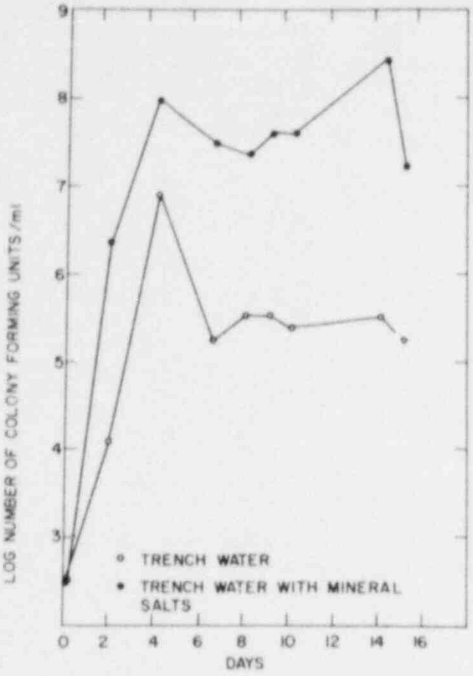

Figure 6.1. Anaerobic growth of mixed culture bacteria in Maxey Flats trench 26 water sample.

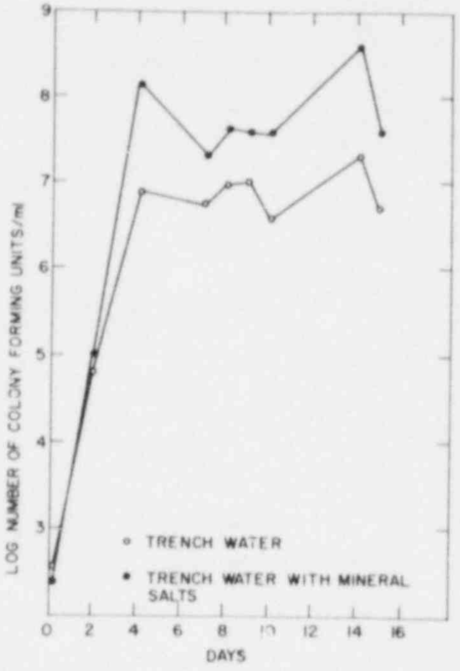

Figure 6.2. Anaerobic growth of mixed culture bacteria in Maxey Flats trench 32 water sample.

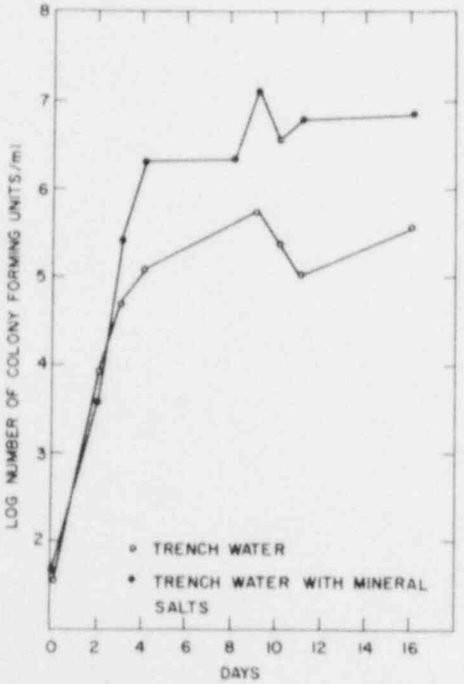

Figure 6.3. Anaerobic growth of mixed culture bacteria in West Valley trench 3 water sample.

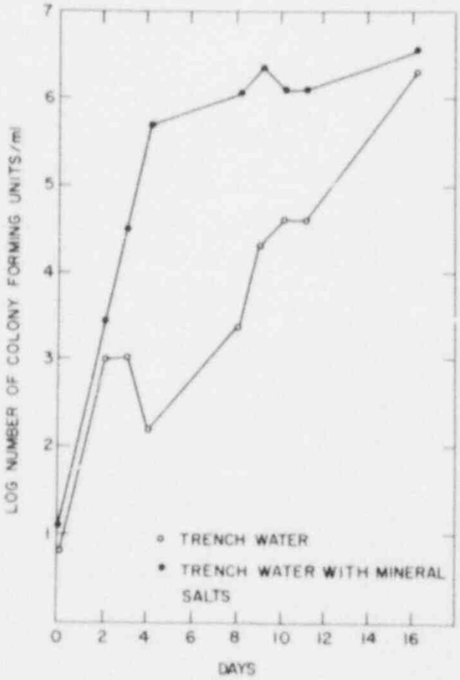

Figure 6.4. Anaerobic growth of mixed culture bacteria in West Valley trench 5 water sample.

Table 6.6

Composition of Mineral Salts Medium

Component	Amount
$(NH_4)_2SO_4$	0.45 g
NaCl	0.9 g
$MgSO_4 \cdot 7H_2O$	0.18 g
$CaCl_2 \cdot 2H_2O$	0.1 g
NH_4Cl	0.5 g
KH_2PO_4	1.5 g
K_2HPO_4	2.2 g
Distilled Water	1000 mL
pH	7.2

of radioactivity. Therefore, the threshold level of radioactivity beyond which the trench water bacteria cannot survive or contribute to the degradation of the buried wastes was determined. For this purpose, a mixture of radionuclides consisting of ^{60}Co, ^{85}Sr, and $^{134,137}Cs$ was prepared in 0.5 M HCl and added to growth media to give total activity concentrations of 2.6×10^2 pCi/mL, 2.7×10^3 pCi/mL, 2.7×10^4 pCi/mL and 2.7×10^5 pCi/mL. Uninoculated media containing radionuclides were acidified with 10 mL of 6 M HCl and were standardized by gamma ray analyses using a Ge(Li) detector and multichannel analyzer system. The levels of each isotope added to the bacterial growth media are shown in Table 6.7. One milliliter of a 4-day old mixed culture of bacteria from Maxey Flats trench 32, grown in filter sterilized trench leachate, was used to inoculate 50 mL of medium in 300-mL nephlo flasks. The medium consisted of NH_4NO_3, 0.5g; $MgSO_4 \cdot 7H_2O$, 0.2g; NaCl, 0.2g; $CaCl_2 \cdot 2H_2O$, 0.025g; $FeSO_4 \cdot 7H_2O$, 0.005g;

Table 6.7

Levels of Radionuclides Added to Bacterial Growth Media

Isotope	Activity (pCi/mL)			
^{60}Co	1.1×10^2	1.0×10^3	1.1×10^4	1.1×10^5
^{85}Sr	8.9×10^0	1.3×10^2	1.4×10^3	1.4×10^4
^{134}Cs	3.8×10^1	3.9×10^2	3.4×10^3	3.4×10^4
^{137}Cs	1.0×10^2	1.2×10^3	1.1×10^4	1.1×10^5
Total	2.6×10^2	2.7×10^3	2.7×10^4	2.7×10^5

$(NH_4)_2SO_4$, 0.4g; K_2HPO_4, 4.8g; KH_2PO_4, 1.2g; dextrose, 5.0g; yeast extract, 2.5g; and distilled H_2O, 1000 mL. The growth of bacteria was monitored by measuring the optical density at 525 nm in a Spectronic-20 spectrophotometer.

The effect of a mixture of the radionuclides on the growth of a mixed culture bacteria isolated from trench 32 at Maxey Flats is shown in Figure 6.5. There is no significant difference in effect on the growth of bacteria between the control, containing no radionuclides, and the media, containing 2.6×10^2 and 2.7×10^3 pCi/mL of radioactivity. The levels of radionuclides added to these bacterial growth media were of the same order of magnitude as those radionuclides found in Maxey Flats trench leachates. At a concentration of 2.7×10^4 pCi/mL the growth of bacteria was inhibited, and two distinct growth curves were observed. This is probably due to selection of radio-resistant strains or mutants of bacteria. However, growth of bacteria was completely inhibited at 2.7×10^5 pCi/mL of radioactivity.

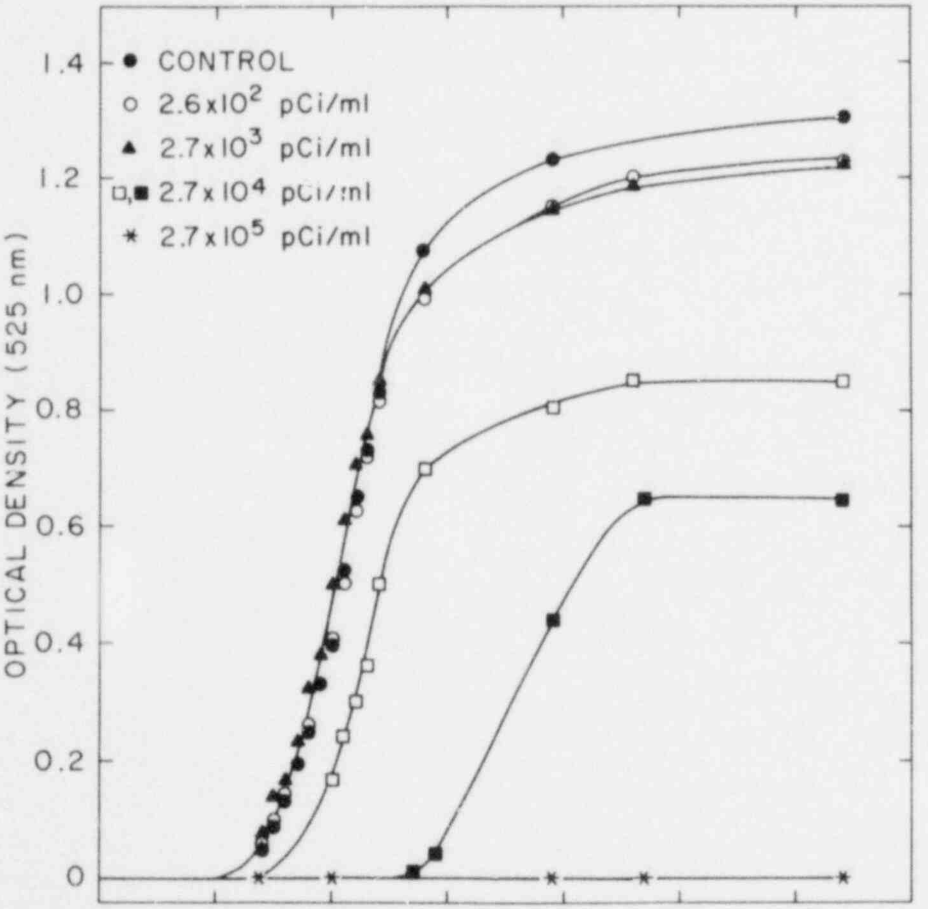

Figure 6.5. Effect of ^{60}Co, ^{85}Sr, and $^{134,137}Cs$ on growth of mixed culture bacteria from trench 32 at the Maxey Flats, Kentucky, Disposal Site.

6.6 Microbial Degradation of Organic Compounds Present in Trench Leachates

The organic compounds present in the leachate samples may play a major role in the transport of radionuclides by leaching, solubilization, and formation of organoradionuclide complexes. For example, chelating agents such as EDTA have been reported in the transport of ^{60}Co from radioactive waste disposal sites.(10) Several organic acids from the decomposition of organic materials are involved in the solubility and leachability of heavy metals in forest soils.(11) Microbial degradation of the organic constituents of the waste under anaerobic conditions results in the production of gases such as carbon dioxide, hydrogen, methane, and several organic acids and alcohols which may influence the mobility of buried radionuclides. The chemical and biological stability of the synthetic (decontamination agents), naturally occurring and microbiologically synthesized complexing agents, and the radionuclide complexes are among the critical factors which determine the mobility of the radionuclides from the burial environment into the biosphere. Lack of such information often complicates studies that deal with prediction of soil retention characteristics of radionuclides. Furthermore, a comprehensive information on the behavior of the contaminated organic compounds in the disposal environment may aid in the formulation of guidelines that will either restrict or allow certain kinds of compounds for shallow-land disposal.

Although microbial degradation of organic materials in anaerobic environments proceeds albeit slowly, it is not clear which of the organics found in the leachates are further degraded and the extent of decomposition. For this purpose, leachate samples collected from trenches 26 and 32 at Maxey Flats were filter sterilized. A mixed culture bacteria isolated from each of trenches 26 and 32 was used to inoculate 100 mL of the respective filter-sterilized trench waters, in serum bottles filled with N_2. Uninoculated, filter-sterilized control samples were incubated under identical conditions. After 30 days of incubation at 28°C, the inoculated and the control samples were analyzed for the organic constituents by gas chromatography and mass spectrometry as described in the organic analyses section of this report (Appendix D). The changes in concentration of several organic constituents due to microbial action are shown in Tables 6.8 and 6.9. Changes in concentrations of several acidic compounds were observed in both the leachate samples. However, little degradation of tributyl phosphate and α-terpineol were observed. These compounds may play an important role in the transport of radionuclides. Several of the low molecular weight organic acids are formed due to breakdown of complex organic materials and are further metabolized by microorganisms; hence these compounds are in a dynamic state being both synthesized and destroyed.

6.7 Microbial Generation of Tritiated and Carbon-14 Methane from Trench Leachates

Radioactive gaseous compounds such as CH_3T, HTO, HT, other tritiated hydrocarbons, ^{85}Kr, ^{222}Rn, $^{14}CO_2$, $^{14}CH_4$, and other ^{14}C-hydrocarbons have been detected coming from burial trenches at West Valley, N.Y.(12,13) Of these, tritiated methane is one of the most abundant; it has been estimated that one tenth to two curies per year of CH_3T is released to the environment from various trenches at West Valley.(13)

Table 6.8

Anaerobic Degradation of Organic Compounds Present in Maxey Flats Trench 26 Leachate Sample by a Mixed Culture Bacteria

Compound	Initial Concentration (mg/L)	Change in Concentration (%)
2-Methylpropionic acid	3.5	+ 31
2-Methylbutanoic acid	19	+ 16
Valeric acid	4.6	- 100
C_6 acid (unidentified)[a]	N.Q.[b]	+ 5.8
C_6 acid (unidentified)[a]	N.Q.	+ 3.6
Hexanoic acid	1.8	- 100
2-Methylhexanoic acid	1.3	+ 8
Cresol	1.8	+ 11
C_8 acid (unidentified)[a]	N.Q.	- 4
C_8 acid (unidentified)[a]	N.Q.	- 0.5
Benzoic acid	1.1	0
Phenylacetic acid	1.4	- 7
Phenylpropionic acid	1.2	- 100
α-Terpineol	0.16	- 6

[a] Percent change in concentration was determined on the basis of the ratio of the compound with the internal standard.
[b] N.Q. = Not Quantified.

Although much is known about the microbial metabolism of ^{14}C-compounds and production of $^{14}CO_2$ and $^{14}CH_4$, very little is known about the microbial generation of tritiated methane.

Since methane bacteria were detected in several of the leachate samples, the ability of methanogens to produce tritiated methane from trench leachate containing tritium and other radionuclides and from synthetic media containing tritiated water was investigated. For this purpose, a mixed methanogenic bacterial culture was isolated from Maxey Flats trench 19S leachate sample. Trench water aliquots of 30 mL each were transferred to sterile stoppered 60-mL serum bottles filled with 85% N_2, 10% CO_2, and 5% H_2 or with 80% H_2 and 20% CO_2. They were incubated (a) as is, (b) inoculated with mixed methanogenic culture, or (c) with 10% formaldehyde to prevent bacterial growth (control). The rates of methane production by the uninoculated and inoculated samples incubated in the N_2 + CO_2 + H_2 and CO_2 + H_2 atmospheres are shown in Figure 6.6. At the conclusion of the experiment, the gas samples were analyzed for the presence of carbon-14 and tritium activity in the methane fraction. The samples incubated under H_2 + CO_2 produced more methane with higher $^{14}CH_4$ and CH_3T activity than the samples incubated under N_2 + CO_2 + H_2 (Table 6.10). Furthermore, significant quantities of

Table 6.9

Anaerobic Degradation of Organic Compounds Present in Maxey Flats Trench 32 Leachate Sample by a Mixed Culture Bacteria

Compound	Initial Concentration (mg/L)	Change in Concentration (%)
2-Methylpropionic acid	5.9	- 2
2-Methylbutyric acid	21	- 52
3-Methylbutyric acid	9.9	0
Valeric acid	5.5	+ 27
2-Methylpentanoic acid[a]	N.Q.[b]	- 24
C_6 acid (inidentified)[a]	N.Q.	- 27
Phenol	1.1	- 27
Hexanoic acid	5.1	- 45
2-Methylhexanoic acid	3.0	- 10
Cresol (isomers)	3.9	- 21
C_8 acid (unidentified)[a]	N.Q.	- 13
Benzoic acid	1.9	- 26
Octanoic acid	1.9	- 21
Phenylacetic acid	3.8	- 50
Phenylpropionic acid	9.3	- 53
Phenylhexanoic acid	N.Q.	- 11
α-Terpineol	0.26	- 12
Tributyl phosphate	0.24	0

[a] Percent change in concentration was determined on the basis of the ratio of the compound with the internal standard.

[b] N.Q. = Not Quantified.

tritiated methane were produced from synthetic media containing 2 mCi of tritium as HTO or $CH_2TCOONa$ (tritiated acetate). The levels of tritium used in this study had no apparent effect on methanogenesis. Although the same levels of tritium as HTO and tritiated acetate were added to the media, increased levels of tritiated methane were produced from media containing tritiated acetate (Figure 6.7). This is due to preferential utilization of acetate by methanogens in the biosynthesis of methane. In nature, acetate is converted to methane via a reaction in which the methyl group is reduced to methane while the carboxyl group is oxidized to CO_2 and H_2O. There was no detectable direct chemical exchange of tritium from HTO to CH_4 in incubation bottles containing uninoculated media, sterile methane, and 1.4 mCi of tritium as HTO. The mechanism of incorporation of tritium from HTO to the methane fraction is not clearly understood. Nevertheless, tritium may exchange with hydrogen atoms of the organic compounds, such as acetate, or the bacteria are able to use tritium or hydrogen from water in methane biosynthesis by enzymatic reactions.

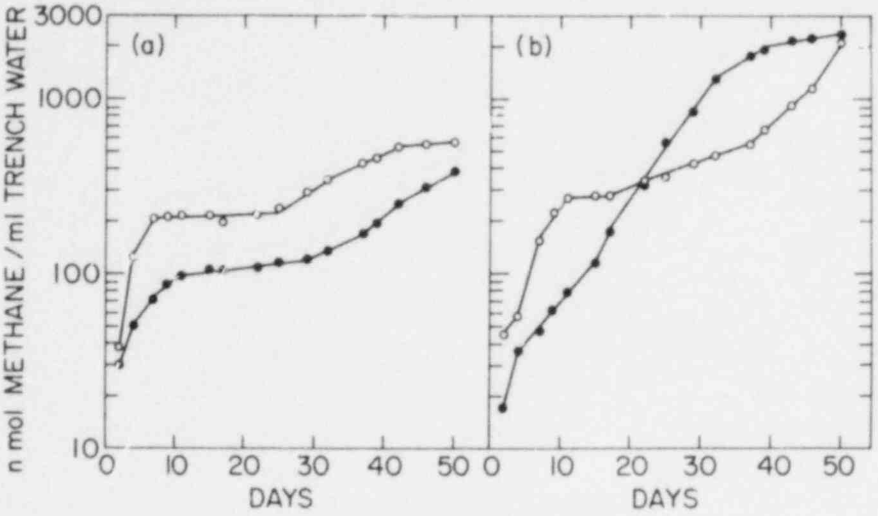

Figure 6.6. Microbial generation of methane from Maxey Flats trench 19S leachate (a) gas phase 85% N_2, 10% CO_2 and 5% H_2; (b) gas phase 80% H_2 and 20% CO_2; ○ - inoculated with mixed culture methane bacteria; ● - uninoculated raw trench leachate.

Table 6.10

Microbial Production of $^{14}CH_4$ and CH_3T From Maxey Flats Trench 19S Leachate Sample

Sample[a]	Methane Produced (nmol)	Total Activity (pCi)	
		$^{14}CH_4$	CH_3T
Control	980	0.5	0.03
Inoculated (N_2 + CO_2 + H_2)	18,000	0.59	1.0
Inoculated (CO_2 + H_2)	68,000	12	57

[a] 30 mL of trench leachate in 60-mL bottle.

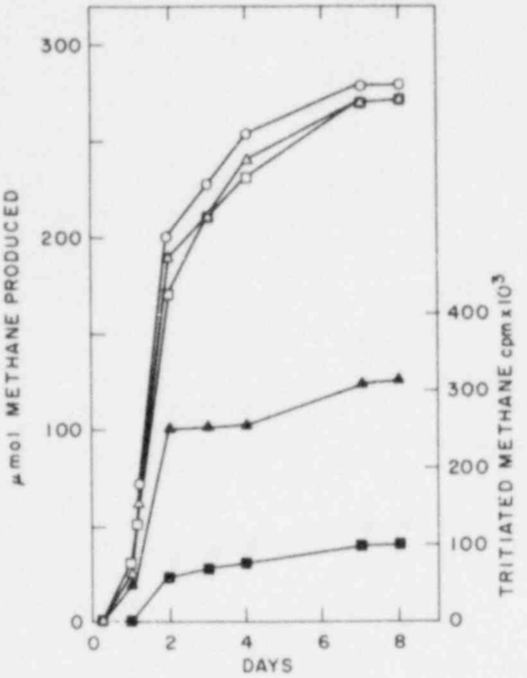

Figure 6.7. Microbial production of tritiated methane from HTO and tritiated acetate (CH_2TCOO^-). Methane production from ○, control; □, 2 mCi HTO; and △, 2 mCi tritiated acetate. Tritiated methane production from ■, 2 mCi HTO; and ▲, tritiated acetate.

Various microbial processes may bring about changes in the forms of radionuclides, such as oxidation-reduction reactions, solubilization, leaching, formation of radionuclide complexes of microbial metabolites, and degradation of organic components of the waste including chelating agents. The finding of active microflora in the trench leachates suggest that they may play a significant role in the transformation of radionuclides and the organic constituents of the waste, and thus affect the long-term storage, mobility and migration of radionuclides from the waste disposal sites into the biosphere.

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7 GEOCHEMICAL CONSIDERATIONS

(K. Czyscinski)

Introduction

The migration and retention of radionuclides is largely a geochemical problem involving the interaction of local radionuclide-bearing groundwaters with the solid components of the geological media. An important aspect of these processes is the ability of the solid phases to selectively remove radionuclides from the water, the property loosely referred to as sorption. Investigations of the sorption process have numbered in the hundreds and involved both laboratory and field studies. The review by Ames and Rai(1) illustrates the magnitude of this effort over the years.

The present study is unique in that site specific materials are used in the laboratory experiments. Waters collected from commercial shallow land burial trenches are used as the aqueous phase in the sorption experiments. The solid phases consist of samples of the lithosphere, also taken from these disposal sites, at depths comparable to the trenches. Using these materials offers the opportunity to perform laboratory experiments which duplicate the actual field conditions as closely as possible. In addition to these laboratory studies, cores taken from beneath disposal trenches at various sites, (as part of the U.S. Geological Survey modeling studies) are also to be analyzed in terms of their radionuclide content. The efficiency of the geological media in retarding radionuclide migration can be directly determined by analysis of these cores. In addition, the mechanisms which control sorption results observed in laboratory experiments can be checked by looking for confirmatory evidence in the trench cores. Such a combination of laboratory experiments with field verification has seldom been reported in the open literature.

Some important information of direct concern in NRC licensing functions can be obtained from this study. Results from this study will have direct bearing on the following aspects of shallow land burial:

1) designing useful, reliable, testing procedures (such as batch vs. column tests) for measuring sorptive behavior which are in turn used in selecting potential disposal sites, and in modeling studies,

2) establishing siting criteria for future disposal sites, based on mineral-pore water-radionuclide associations which will maximize retention by the geologic media,

3) designing burial procedures, such as using trench lining materials, in order to improve the retention capacity of the geological media.

The geological media of any potential disposal site would require testing to determine its sorptive characteristics as a part of any site evaluation study. Modeling efforts also require information of this kind. An extensive literature exists on "batch" and "column" tests, but critical comparisons of the two methods are not common. The majority of studies use only one procedure. Performing batch and column tests with the same starting materials offers a unique opportunity for critical comparison. Furthermore, the radiochemical analysis of the trench cores offers an opportunity to compare laboratory results with the field situation. This is the ultimate test of these procedures in terms of their predictive application.

Proper site selection criteria are of concern for the obvious environmental contamination problems. The host geologic media must be selected, not only with respect to favorable hydrologic and tectonic conditions, but also based on geochemical considerations. The environment in and around the trenches should be maximized in terms of mineral-pore water associations favorable to radionuclide retention. These associations can be identified by the closely interrelated approach described, and the information applied as a predictive tool in other similar geochemical environments.

The number of potential disposal sites will be limited due to restrictions imposed by hydrogeologic, tectonic, and socio-political considerations. Sites which satisfy these requirements may not have optimum mineralogical properties for radionuclide retention. Such sites could be "engineered" by adding materials to the trenches during construction to enhance radionuclide retention. The selection of proper materials for use as trench liners also requires knowledge of favorable mineral-pore water-radionuclide associations. Again, the results of a closely interrelated laboratory and field study are critical in this respect.

This chapter describes previous work concerning sorption experiments, current experiments, and future plans in this area. The chapter consists of three major divisions: (i) characterization of the solid materials used in the batch sorption tests (trench water used as the liquid phase in the experiments has already been described), (ii) the results of experimental work particularly as they relate to migration and retention of radionuclides, and (iii) future sorption experiments are described in the light of information gained from the past work. The last section also describes the analytical plan to be used in studying the cores taken from beneath the burial trenches. How the laboratory experiments can be related to the field data is discussed, along with some comments on their practical application.

7.1 Sediment Characterization (K. Czyscinski)

7.1.1 Introduction

Characterization of the solid phases used in sorption (K_d) experiments is an integral part of the experimental procedure. Such data supplies necessary input toward interpretation of the experimental results, and allows comparison with the results of similar studies reported in the literature.

For the sedimentary materials used in past and future sorption experiments, the following parameters have been chosen for characterization:

Particle Size Distribution
Surface Area
Mineralogy
Extractable Iron Content
Organic Carbon
Carbonate Content
Cation Exchange Properties

Reasons for selecting these parameters are enumerated in the following pages, along with the results for site-specific materials from the West Valley and Maxey Flats disposal sites. Bulk samples of sedimentary material from the sites were used for characterization, as well as ground and sieved (100-200 mesh fractions) material used for some of the sorption experiments. Analytical procedures used are listed in Appendix E, along with any modifications made to these published procedures.

Preliminary results are reported here for shale and "sandstone" samples from the Maxey Flats disposal site, along with till samples from the West Valley facility. Complete characterization will be reported in future reports when completed.

The disposal site at West Valley is situated in a till complex of late Wisconsin age within a sequence of glacio-fluvial sediments. Material used for the sorption experiments was unoxidized till (Lavery till) recovered from bore hole A2, at depths of 27-35 feet (U.S. Geologic Survey drilling program, 1975, supplied by D. Prudic). Drilling logs describe the material as a very fine-grained, moist, plastic, medium olive gray till (N5-5Y5/1), (D. Prudic, personal communication, 1979). The sample used for experiments was dried and hard.

The Maxey Flats disposal site is located in the Nancy shale which consists of a largely fine-grained shale with interbedded sandstone and siltstone lenses. Samples of the "sandstone" and shale were recovered from depths of approximately twelve and twenty feet, respectively, during the course of U.S. Geological Survey investigations of the site. Bulk samples of the material were furnished to Brookhaven for use in sorption experiments (samples obtained from H. Zehner, U.S. Geol. Survey, 1977).

The term "soil" will be used in this report to designate the solid material used in sorption experiments, or in which a disposal site is located, whether this material is soil by the pedologic definition or lithified material. Results presented here aply only to the material used in the sorption experiments. These results are not meant to be characterizations of the entire sedimentary units from which the test materials were collected.

7.1.2 Particle Size Distribution

This is a basic parameter for the description of any sedimentary material, and is chosen for determination when only limited characterizations are performed. Variations in grain size have been observed to affect sorptive behavior in numerous cases. The data are presented graphically on the standard sand-silt-clay triangular diagram (Figure 7.1).

There is not a marked difference between the Maxey Flats shale and "sandstone" (which would be properly called a siltstone), and the West Valley till used in the experiments. The "sandstone" samples used in early sorption experiments were probably incorrectly labeled. The term sandstone is retained only for consistency with earlier reports. However, a significant difference is evident between ground and sieved material, compared to the bulk samples. Although the 100-200 mesh fraction is in the sand size range, these materials are actually richer in fine-grained material than the bulk samples. Grinding has

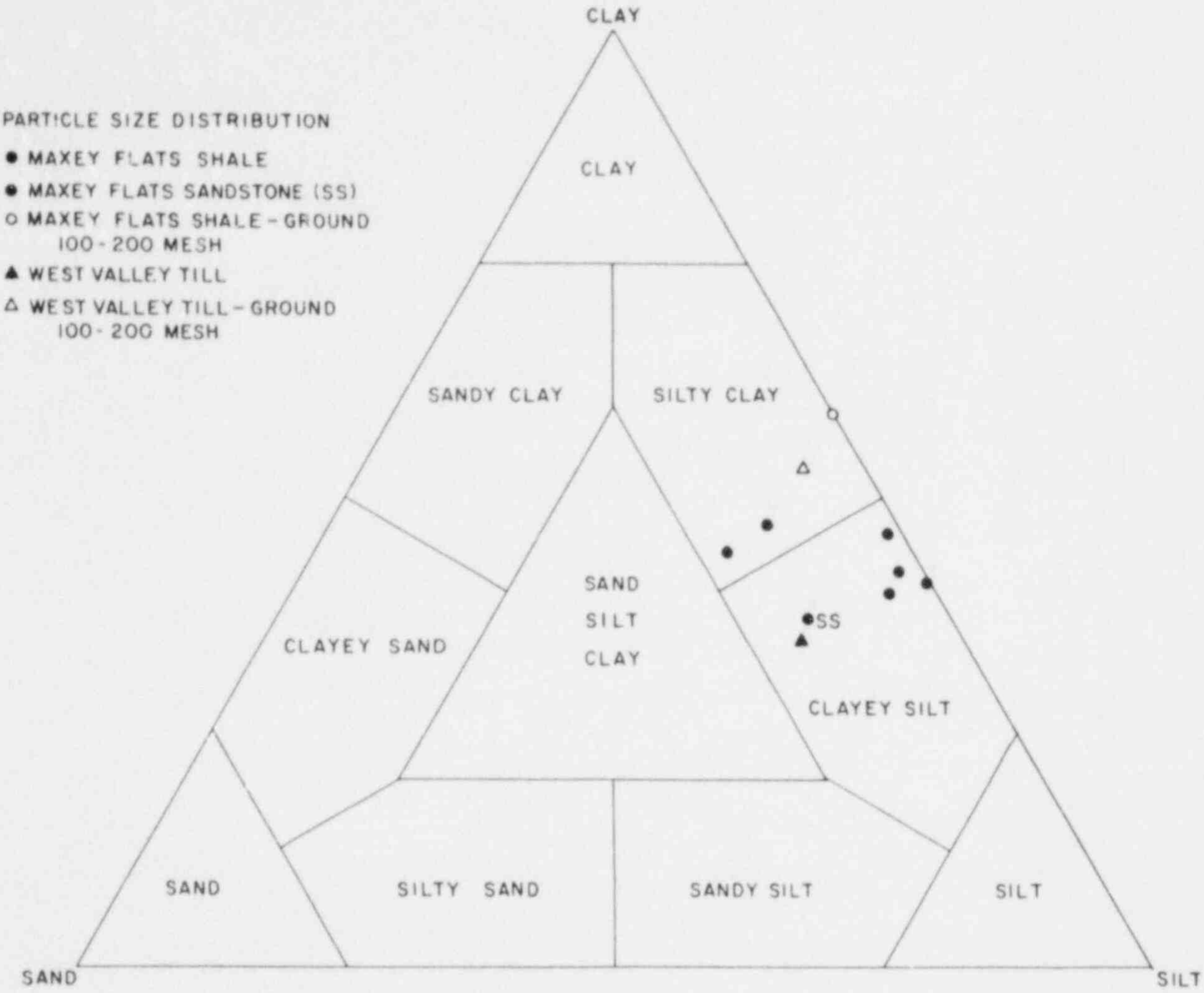

Figure 7.1. Particle size distributions data for Maxey Flats and West Valley samples.

apparently created sand size aggregates of silt and clay size material which are then retained on the sieves.

7.1.3 Surface Area

Sorption of ions from solution can take place by electrostatic attraction arising from broken bonds along the surfaces of solid materials. The amount of available surface area would therefore be a parameter affecting the sorptive behavior of solids. Numerous methods for measuring surface area exist, he most common involving sorption of organic molecules and inert gases. Adsorption of ethylene glycol (EG) and gaseous nitrogen (BET) are the most widely used techniques. Ethylene glycol adsorption is thought to measure both internal and external areas of layer silicates, whereas the N_2 adsorption technique measures external surface alone. Because sedimentary materials almost always contain layer silicates (clay minerals), often in high percentages, the EG technique would be most appropriate for these materials as opposed to the BET measurement. Better correlation of EG measurements with other parameters such as cation exchange capacity and sorption distribution coefficients has also been reported.(2) A quicker procedure using ethylene glycol monoethyl ether (EGME) was also used and gave numbers comparable to the EG results for equivalent samples (Maxey Flats and West Valley bulk samples). Several BET measurements were performed for comparison with the EG results. As expected, large variations between EG and BET results (Table 7.1) are apparent for equivalent samples. The ground and sieved samples have a larger surface area than the bulk material due to the higher content of fine-grained material, as shown by the size distribution data.

Table 7.1

Soil Surface Area Measured by EG, EGME and BET Methods
(m^2/g)

Soil	West Valley Till			Maxey Flats Shale		
	EG	EGME	BET	EG	EGME	BET
	Range			Range		
Ground	27.6-34.0	19.7-22.2	12.1	31.4-42.3	12.1-17.8	12.1
	Average			Average		
	30.9	21.3		41.0	17.4	
	Range			Range		
Bulk	21.8-30.5	21.8-24.3	9.4	19.3-36.3	22.2-34.5	8.8
	Average			Average		
	22.7	22.6		19.8	25.7	

Prior to surface area determination, the ground and sieved samples used for sorption experiments were exhausted and new material had to be prepared. Differences between EG and EGME results for these samples are presumably due to the difficulty in reproducing the grinding and sieving process.

7.1.4 Mineralogy

The mineral composition of the sediment is the most fundamental property relating to its sorptive behavior both qualitatively and quantitatively. Presence or absence of strongly sorbing minerals greatly influences the retention capability of the geologic media. Interactions between minerals and pore waters will control the composition and chemical behavior of the waters, in terms of ion concentrations, pH, redox potential, and subsequent ion speciation. Minerals such as sulfides, present in only minor concentrations, can greatly affect the behavior of the soil (or rock) - pore water system. At the minimum, materials used in sorption experiments must be qualitatively analyzed as to their mineralogy. Mineralogical analyses of the sedimentary materials of concern in this work will be presented in terms of sand, silt, and clay size fractions of the bulk material. Site specific samples were used and the fractionations carried out by ultrasonic disaggregation, followed by appropriate sieving and column settling and decantation procedures.

Qualitative x-ray and microscopic analysis of the shale from Maxey Flats and the till from the West Valley disposal site are given at this time (Table 7.2). More detailed analyses will be performed in the future. Samples from both sites are quite similar in terms of major components, the only significant difference being the high carbonate content of the West Valley tills.

Table 7.2

Qualitative Mineralogical Analyses of
Maxey Flats Shale and West Valley Till

	Maxey Flats Shale and "Sandstone"	West Valley Till (Hole A2 27-28 ft)
Sand Fraction $> 63\mu m$	Quartz Mica ("illite") Feldspars	Quartz Mica ("illite") Calcite Dolomite Feldspars
Silt Fraction $62.5\text{-}4\mu m$	Quartz Mica ("illite") Feldspars	Quartz Mica ("illite") Calcite Dolomite Feldspars
Clay Fraction $< 4\mu m$	Quartz Mica ("illite") Kaolinite Chlorite (minor)	Quartz Mica ("illite") Kaolinite Mixed Layer Clays (minor)

7.1.5 Extractable Iron Content

The extractable iron fraction of a sediment consists of amorphous iron and aluminum compounds and more crystalline iron oxide, and oxyhydroxides. Iron precipitation in the sediment pore spaces can act as a scavenging mechanism for radionuclides; and iron redox chemistry plays an important role in natural systems. Cobalt may be expected to follow the behavior of iron in natural systems, and plutonium has been reported to show an affinity for iron phases in sediments. For these reasons, the amount of highly reactive iron in a sediment is potentially an important consideration.

Results (Table 7.3) show the West Valley till to be twice as iron rich as the shale from Maxey Flats.

Table 7.3

Carbonate, Organic Carbon, and Extractable Iron Content of Disposal Site Materials

	Carbonate (wt. %)	Organic C (wt. %)	Ext. Fe (wt. %)
Maxey Flats Shale	N.D.[a]	0.8	0.15
West Valley Till	14.2	1.7	0.35

---

[a] Not detectable

7.1.6 Organic Carbon

Organic material in sedimentary material affects the cation exchange behavior. Organic material also reacts with pore waters in terms of exchange and complexing reactions which may influence the sorptive properties of the sediment water system. Numerous procedures exist for organic carbon analysis. The relatively simple dichromate oxidation procedure was chosen because it has a long history of use in soil studies and is easily performed. In comparison to the amount and complexity of the organic fraction found in trench waters, the contribution from the soil organic fraction would be relatively minor. As was the case with extractable iron, the West Valley samples are approximately twice as high in carbon as the shales (Table 7.3). This is attributable to the difference in ages between the sedimentary material in these areas. Additional characterization of the organic content (% humic and fulvic acid fractions) of the materials can be performed if necessary.

7.1.7 Carbonate Content

Carbonate minerals can exert a strong influence on the sediment-pore water system. The pH and concentrations of alkaline earth ions in many natural waters are a function of the carbonate content. Carbonate-bearing sediments also show strong pore water buffering capacities. Qualitative identification of carbonate minerals was accomplished by standard petrographic and x-ray analysis techniques, and quantified by a gravimetric procedure. The carbonate content of the West Valley tills is high, reflecting their source area (Table 7.3) in the complex of Palaeozoic sandstone, shales, and limestones of the region.

7.1.8 Cation Exchange Properties

Cation exchange behavior is probably the most complex and poorly understood of the parameters mentioned. The capacity of a sediment to exchange cations is obviously significant in terms of radionuclide retention, but choosing quantitative measures of this behavior is not an easy task. Exchange determination results are strongly influenced by the experimental technique(3,4) so that internal consistency is essential if results for different sediments are to be compared.

A standard sodium displacement technique was used to determine the total exchange capacity (CEC_T) at pH's of 8.2 and 4.5. The pH-dependent portion (ΔpH) of the cation exchange is simply the difference between the two values. Total exchange capacities for strontium (CEC_{Sr}) were also determined. Pretreatments of the sediments prior to the actual determinations were avoided.

Little difference is apparent between sieved and bulk samples (Table 7.4) in terms of total exchange capacity. Exchange capacities at pH 4.5 are consistently lower than at higher pH. An approximate 2-fold decrease is evident for strontium exchange capacities.

Table 7.4

Cation Exchange Data of Disposal Site Materials

(meq/100 g)

	Maxey Flats			West Valley	
	Shale		Sandstone	Till	
	Ground	Bulk		Ground	Bulk
CEC_T (pH 8.2)	10.9	10.9	7.3	8.3	7.4
CEC_T (pH 4.5)	10.5	7.8	6.6	7.0	6.1
ΔpH	0.4	3.1	0.7	1.3	1.3
CEC_{Sr}	6.5	3.9		2.8	4.1

7.2 Determination of Sorption Coefficients (K_d) with Waters and Soils Collected at Low-Level Radioactive Waste Disposal Sites

(R.F. Pietrzak and K. Czyscinski)

7.2.1 Introduction

At present, the ultimate container for long-term storage of low-level radioactive wastes buried in shallow land disposal sites is the geologic media of the disposal site. The materials in which the wastes are presently buried will eventually deteriorate due to weathering and corrosion. Isolation of the buried radionuclides for long periods of time will depend upon several factors, such as the stability of the geologic environment, the hydrological conditions at the site, and interactions of the radionuclides with the geologic media. Retention of radionuclides by geologic media is summarized by the commonly used term "sorption". The mechanisms by which sorption takes place depend upon the chemical and physical interactions between the geologic media and the matrices containing the radionuclides. The geologic media is a complex mixture of water, minerals, and organic matter. Trench waters at the shallow land disposal sites are complex solutions containing a variety of dissolved components which can influence radionuclide sorption reactions. Evaluation of the interactions of these materials is essential to the understanding of sorption mechanisms and for predicting radionuclide behavior in these environments.

To evaluate the potential for radionuclide migration, one of the parameters that must be quantified is the distribution of the radionuclides between the complex solid and liquid phases. This distribution is expressed as an experimentally determined distribution coefficient, K_d, for each element. The K_d parameter, which is included in all groundwater solute transport models, is generally determined by batch or column methods. Batch and column experiments will be conducted using site specific soils and trench waters from the low-level radioactive waste disposal sites. Column studies will be conducted by passing trench water through representative cores obtained from the burial sites and mapping the resultant radionuclide distribution along the lengths of the cores. These data will be compared to the distribution of radionuclides in cores taken from beneath the burial trenches at the disposal sites. The results of batch K_d determinations using site specific soils and trench waters from the Maxey Flats, Kentucky and West Valley, New York disposal sites, are presented in this report.

In this study, the K_d of a radionuclide is defined as the ratio of specific activity in the soil to specific activity in the water after the two phases have been in contact for a given length of time.

$$K_d = \frac{\text{Soil Activity/Weight of Soil}}{\text{Liquid Activity/Volume of Liquid}} \qquad (1)$$

Theoretically, K_d is the value of this ratio when a state of equilibrium exists between the two phases. However, if the contact time is long enough to approach equilibrium, the measured K_d will be a good approximation of the theoretical value.

Sorption studies have generally been performed under oxic conditions. When sorption was studied under both oxic and anoxic conditions, the results differed by as much as an order of magnitude.(5)

The K_d is dependent upon the physio-chemical state of the solid-liquid system. Variables such as Eh, pH, dissolved ion concentrations, soil exchange capacity, surface area and mineralogy are likely to have a strong effect on the sorptive behavior of the system.

Anoxic regimes are frequently present in groundwaters, particularly when water movement is slow, both above and below the water table. Dissolved oxygen in the original meteoric waters is rapidly consumed by bacterial action with the resulting onset of anoxic conditions. Such situations are frequently strongly reducing chemical environments with chemistries strikingly different from oxic regimes.

Reducing conditions exist in the trenches at low-level disposal sites due to microbiological degradation of buried organic wastes. As a result, the Eh and dissolved oxygen in trench waters are low. In order to measure K_d under conditions similar to those existing at the disposal sites, batch experiments were performed in an anoxic environment using actual trench water and unweathered soil from the sites.(6)

Changes in environmental conditions such as pH, redox state (oxidizing or reducing regimes), ion concentrations, soil to solution ratio, etc., would be expected to produce changes in the sorptive behavior of the solid-liquid system. In order to assess the magnitude of such changes, a series of experiments were designed to measure these effects. Anoxic conditions were also to be maintained during some of these experiments in order to more closely simulate field conditions.

Precipitation of iron oxyhydroxides is a sensitive indicator for the onset of oxic conditions in the original anoxic trench waters. Due to the very low solubility of ferric oxyhydroxide, ($Fe(OH)_3$ $K_{sp} = 1.5 \times 10^{-36}$), any oxidation of dissolved ferrous iron in the trench water generally produces a red precipitate.(7,8)

7.2.2 Experimental

7.2.2.1 Water Solution

Water solutions used to prepare samples for the determination of K_d were collected at disposal sites by an anoxic collection procedure described in Appendix B. The waters were stored at approximately 4°C in glass collection bottles under a nitrogen atmosphere to preserve the reducing conditions (low oxygen concentration and low Eh). A list of the water solutions used in the K_d experiments are given in Table 7.5. Water solutions in the original collection condition are referred to in this report as "anoxic trench waters". Analytical data for the anoxic trench waters are given in Chapter 5 of this report.

Table 7.5

Water Used to Prepare Samples for the Determination of K_d

Sample Number	Disposal Site	Site Location	Collection Date
WV-36	West Valley, New York	Trench 4	November 1977
WV-37	West Valley, New York	Trench 5	November 1977
WV-40	West Valley, New York	Trench 2-1A	November 1977
MF-155	Maxey Flats, Kentucky	Trench 19S	May 1978
MF-156	Maxey Flats, Kentucky	Trench 27	May 1978
MF-157	Maxey Flats, Kentucky	Trench 33L-4	May 1978
MF-158	Maxey Flats, Kentucky	Trench 33L-18	May 1978
MF-159	Maxey Flats, Kentucky	Well UB1-A	May 1978

Trench waters which existed under reducing conditions at the disposal sites must be handled in a low oxygen atmosphere to prevent precipitation of ferric hydroxide. An inert atmosphere was used during the determination of the K_d sorption coefficient, to simulate the anoxic conditions existing in the burial trenches. Since the preservation of samples for K_d determination for a month was quite difficult, an alternative procedure of working in an oxidizing atmosphere was tried. Trench waters were exposed to the air to precipitate ferric hydroxide. The precipitate was removed by filtration through glass fiber filter paper followed by 0.45 μm membrane filter paper. The resulting water was used to prepare samples for K_d determination. Such air exposed and filtered waters are referred to as "oxic trench waters" in this report.

Dilutions (1/10 v/v) of trench waters under an inert atmosphere (nitrogen or argon) were made by transferring 10 mL of filtered anoxic trench waters, using the manifold procedure described in Appendix F, to 90 mL of distilled water containing additional amounts of the radionuclides being studied.

7.2.2.2 Soil Samples

The U.S. Geological Survey collected bulk soil samples of unweathered till from the West Valley, New York, Disposal Site and unweathered Nancy shale and sandstone from the Maxey Flats, Kentucky, disposal site.(9) These soils were intact, nonhomogeneous bulk cores listed in Table 7.6. Chemical and mineralogical data are given in Section 7.1. The first approach was to grind the material in a ball mill and sieve the resulting powder to remove coarse materials. A 100-200 mesh fraction (149 μm-74 μm) was used to prepare samples for the determination of K_d. Such samples will be referred to as containing a "100-200 mesh fraction" of soil in this report.

Table 7.6

Soils Used to Prepare Samples for the Determination of K_d

Sample	Disposal Site	Site Location	Collection Date
WV-A2 Unweathered Till	West Valley, New York	Trench 2, east end Test Hole A2 at 34.8 to 35.1 feet	1975
MF-II Sandstone	Maxey Flats, Kentucky	Trench 46 at ∿ 12 feet	1977
MF-III Nancy shale Unweathered	Maxey Flats, Kentucky	Trench 46 at ∿ 20 feet	1977

The process of grinding and sieving involved a considerable risk of obtaining misleading K_d results because the grinding process can increase the surface area of the material(1,10). Also, the sieving of the ground till, to obtain a uniform sample, can produce separations of the clay, sand and silt constituents. The alternative process was to prepare K_d samples from chips of the bulk soil and to disaggregate the soil by vibrating the prepared K_d samples in an ultrasonic bath. The disadvantage of the ultrasonic method is that the samples are not necessarily uniform.

7.2.2.3 Sample Preparation Procedure

The general method of preparing samples for the determination of the sorption coefficient K_d was to first add filtered trench water to a small volume of radionuclide "spike" solution containing ^{241}Am, ^{85}Sr, ^{134}Cs, ^{137}Cs, ^{59}Fe, ^{60}Co or ^{152}Eu. Aliquots of the spiked trench water solution were added to soil in a reaction container. Another aliquot of a spiked trench water solution was added to a reaction container not containing soil and reserved as a "control" sample to measure the initial radionuclide concentrations. A manifold was constructed to perform a series of anoxic operations with trench water. These operations included: (a) filtration, (b) dilution, (c) pH adjustment, (d) addition of specific radionuclides, and (e) transfer to reaction vessel containing soil.

The samples were tumbled to achieve a radionuclide equilibrium between the soil and the solution. The activity remaining in the liquid phase after mixing with the solid was determined by gamma-ray spectroscopy using a Ge(Li) detector. A description of the general procedure is given in Appendix F. Modifications of the general procedure are described in the individual experimental results section.

7.2.3 Results

7.2.3.1 Effect of Dilution and Oxidation of Trench Water

Preliminary experiments were designed to assess the effect of differences in redox state and large changes in ionic composition on the sorptive behavior of a specific trench water and soil system.

K_d sorption coefficients were measured with the following water samples:

(1) Anoxic trench 5 water
(2) 1:10 dilution of anoxic trench water
(3) Trench water exposed to air, after which the $Fe(OH)_3$ precipitate was filtered from solution. Oxic trench 5 water.
(4) Deionized water ($\sim 5 \times 10^{-4}$ M HCl).

K_d results are listed in Table 7.7.

Table 7.7

Sorption Coefficient of Trench 5 Water and Soil
From West Valley, New York, Disposal Site
(Anoxic Versus Oxic Water)

		K_d (mL/g)[a]			
Liquid Phase	Container	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co
Anoxic Trench Water	Teflon	11 ± 1	30 ± 4	38 ± 4	22 ± 1
	Glass	<1	39 ± 2	34 ± 3	9 ± 1
Anoxic Trench Water 1:10 dilution	Teflon	8 ± 1	121 ± 3	120 ± 8	116 ± 12
Air Exposed & Filtered Trench Water	Glass	<1	22 ± 1	23 ± 2	29 ± 3
Deionized Water (5×10^{-4} M HCl)	Glass	20	> 1800	> 1800	> 900

Trench Water:	Trench 5 water (WV-37)
Solid Phase:	Unweathered till, (WV-A2), 100-200 mesh fraction.
Water/Soil Ratio:	20 mL/g
Equilibration Time:	18 hours

[a] K_d is reported as an average ± one standard deviation of the observed results.

Doubt as to the totally anoxic condition of the samples arose because of the presence of some red ferric hydroxide precipitate on the walls of the Teflon containers.

Sorption of carrier free radionuclides from deionized water (~ 5×10^{-4} M HCl) was very large. The K_d is reported as greater than the listed value due to the low residual activity in the water phase, and because of possible contribution of counts from the soil.

The K_d value from a 1:10 dilution of trench water is intermediate between anoxic trench water and deionized water for ^{134,137}Cs and ^{60}Co. One possible explanation is that the trench water contains dissolved components which compete with radionuclides for sorption sites on the solids. Complexing agents in the trench water may also keep radionuclides in the liquid phase. Diluted trench water will have less of these components, some of which may be carrier metal ions, complexing agents or organic species in trench waters from the disposal sites.

7.2.3.2 Effect of Water/Soil Ratio

The ultimate purpose of K_d determinations is to estimate the retardation of nuclides by sorption on the geological media of the burial site. The purpose of this experiment was to measure the sensitivity of the batch K_d method to changes in the water/soil ratio.

Samples were prepared in glass test tubes. The septum-sealed glass tubes shown in Appendix F, Figure F.7, preserved the anoxic condition of the trench water.

When varying amounts of soil were equilibrated with a fixed volume of anoxic trench water for 18 hours, the K_d values were not constant. K_d results are given in Table 7.8 for trench water samples and in Table 7.9 for distilled water samples. The change in K_d versus water/soil ratio for ^{60}Co, ^{85}Sr, and ^{134,137}Cs are shown in Figures 7.2, 7.3, and 7.4, respectively. The straight line logarithmic relationship between K_d and water/soil ratio resembles the Freundlich adsorption isotherm for sorption of solutes from solution onto solids. No explanation is given at this time for the exceptional behavior of ^{60}Co in deionized water (Figure 7.2). The K_d's for ^{60}Co and ^{134,137}Cs from 1:10 diluted anoxic trench water are shown in Figures 7.2 and 7.3 for a water/soil ratio of 20 mL/g. K_d values for ^{85}Sr as a function of water/soil ratio with anoxic trench water were not obtained in this series.

These preliminary results do not indicate a limiting value of K_d with decreasing water to soil ratio. This seems to imply that it is necessary to obtain chromatographic K_d values from soil cores and trench water under field conditions. The batch method nevertheless provides a rapid method for determining relative K_d values of a group of radionuclides under the same experimental conditions, and for studying general properties of trench water-soil systems at the disposal sites.

Table 7.8

Sorption Coefficients of Trench 5 Water and Soil From West Valley, New York, Disposal Site (Solution/Soil Ratio Study)

Solution/Soil Ratio (mL/g)	K_d (mL/g)		
	^{134}Cs	^{137}Cs	^{60}Co
290	< 1	15	26
163	15	23	16
68	24	29	14
30	33	36	13
24	35	42	13
20	37	42	13
18	41	37	13
11	54	49	12

Trench Water: (WV-37) Trench 5, Anoxic
Solid Phase: Unweathered till (WV-A2), 100-200 mesh fraction.
Reaction Containers: Screw cap, septum sealed, glass test tubes (Bellco 2047-16125), Appendix F, Figure F.7
Equilibration Time: 18 hours

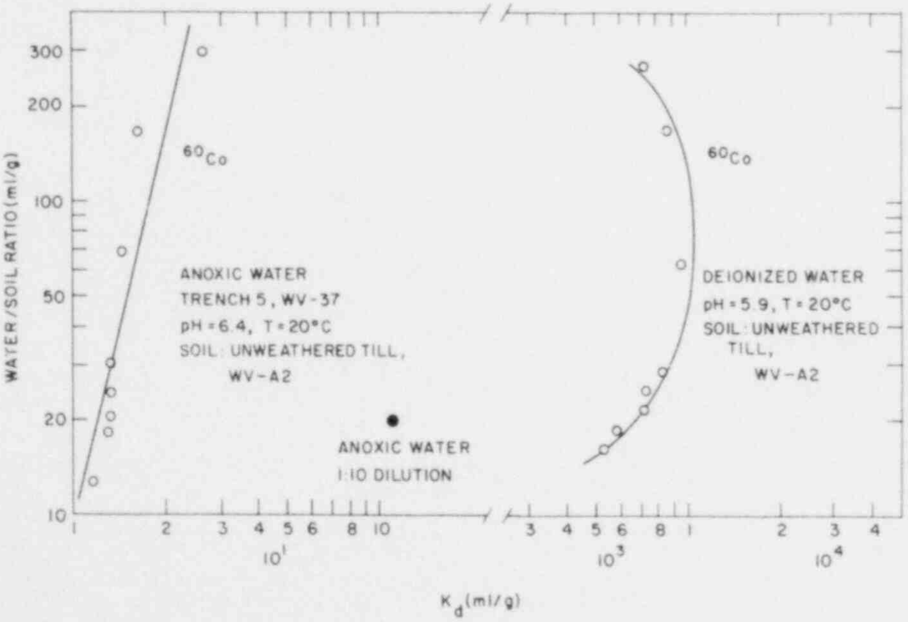

Figure 7.2. K_d sorption coefficient versus water/soil ratio for ^{60}Co.

Table 7.9

Sorption Coefficients of Distilled Water and Soil From West Valley, New York, Disposal Site (Effect of Changes in the Solution/Soil Ratio)

Solution/Soil Ratio (mL/g)	K_d (mL/g)			
	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co
272	44	27,500	26,200	6,200
168	47	19,300	20,800	8,700
63	30	10,000	10,400	9,500
28	24	7,000	6,800	8,300
25	21	6,900	6,300	7,300
21	21	6,700	5,600	7,100
18	21	4,300	5,100	5,900
17	20	---	5,300	5,200

Distilled Water:	∿ 5×10^{-4} M HCl
Solid Phase:	Unweathered till (WV-A2), 100-200 mesh fraction.
Reaction Containers:	Screw cap septum sealed, glass test tubes, (Bellco 2047-16125), Appendix F, Figure F.7
Equilibration Time:	18 hours

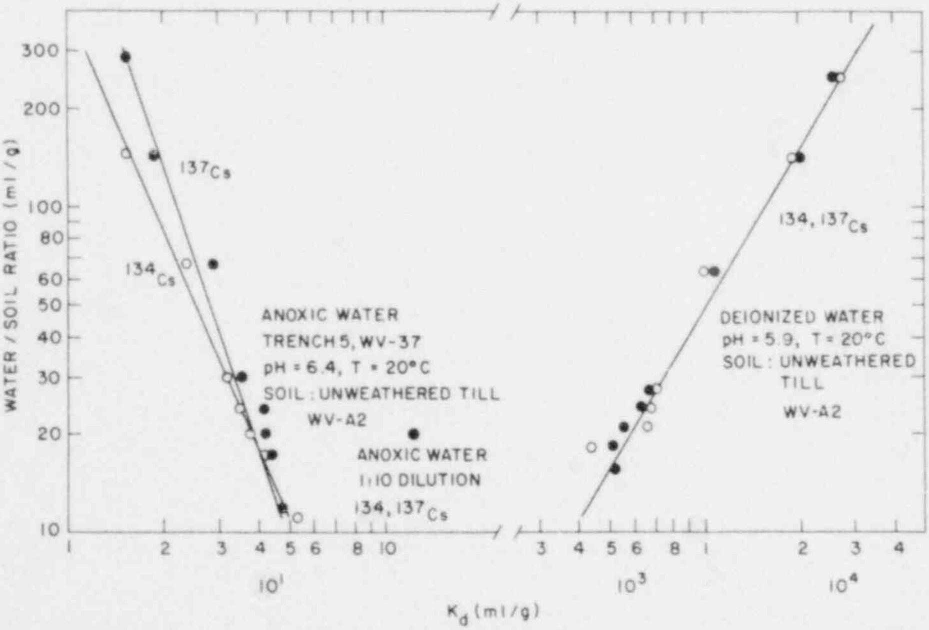

Figure 7.3. K_d sorption coefficient versus water/soil ratio for $^{134,137}Cs$.

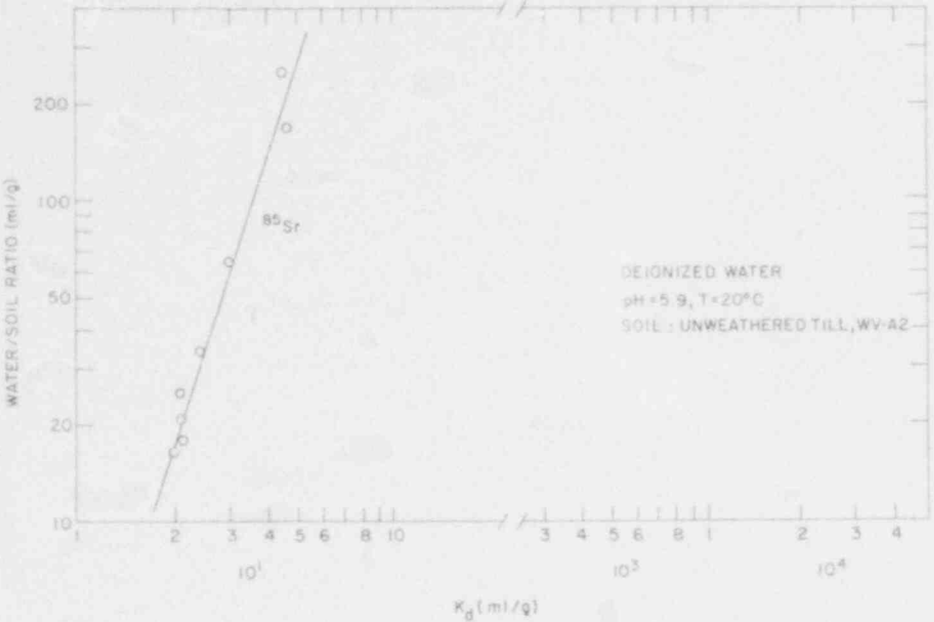

Figure 7.4. K_d sorption coefficient versus water/soil ratio for ^{85}Sr.

7.2.3.3 Variation of K_d with Solution Acidity

The change in radionuclide sorption, K_d, after the addition of small amounts of acid or base to trench water was investigated.

Samples for K_d determinations were prepared in glass test tubes shown in Appendix F, Figure F.7. The septum sealed glass tubes preserved the anoxic condition of the trench water.

Addition of small volumes (0.1 mL) of nitric acid (0.1 M) or sodium hydroxide (0.1 M) to the septum sealed glass sample tubes was made by means of a hypodermic syringe.

Radionuclide K_d results for addition of acid or base are given in Table 7.10 and Table 7.11, respectively. Trench 5 water (WV-37) maintained a constant pH of 6.4 in spite of the addition of sodium hydroxide or nitric acid, because the solution is a highly buffered system (see titration curves in Section 5.3.2.2). However, significant changes in the sorption coefficients, K_d, of radionuclides were observed. A graph of these K_d versus addition of acid or base results is given in Figure 7.5.

Table 7.10

Sorption Coefficients of Trench 5 Water and Soil from West Valley, New York, Disposal Site (Modified by Addition of Nitric Acid)

HNO_3 mmoles/mL	K_d (mL/g)			
	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co
0	-	39	34	9.3
0.7×10^{-4}	21	45	39	10
1.4×10^{-4}	32	36	33	5.9
2.0×10^{-4}	15	33	34	6.6
2.8×10^{-4}	15	40	42	8.1

Trench Water: Anoxic Trench 5 (WV-37)
Solid Phase: Unweathered till (WV-A2), 100-200 mesh fraction.
Solution/Soil Ratio: 20 mL/g
Reaction Containers: Screw cap, septum sealed, glass test tubes (Bellco 2049-16125) Appendix F, Figure F.7
Equilibration Time: 18 hours

Table 7.11

Sorption Coefficients of Trench 5 Water and Soil from West Valley, New York, Disposal Site (Modified by Addition of Sodium Hydroxide)

NaOH mmoles/mL	K_d (mL/g)			
	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co
0	-	39	34	9.3
0.7×10^{-4}	11	34	37	9.0
1.3×10^{-4}	33	42	38	11
2.0×10^{-4}	36	43	39	15
2.8×10^{-4}	24	45	41	32

Trench Water: Anoxic Trench 5 (WV-37)
Solid Phase: Unweathered till (WV-A2), 100-200 mesh fraction.
Solution/Soil Ratio: 20 mL/g
Reaction Containers: Screw cap, septum sealed, glass test tubes (Bellco 2047-16125) Appendix F, Figure F.7
Equilibration Time: 18 hours

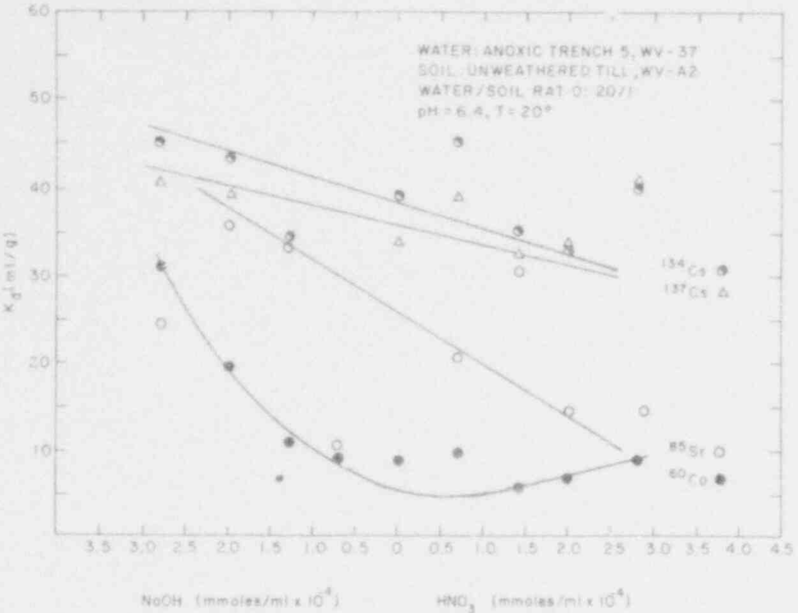

Figure 7.5. K_d sorption coefficient versus addition of acid or base.

It is evident that addition of $5x10^{-5}$ mmoles/mL of H^+ by the spike solution to the trench water is sufficient to significantly affect the K_d. Radionuclide spike solutions mixed initially with trench 5 water (WV-37) should not exceed an addition of $1x10^{-5}$ mmoles/mL of H^+. Consequently, the preferred method for preparing samples for K_d determinations would be to evaporate all the acid from the radionuclide carrier solution before mixing with trench water.

The fact that addition of acid or base to the experimental system did produce a change in the observed K_d results, but did not change the pH, is not easily explained. One possible explanation is that the added acid or base was consumed to produce changes in the water chemistry which in turn affected the sorption capacity. An alternate explanation involving the solid phases may also be possible. The acid or base may compete directly with the radionuclides for the available exchange sites on the soil, or may modify the exchange sites themselves. Hydrogen ion can preferentially displace other cations from exchange sites(11). Destruction of layer silicates (clay minerals) by acid attack, and subsequent lowering of the total exchange capacity, has been observed during acid sulfate soil development(12).

A systems approach to the sorption experiment must be adopted to resolve this question. Water chemistry should be understood in terms of chemical systems operative in the trench waters. In this way, interactions with additional chemical components can be assessed, and interactions between specific soil minerals and the liquid phase also understood. Both the liquid and solid phases of this experiment should be thoroughly analyzed after, as well as before the experiment to determine which of the above explanations is correct. Once the mechanism for the observed results is determined, this information can be applied as a predictive tool in transport modeling.

7.2.3.4 Sorption Coefficients Versus Time

The efficiency of the geologic media for retaining radionuclides will depend, in part, upon the flow rates of the groundwaters in the field situation. Longer mineral-solution contact times will favor enhanced sorption because the sorption process is not instantaneous. This series of experiments attempts to examine the kinetic effect by determining K_d as a function of time.

Trench waters at the West Valley and Maxey Flats burial sites contain appreciable amounts of ferrous ion which oxidizes when exposed to air and precipitates as ferric hydroxide. Since radionuclides could coprecipitate with the iron hydroxide an attempt was made to design an improved reaction bottle. A thick walled, o-ring and septum-sealed TFE Teflon bottle was made, as shown in Figure F.9. Samples were prepared using the manifold technique described in Appendix F. The sealed samples were tumbled in the lucite chamber shown in Figure F.10 which was flushed with a stream of nitrogen. After each period of tumbling the samples were centrifuged and counted with a Ge(Li) detector while shielding the detector from the soil with a lead collimator.

After 235 hours of tumbling the samples were opened in a nitrogen atmosphere glove box. The Eh of each sample was measured with a platinum electrode. The solution from each sample was filtered through a 0.45 μm membrane filter and a 10-mL aliquot was acidified for counting. Counting only the liquid phase from each equilibrated sample gives the best value for the sorption coefficient by eliminating any contribution to the liquid phase counts from the activity in the soil phase.

An identical experiment was performed with a 1/10 dilution of trench 4 water (WV-36) with distilled water.

Sorption coefficients for the trench 4 water (WV-36) equilibrated with unweathered till are given in Table 7.12 and Figure 7.6. The sorption of ^{134}Cs and ^{137}Cs appeared to have reached a constant value after 130 hours. No significant changes in the sorption of ^{59}Fe, ^{60}Co or ^{85}Sr were observed with time. After 235 hours of equilibration the samples were opened in a glove box containing a nitrogen atmosphere. The integrity of the anoxic solution appeared to have been breached, as some reddish precipitate, possibly ferric hydroxide, was observed. Eh measurements of the solution with a platinum electrode confirmed that the solutions were indeed oxic. Consequently, some of the radionuclide content of the control and sample solutions could have been coprecipitated. The solution was filtered through a 0.45 μm membrane filter and a 10-mL aliquot of the filtrate was acidified. The results of counting only the liquid phase are listed at the bottom of Table 7.12.

Table 7.12

Sorption Coefficient Versus Time of Trench 4 Water and Soil From West Valley, New York, Disposal Site (Equilibration Time Study)

Time Elapsed (hours)	K_d (mL/g)[a]				
	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co	^{59}Fe
50[b]	36±4	220±50	220±50	64±9	190±30
72	39±6	500±220	530±170	59±7	220±50
130	46±10	950±160	930±200	57±8	190±20
235	37±6	860±140	770±110	52±1	340±80
10 mL[c] aliquot	2.2±0.3	520±40	510±40	12±1	---

Trench Water: West Valley, New York, Anoxic Trench 4 (WV-36)
Solid Phase: West Valley, New York, Unweathered till (WV-A2) 100-200 mesh fraction
Reaction Containers: o-ring sealed TFE Teflon bottles, Appendix F, Figure F.9
Solution/Soil Ratio: 20 mL/g

[a] K_d is reported as an average ± one standard deviation of the observed results.

[b] Results were obtained by shielding the soil from a Ge(Li) detector.

[c] Results were obtained by counting a 10-mL aliquot of the liquid phase.

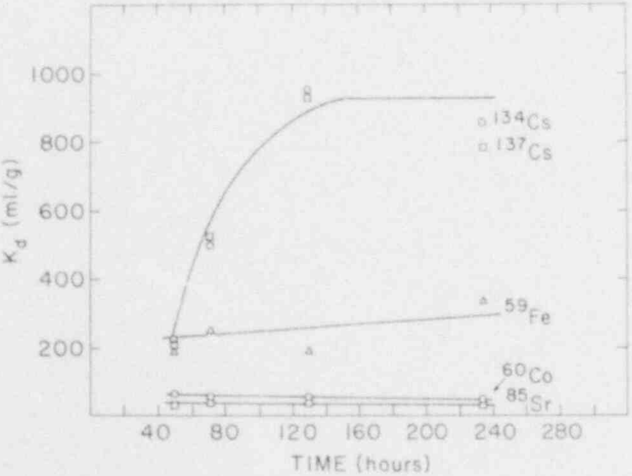

Figure 7.6. K_d radionuclides sorption coefficients versus time for trench water and soil from West Valley, New York, disposal site.

Sorption coefficients for a 1/10 dilution of trench 4 water (WV-36) with distilled water equilibrated with unweathered till are given in Table 7.13 and Figure 7.7. The sorption coefficients for ^{134}Cs, ^{137}Cs and ^{59}Fe appear to have slightly increased with time during equilibration. No significant increase with time was observed for ^{60}Co or ^{85}Sr. No red precipitate of ferric hydroxide was seen when the samples were opened in a nitrogen atmosphere glove box. The aqueous phases were filtered through a 0.45 µm membrane filter and a 10-mL aliquot was acidified with nitric acid. The results of counting the liquid phase only are listed at the bottom of Table 7.13.

Table 7.13

Sorption Coefficient Versus Time of Trench 4 Water
and Soil From West Valley, New York, Disposal Site
(Effect of a 1/10 Dilution)

Time Elapsed (hours)	K_d (mL/g)[a]				
	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co	^{59}Fe
50[b]	16±3	430±8	400±30	130±20	250±50
72	16±1	400±220	380±200	140±45	280±150
130	17±1	500±38	330±10	150±5	260±34
235	18±1	500±7	480±110	160±15	360±80
10 mL[c] aliquot	12±2	630±70	620±60	240±20	---

Trench Water: West Valley, New York, Trench 4 (WV-36) anoxic diluted 1/10 with distilled water.
Solid Phase: West Valley, New York, Unweathered till (WV-A2), 100-200 mesh fraction.
Solution/Soil Ratio: 20 mL/g
Reaction Containers: o-ring sealed TFE Teflon bottles.

[a] K_d is reported as an average ± one standard deviation of the observed results.

[b] Results were obtained by shielding the soil from a Ge(Li) detector.

[c] Results were obtained by counting a 10-mL aliquot of the liquid phase.

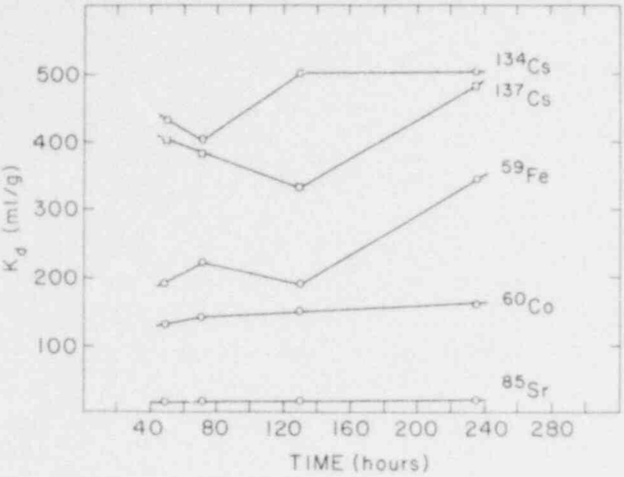

Figure 7.7. K_d radionuclides sorption coefficients for diluted (1/10) trench 4 water and soil from West Valley, New York, disposal site.

The K_d results for the diluted trench water are significantly higher for ^{85}Sr and ^{60}Co than the K_d results for the anoxic trench water. This is again probably due to the competition effect from other ions in the trench water which compete with the radionuclides for exchange sites on the solids. The diluted water contains less competing ions and therefore produces a larger K_d.

7.2.3.5 Anoxic Versus Oxic Trench Water

Waters from the West Valley trenches are chemically reducing, anoxic solutions, frequently containing high ferrous iron contents. Exposure to air causes the ferrous iron to oxidize and precipitate, as commonly observed. This reaction produces hydrogen ion which in turn affects the other charged species in solution. Upon exposure to air, carbon dioxide will also be released from solution, thereby readjusting the carbonate equilibria. The chemical system in anoxic waters is obviously quite different than that in the air exposed waters. A series of experiments designed to assess the effect of these two different water chemistries on sorption behavior were conducted.

Difficulties were experienced in attempting to completely preserve the integrity of the anoxic trench waters during K_d determinations. Consequently, heavy walled, o-ring sealed TFE Teflon bottles were constructed (see Appendix F.3.3.3, Figure F.9). An earlier experiment with a water from the West Valley, New York, disposal site, trench 4 (WV-35), was not completely successful using these bottles. During the current experiment an effort was made to minimize the exposure of the Teflon vessels to air after preparation of the samples by the manifold method as described in Appendix F. The prepared samples were transferred to an argon atmosphere glove box, sealed in the tumbling chamber, removed from the glove box, and tumbled for 456 hours. The samples were transferred back to argon atmosphere glove box, opened, and the solutions were filtered through a 0.45 μm membrane filter. The pH and Eh of each solution was measured. A 10-mL aliquot of each sample solution was acidified with 1-mL of 8 M HNO_3 for gamma ray spectroscopy using a Ge(Li) detector.

K_d results were compared among three sets of samples as follows:

1) Anoxic trench 2-1A water (WV-40),
2) A 1/10 v/v dilution of trench 2-1A water (WV-40) diluted with distilled water,
3) Oxic trench 2-1A water (WV-40).

The Teflon containers were opened in an argon atmosphere glove box and visually inspected for evidence of ferric hydroxide precipitation. No reddish brown colorations due to the oxidation of Fe^{+2} and consequent precipitation of ferric hydroxide was found. The pH and Eh of each sample was measured. The Eh results were calculated from platinum electrode potentials which had reached a steady state value in contact with the sample solution. The time response behavior is shown in Figure 7.8. Results of the Eh and pH measurements are given in Table 7.14. The Eh difference between any oxic or anoxic sample is not significant. This would imply that the anoxic samples had been partially oxidized during the preparation process. However, no visible ferric hydroxide precipitate had formed.

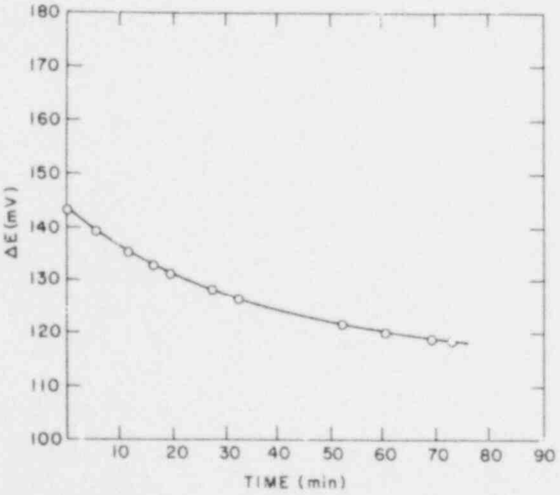

Figure 7.8. Oxidation potential versus time. ΔE(mv) is the measured potential difference between a platinum electrode and silver/silver chloride reference electrode. The trench 2-1A water (WV-40) from the West Valley, New York, disposal site had been equilibrated with unweathered till (WV-A2) for 550 hours.

Table 7.14

pH and Eh of K_d Samples of Trench 2-1A Water and Soil From West Valley, New York, Disposal Site (Comparing Oxic and Anoxic Conditions)

Americium Spiked Solutions

Sample	pH		Eh (mV)	
	control	sample	control	sample
Oxic	7.95	7.85	315	357
Anoxic	8.16	8.41	320	309

^{85}Sr, ^{134}Cs, ^{60}Co Spiked Solutions

Sample	pH		Eh (mV)	
	control	sample	control	sample
Oxic	8.23	8.13	316	390
Anoxic	8.16	8.14	309	371

Trench Water: West Valley, New York, disposal site Trench 2-1A (WV-40)
Soil: West Valley, New York, disposal site Unweathered till, Test Hole A2 (WV-A2), 100-200 mesh fraction
Control: Solution only
Sample: Solution plus soil (20 mL/g)
Oxic: Trench 2-1A water (WV-40) was exposed to air to precipitate ferric hydroxide. Samples for K_d determination were prepared from the solution after the precipitate was removed by filtration.
Anoxic: Samples maintained in an argon atmosphere

A comparison of results for the "anoxic", "anoxic 1/10 dilution" and "oxic" sample sets prepared from trench 2-1A water (WV-40) are given in Table 7.15. The major difference between K_d results for anoxic and oxic solution was the large sorption of ^{241}Am from anoxic solution. Sorption from an anoxic solution diluted with distilled water gave generally higher K_d results for all radionuclides measured except ^{241}Am.

Table 7.15

Sorption Coefficients for Trench 2-1A Water and Soil
From West Valley, New York, Disposal Site
(Comparison Oxic and Anoxic Conditions)

	K_d (mL/g)[a]				
Sample	^{241}Am	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co
Anoxic	8000 ±2000	14±2	56±5	56±4	1.6
Anoxic 1/10 Dilution	290±20	14.2±0.5	380±36	378±38	24±2
Oxic	0.3	12±1	55±4	55±4	< 1

Trench Water:	West Valley, New York, disposal site, Trench 2-1A (WV-40), Collected anoxically, November 1977.
Soil:	West Valley, New York, disposal site, Unweathered till, Test Hole A2 (WV-A2), 100-200 mesh fraction
Solution/Soil Ratio:	20 mL/g
Reaction Containers:	TFE Teflon septum bottles in an argon filled tumbling chamber
Equilibration Time:	456 hours
Anoxic:	Original materials maintained in an argon atmosphere
Oxic:	Trench water was exposed to air to precipitate ferric hydroxide. Samples for K_d determination were prepared from the solution after the precipitate was removed by filtration.

[a] K_d is reported as an average ± one standard deviation of results.

Since both the "oxic" and "anoxic" waters were chemically oxidizing (positive Eh) at the conclusion of the experiment, the Am sorption has apparently arisen due to a change in the water chemistry of the breached "anoxic" sample. A speciation change for americium may have occurred, or some other water chemistry change which could affect the sorption behavior less directly. In order to explain these results the liquid phase would have to be analyzed at the end of the experiment also. The effect of anoxic conditions could not be evaluated from these results.

7.2.3.6 Equilibration Time

A K_d versus time study has also been performed using waters and soil samples from the Maxey Flats disposal facility. In this study bulk samples of the shale and "sandstone" were used because they are more representative of the site-specific material. Ground and sieved material is significantly different than the bulk samples in terms of particle size distribution, and surface area, (Section 7.1).

The amount of time necessary to achieve an equilibrium concentration of radionuclides in solution by sorption on burial site soils was determined by observing the apparent K_d change with time.

Oxic samples for K_d determination were prepared from five trench waters and two soils obtained from the Maxey Flats, Kentucky, waste disposal site. The soils (shale and sandstone) are very similar in composition and grain size. Filtered, air oxidized trench water was spiked with ^{241}Am, ^{85}Sr, ^{134}Cs, ^{137}Cs and ^{60}Co, and added to granules of soil in TFE Teflon bottles. The granules of soil were disaggregated by vibrating the samples in an ultrasonic bath. The activity remaining in solution, after each tumbling period, was used to calculate an apparent K_d.

Plots of the apparent K_d as a function of time are shown in Figures 7.9 to 7.13 for each radionuclide. ^{241}Am continued to be sorbed from solution after 800 hours for the majority of water and soil combinations in Figure 7.9. ^{134}Cs and ^{137}Cs also showed a similar behavior in Figures 7.11 and 7.12. ^{90}Sr and ^{60}Co sorption did not increase significantly after 200 hours of equilibration. Similar behavior was also observed for these radionuclides in the West Valley "K_d versus time" study.

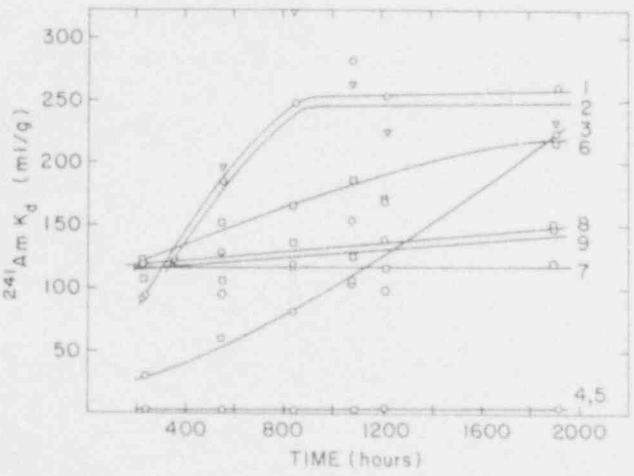

Figure 7.9. ^{241}Am K_d sorption coefficient versus time for waters and soils From Maxey Flats, Kentucky, Disposal Site.

Water:	Oxic
Soil:	Ultrasonicated
Solution/soil ratio:	20 mL/g
Reaction Container:	TFE Teflon

Experiment	MF Code	Water	Soil
1 ○	155	19S	shale
2 ▽	155	19S	sandstone
3 ○	156	Well UB1A	shale
4 ○	157	27	shale
5 ○	157	27	sandstone
6 □	158	33L-4	shale
7 □	158	33L-4	sandstone
8 ○	159	33L-18	shale
9 □	159	33L-18	sandstone

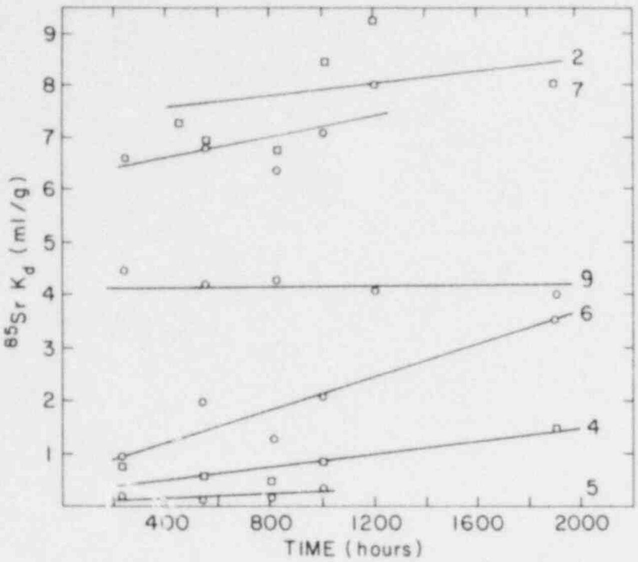

Figure 7.10. ^{85}Sr K_d sorption coefficient versus time for waters and soils from Maxey Flats, Kentucky, disposal site.

Water:	Oxic
Soil:	Ultrasonicated
Solution/soil ratio:	20 mL/g
Reaction Container:	TFE Teflon

Experiment[a]	MF Code	Water	Soil
1	155	19S	shale
2 □	155	19S	sandstone
3	156	Well UB1A	shale
4 □	157	27	shale
5 ○	157	27	sandstone
6 ○	158	33L-4	shale
7 ○	158	33L-4	sandstone
8	159	33L-18	shale
9 ○	159	33L-18	sandstone

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[a] Experiments 1, 3, and 8 were not performed.

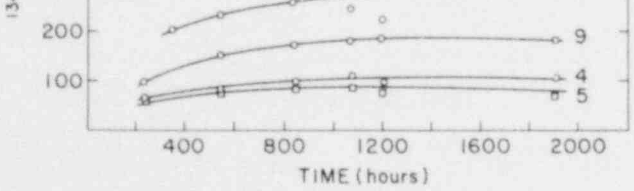

Figure 7.11. ^{134}Cs K_d sorption coefficient versus time for waters and soils from Maxey Flats, Kentucky, disposal site.

Water:	Oxic
Soil:	Ultrasonicated
Solution/soil ratio:	20 mL/g
Reaction Container:	TFE Teflon

Experiment[a]	MF Code	Water	Soil
1	155	19S	shale
2 ○	155	19S	sandstone
3	156	Well UB1A	shale
4 ○	157	27	shale
5 □	157	27	sandstone
6 ○	158	33L-4	shale
7 □	158	33L-4	sandstone
8	159	33L-18	shale
9 ○	159	33L-18	sandstone

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[a] Experiments , 3, and 8 were not performed.

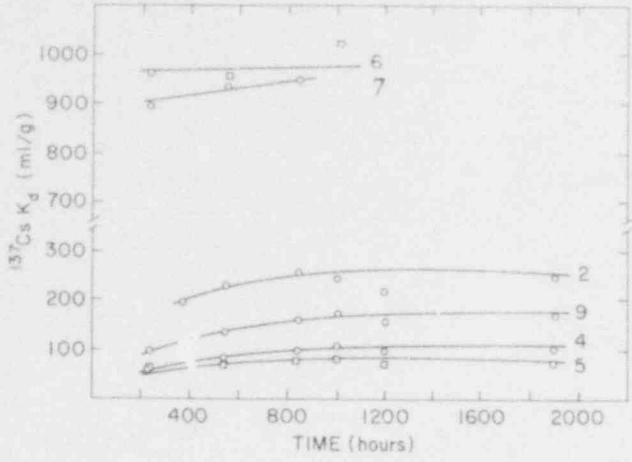

Figure 7.12. ^{137}Cs K_d sorption coefficient versus time for waters and soils from Maxey Flats, Kentucky, disposal site.

Water:	Oxic
Soil:	Ultrasonicated
Solution/soil ratio:	20 mL/g
Reaction Container:	TFE Teflon

Experiment[a]	MF Code	Water	Soil
1	155	19S	shale
2 ○	155	19S	sandstone
3	156	Well UB1A	shale
4 ○	157	27	shale
5 □	157	27	sandstone
6 □	158	33L-4	shale
7 ○	158	33L-4	sandstone
8	159	33L-18	shale
9 ○	159	33L-18	sandstone

---

[a] Experiments 1, 3, and 8 were not performed.

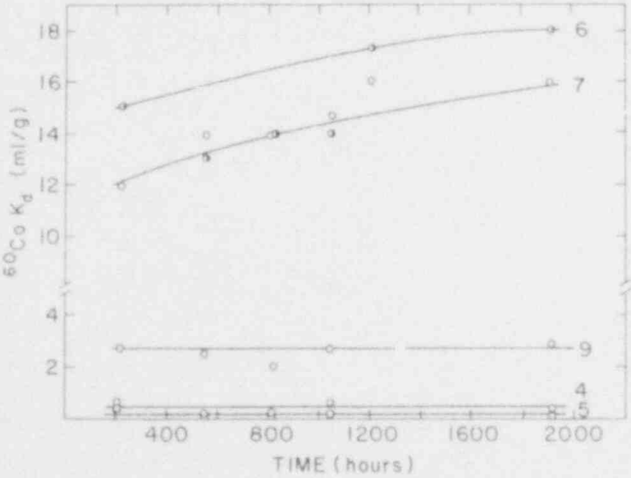

Figure 7.13. ^{60}Co K_d sorption coefficient versus time for waters and soils from Maxey Flats, Kentucky, disposal site.

Water:	Oxic
Soil:	Ultrasonicated
Solution/soil ratio:	20 mL/g
Reaction Container:	TFE Teflon

Experiment[a]	MF Code	Water	Soil
1	155	19S	shale
2[b]	155	19S	sandstone
3	156	Well UB1A	shale
4 ○	157	27	shale
5 □	157	27	sandstone
6 ○	158	33L-4	shale
7 ○	158	33L-4	sandstone
8	159	33L-18	shale
9 ○	159	33L-18	sandstone

---

[a] Experiments 1, 3, and 8 were not performed.

[b] Erratic results for experiment 2 were not reported.

Apparent K_d versus time for sample sets of sandstone and shale paralleled each other for the same trench water. Differences between the sandstone and shale are probably due to small variations in particle size or surface area.

The pH of the original trench waters was a significant property which correlated with the apparent K_d's for ^{134}Cs, ^{137}Cs and ^{60}Co. Plots of apparent K_d at 800 hours versus pH showed a regular trend with pH (Figures 7.14 and 7.15). The water from Trench 33L-18 (MF-159) was very acidic (pH = 2.0). At low pH, hydrogen ion may be a more efficient competitor than the radionuclides for the soil exchange sites. It is equally possible that the clay mineral structures are being destroyed by the high acidity, thereby lowering the soil exchange capacity and changing the trend of the observed K_d versus pH line. This effect has been observed in nature during the formation of acid sulfate soils(11). This change would account for the ^{137}Cs K_d and ^{60}Co K_d being much larger.

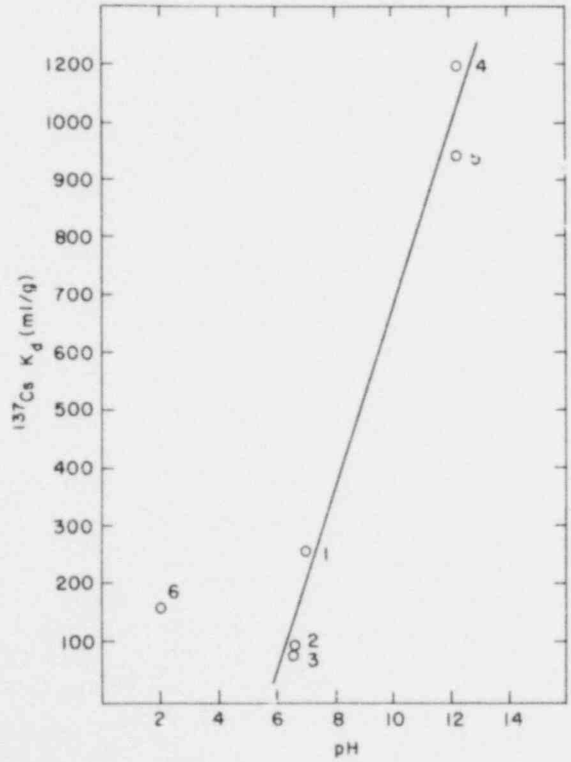

Figure 7.14. ^{137}Cs K_d sorption coefficient versus pH for trench waters and soils from Maxey Flats, Kentucky, disposal site.

Oxic trench waters/
ultrasonicated soils:
Solution/soil ratio: 20 mL/g
Reaction Containers: TFE Teflon
Equilibration Time: 822 hours

Experiment	MF Code	Trench Water	Soil
1	155	19S	sandstone
2	157	27	sandstone
3	157	27	shale
4	158	33L-4	shale
5	158	33L-4	sandstone
6	159	33L-18	sandstone

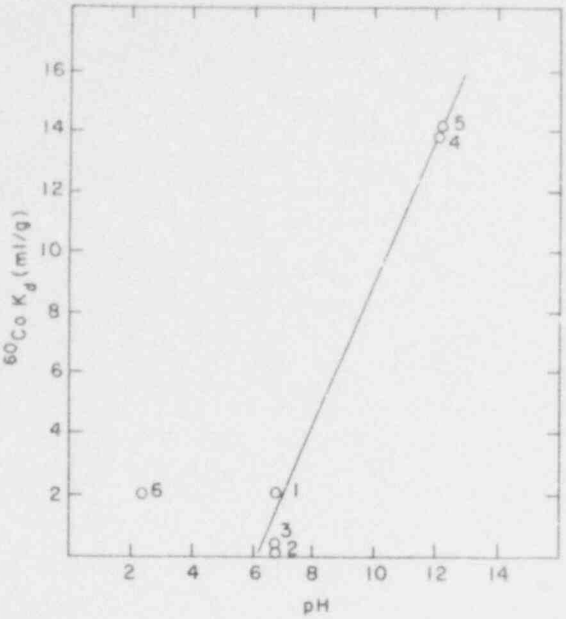

Figure 7.15. ^{60}Co K_d sorption coefficient versus pH for trench waters and soils from Maxey Flats, Kentucky, disposal site.

Oxic trench waters/
ultrasonicated soils:
Solution/soil ratio: 20 mL/g
Reaction Containers: TFE Teflon
Equilibration Time: 822 hours

Experiment	MF Code	Trench Water	Soil
1	155	19S	sandstone
2	157	27	sandstone
3	157	27	shale
4	158	33L-4	sandstone
5	158	33L-4	shale
6	159	33L-18	shale

7.2.3.7 Comparison of K_d Results for Glass and Teflon Containers

Determination of the sorption coefficient K_d was made by gamma-ray counting the solution with a Ge(Li) detector while shielding the detector from the soil. An error in K_d determination can be caused by any appreciable amount of radionuclides adsorbed on the container walls, which would appear to be in solution. The calculation of isotopic K_d from the radionuclide concentration in solution would be systematically in error due to the wall adsorption. TFE Teflon does not significantly adsorb radionuclides from solution. However, low Eh trench waters cannot be preserved because oxygen diffuses rapidly through TFE Teflon walls. Screw cap, septum sealed, glass test tubes (Bellco, 2047-16125) were excellent for protecting trench water from oxygen. In spite of the adsorption of radionuclides onto the glass walls, the glass test tubes offer a great experimental convenience. Therefore, a comparison of isotopic K_d results for glass and Teflon containers was made to see if the K_d results were within the experimental error.

Trench 19S (MF-155), and trench 33L-18 (MF-159) waters from the Maxey Flats, Kentucky, disposal site, were exposed to air in the laboratory. The ferric hydroxide precipitate was removed by filtration and the oxic solution was used to prepare samples for isotopic K_d determination. Shale, also from Maxey Flats, was used with the oxic trench water. Four types of sample sets were prepared in glass and Teflon test tubes as follows:

Trench Water	+ Soil
1. Oxic Trench 19S (MF-155)	+ Shale (MF-III), 100-200 mesh fraction
2. Oxic Trench 19S (MF-155)	+ Shale (MF-III), chips of core disaggregated by ultrasonic vibration
3. Oxic Trench 33L-18 (MF-159)	+ Shale (MF-III), 100-200 mesh fraction
4. Oxic Trench 33L-18 (MF-159)	+ Shale (MF-III), chips of core disaggregated by ultrasonic vibration

The effect of pH changes in the solutions as well as dilution of the trench water was examined by preparing sample sets in glass test containers.

After the sample sets had been tumbled to equilibrate the solution with the soil, a 10.0-mL-filtered (0.45 μm membrane filter) aliquot was acidified with 1-mL of nitric acid (8 M) and counted using a Ge(Li) gamma ray detector.

K_d results are given in Tables 7.16 to 7.19. The underlying assumption in the comparison of results for glass and Teflon containers is that glass adsorbs radionuclides and consequently would result in lower K_d values. The K_d results for ^{241}Am and ^{134,137}Cs, were significantly lower for glass containers as shown in Table 7.19. The K_d results for ^{241}Am, (Tables 7.16 and

Table 7.16

Sorption Coefficients for Trench 33L-18 Water and Disaggregated Soil
From Maxey Flats, Kentucky, Disposal Site
(Teflon Versus Glass, Effect of pH)

		K_d (mL/g)[a]					
pH	Container	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co	^{59}Fe	^{241}Am
2.1	Teflon	1.4±0.3	105±2	104±2	< 0.1	0.90±0.04	173±6
2.1	Glass	1.2±0.4	127±2	130±10	< 0.1	2±1	125±6
--	Glass[b]	2.3±0.2	760±70	740±9	0.7±1	9±1	---
3.3	Glass	1.8±0.1	110±10	110±20	0.7±1	< 0.1	104±4
3.7	Glass	0.9±0.3	89±2	94±2	< 0.1	1.3±0.4	---

Trench Water: Maxey Flats, Kentucky, disposal site
Trench 33L-18 (MF-159), collected May 1977
Exposed to air and filtered to remove ferric hydroxide precipitate
Soil: Maxey Flats, Kentucky, disposal site
Shale (MF-III)
Chips of Core Disaggregated by Ultrasonic Vibration
Solution/Soil Ratio: 20 mL/g
Reaction Containers: TFE Teflon - Test tubes fabricated at BNL, Appendix F, Figure F.8
Glass - Screw cap, septum sealed test tubes (Bellco 2047-16125), Appendix F, Figure F.7
Equilibrium Time: 110 hours
Sample Counted: 10-mL filtered and acidified aliquot of aqueous phase

[a] K_d is reported as an average ± one standard deviation of the results.

[b] Results are for a 1/10 v/v dilution of trench 33L-18 water with distilled water.

Table 7.17

Sorption Coefficients for Trench 33L-18 Water and Soil (100-200 Mesh Fraction) From Maxey Flats, Kentucky, Disposal Site (Teflon Versus Glass, Effect of pH)

		K_d (mL/g)[a]					
pH	Container	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co	^{59}Fe	^{241}Am
2.1	Teflon	0.8±0.4	252±2	230±20	< 0.1	9±1	150±60
2.1	Glass	1.3±0.1	210±20	210±20	< 0.1	7±1	150±60
--	Glass[b]	5.8±0.4	790±30	750±120	8±1	150±20	---
3.3	Glass	1.4±0.1	130±20	130±10	0.4±0.2	4±1	200±50
3.7	Glass	0.7±0.2	80±3	77±3	< 0.1	< 1	---

Trench Water: Maxey Flats, Kentucky, disposal site
Trench 33L-18 (MF-159), collected May 1977
Exposed to air and filtered to remove ferric hydroxide precipitate
Soil: Maxey Flats, Kentucky, disposal site
Shale (MF-III), 100-200 mesh fraction
Solution/Soil Ratio: 20 mL/g
Reaction Containers: TFE Teflon - Test tubes fabricated at BNL, Appendix F, Figure F.8
Glass - Screw cap, septum sealed test tubes (Bellco 2047-16125), Appendix F, Figure F.7
Equilibrium Time: 110 hours
Sample Counted: 10-mL filtered and acidified aliquot of aqueous phase

[a] K_d is reported as an average ± one standard deviation of the observed results.

[b] Results are for a 1/10 v/v dilution of trench 33L-18 water with distilled water.

7.18), were also significantly lower in glass containers. The lower K_d results, Table 7.16, ^{134,137}Cs, in Teflon containers, reflect additional unidentified experimental problems other than wall adsorption such as soil adhering to the Teflon walls which was not observed with glass containers. Although the differences, in K_d between glass and Teflon containers, are less than an order of magnitude, and not always consistent, the use of Teflon containers to avoid systematic errors due to wall adsorption appears to be prudent.

The effect of a 1/10 v/v dilution of the original solution with distilled water greatly enhanced the sorption onto the soil. Changes in solution pH by addition of HNO_3 or NaOH, did not produce a clear trend in sorption of radionuclides.

Table 7.18

Sorption Coefficients for Trench 19S Water and Disaggregated Soil
From Maxey Flats, Kentucky, Disposal Site
(Teflon Versus Glass, Effect of pH)

		K_d (mL/g)[a]				
pH	Container	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co	^{241}Am
8.0	Teflon	4.3±0.2	240±10	230±10	< 0.1	21
8.0	Glass	4.3±0.2	260±20	270±40	0.7±0.1	3±1
--	Glass[b]	15±3	2260±60	2140±90	< 0.1	---
7.7	Glass	< 0.1	190±30	190±30	0.11±0.01	---
2.4	Glass	< 0.1	260±20	250±60	0.86±0.04	1.6±0.1

Trench Water: Maxey Flats, Kentucky, disposal site
Trench 19S (MF-155), collected May 1977
Exposed to air and filtered to remove ferric hydroxide precipitate
Soil: Maxey Flats, Kentucky, disposal site
Shale (MF-III)
Chips of Core Disaggregated by Ultrasonic Vibration
Solution/Soil Ratio: 20 mL/g
Reaction Containers: TFE Teflon - Test tubes fabricated at BNL, Appendix F, Figure F.8
Glass - Screw cap, septum sealed glass test tubes (Bellco 2047-16125), Appendix F, Figure F.7
Equilibration Time: 110 hours
Sample Counted: 10-mL filtered and acidified aliquot of aqueous phase

[a] K_d is reported as an average ± one standard deviation of the observed results.

[b] Results are for a 1/10 v/v dilution of trench 19S water with distilled water.

The most significant difference in K_d numbers results from using ultrasonically disaggregated bulk shale versus shale which had been ground in a ball mill. The K_d results for both trench waters were significantly lower with the ultrasonically disaggregated shale. The grinding and sieving process appeared to concentrate the adsorbent materials, clay minerals, in the 100-200 mesh range, (Section 7.1), and artificially increased the surface area.

7.2.3.8 Handling of Sample Materials

The effect of the preliminary preparation of trench water and soil on the K_d sorption coefficient was further examined in this study.

Table 7.19

Sorption Coefficients for Trench 19S Water and Soil (100-200 Mesh Fraction) From Maxey Flats, Kentucky, Disposal Site (Teflon Versus Glass Containers, Effect of pH)

		K_d (mL/g)[a]				
pH	Container	^{85}Sr	^{134}Cs	^{137}Cs	^{60}Co	^{241}Am
8.0	Teflon	26±3	635±1	683±2	44±3	410±40
8.0	Glass	20±1	500±15	500±13	40	190±10
--	Glass[b]	70±17	2520±30	2350±40	370±60	---
7.7	Glass	---	460±160	430±100	< 0.1	---
2.4	Glass	---	620±120	530±40	15±3	19±1

Trench Water: Maxey Flats, Kentucky, disposal site
Trench 19S (MF-155), collected May 1977
Exposed to air and filtered to remove ferric hydroxide precipitate
Soil: Maxey Flats, Kentucky, disposal site
Shale (MF-III), 100-200 fraction
Solution/Soil Ratio: 20 mL/g
Reaction Containers: TFE Teflon - Test tubes fabricated at BNL, Appendix F, Figure F.8
Glass - Screw cap, septum sealed glass test tubes (Bellco 2047-16125), Appendix F, Figure F.7
Equilibration Time: 110 hours
Sample Counted: 10-mL filtered and acidified aliquot of aqueous phase

[a] K_d is reported as an average ± one standard deviation of the observed results.

[b] Results are for a 1/10 v/v dilution of trench 19S water with distilled water.

The results of previous experiments have shown that the experimentally observed K_d is a function of the nature of the water regime. If the water regime is fixed, variation in the observed K_d can be produced by changing the mineral composition of the solid phase, as shown by the last study using ultrasonicated as well as ground and sieved material. An experiment to examine the effects of both soil and water variations on the same system was designed.

Anoxic versus Oxic Trench Water: Trench waters, which existed under reducing conditions at the disposal sites, must be handled in a low oxygen atmosphere to prevent precipitation of ferric hydroxide. An inert atmosphere was used to simulate the anoxic conditions existing in the burial trenches during the determination of the K_d sorption coefficient. Since the preservation of samples for K_d determination for a month was quite difficult, an alternative procedure of working in an oxidizing atmosphere was tried. Trench waters were exposed to the air to precipitate ferric hydroxide. The precipitate was removed by filtration and the resulting oxic water was used to prepare samples for K_d determination. An identical sample set was prepared for comparison using the anoxic water.

Ground versus Ultrasonically Disaggregated Soil: Soil samples of unweathered till were received from the West Valley, New York, disposal site, and unweathered Nancy Shale from the Maxey Flats, Kentucky, Disposal Site. These materials were intact, nonhomogeneous cores. The first approach was to grind the material in a ball mill and sieve the resulting powder to remove coarse materials. The process of grinding and sieving involved a considerable risk of obtaining misleading K_d results because the grinding process can increase the surface area of the material. Also, sieving the ground material to obtain a uniform sample can produce separations of the clay, sand and silt constituents. The alternative process was to prepare K_d samples from chips of the till core and disaggregate the chips by vibrating the prepared K_d sample set in an ultrasonic bath. The disadvantage of the ultrasonic method is that the samples are not necessarily uniform.

Isotopic K_d sorption coefficients for four sets of samples, four combinations of conditions, are shown in Tables 7.20 and 7.22.

These experimental results illustrate the behavior of the trench water-soil geochemical system with respect to variations in soil characteristics and water chemistry which are likely to occur along migration paths.

By comparing the experimental results of ultrasonicated versus ground material for either oxic or anoxic waters, the effect of relatively small changes in the solid phases on the K_d of the system is apparent. In a similar manner, the effect of changing water chemistry can be seen by comparing the results for oxic versus anoxic waters for either ground or sonicated material.

Two comparisons are of particular importance, 1) the comparison of ground-sieved versus ultrasonicated soils under anoxic or oxic conditions, and 2) oxic versus anoxic water regimes for either ultrasonicated or ground-sieved soil. The first comparison applies to the sorptive behavior of the geochemical system as anoxic waters moving away from the immediate trench vicinity, come into contact with soils varying slightly in composition, grain size, etc. Such variations are to be expected due to the inhomogeneity of the geologic media on a small scale. The second comparison mimics what would happen as trench waters move away from the near field trench area and mix with surrounding groundwater. These surrounding waters would not have the high organic contents of trench waters, and consequently they would be much less reducing. Mixing would dilute the trench waters, thereby producing a more oxic water regime as migration continues.

Tables 7.21 and 7.23 give the results of comparisons for combinations of soil conditions and waters. The yes or no response indicates if significant variations in K_d are observed. For example, the K_d results for ^{152}Eu in

Table 7.20

Sorption Coefficients for Trench Water and Soil From West Valley, New York, Disposal Site (Soil and Water Pretreatment)

	K_d (mL/g)[a]			
	Solution Condition			
	Oxic		Anoxic	
	Soil Condition			
Radionuclide	Ultrasonic Disaggregated	Ground 100-200 Mesh Fraction	Ultrasonic Disaggregated	Ground 100-200 Mesh Fraction
^{152}Eu	4300±500	3700±600	600±60	2100±200
^{241}Am	4700±60	4000±600	415±60	1000±150
^{85}Sr	31.9±0.2	25±2	6.9±0.4	7.4±0.2
^{134}Cs	200±9	100±30	49±6	260±7
^{137}Cs	195±10	100±30	48±5	260±7
^{60}Co	2.3±0.2	1.8±0.1	1	5±1

Trench Water:	West Valley, New York, disposal site, Trench 2-1A (WV-40), collected anoxically November 1977
Soil:	West Valley, New York, disposal site Unweathered till, Test Hole A2 (WV-A2) collected July 1975
Solution/Soil Ratio:	20 mL/g
Reaction Containers:	Screw cap, septum sealed, glass test tubes
Equilibration Time:	100 hours
Anoxic:	Original materials maintained in an argon atmosphere
Oxic:	Trench water was exposed to air to precipitate ferric hydroxide. Samples for K_d determination were prepared from the solution after the precipitate was removed by filtration.

[a] K_d is reported as an average ± one standard deviation of observed results.

Table 7.20 show that Eu sorption is affected by differences in water chemistry (oxic versus anoxic) for both the ground-sieved sediment (100-200 mesh), and the ultrasonicated material. Yes responses in Table 7.21 are recorded [illegible] the comparisons in the anoxic and oxic columns. However, under oxic conditions, the sediment variation (100-200 mesh versus ultrasonicated) produces no significant variation in the observed K_d. A no response appears for the comparison in the last column in Table 7.21.

Table 7.21

Does Soil and Water Composition Variation Affect K_d Results for Tench Water and Soil From West Valley, New York, Disposal Site? (See also Table 7.20)

	Comparing K_d Results for:			
	Soil Compositions With		Water Compositions With	
Radionuclide	Anoxic Water	Oxic Water	Ground 100-200 Mesh Soil Fraction	Bulk Soil Ultrasonically Disaggregated
^{152}Eu	YES	YES	YES	NO
^{241}Am	YES	YES	YES	NO
^{85}Sr	YES	YES	NO	NO
^{134}Cs	YES	YES	YES	YES
^{137}Cs	YES	YES	YES	YES
^{60}Co	YES	YES	YES	YES

Trench Water: West Valley, New York, disposal site, Trench 2-1A (WV-40), collected anoxically November 1977

Soil: West Valley, New York, disposal site
Unweathered till, Test Hole A2 (WV-A2)
collected July 1975

If the magnitude of the K_d results are considered, some general predictions can be made concerning migration and retention of the radionuclides. For example, Eu and Am sorption in the West Valley system is affected by soil changes under anoxic conditions, but unaffected under oxic conditions, (Table 7.20). This would indicate that the soil variation is important in controlling sorption around the immediate trench vicinity. However, as the waters move away from the immediate trench vicinity, Am and Eu sorption would be expected to increase due to the chemical regime change. As migration continues, the changes in water chemistry are important in terms of Eu and Am retention.

For Eu and Am in the Maxey Flats experiments, a similar pattern under anoxic conditions is apparent, Table 7.23. Small variations in soil character produce significant changes in the K_d. However, under oxic conditions the sorption is frequently less strong. The reasons for these differences between the West Valley and Maxey Flats experiments are presumably due to differences in water chemistries (oxic versus anoxic) and to some extent, the geological media. In order to explain these differences, the water from the experiments should be analyzed after the conclusion of the experiment as well as before.

Table 7.22

Sorption Coefficients for Trench Water and Shale From Maxey Flats, Kentucky, Disposal Site (Soil and Water Pretreatment)

	K_d (mL/g)[a]			
	Soil Condition			
	Oxic		Anoxic	
	Soil Condition			
Radionuclide	Ultrasonic Disaggregation	Ground 100-200 Mesh Fraction	Ultrasonic Disaggregation	Ground 100-200 Mesh Fraction
^{152}Eu	450±30	480±120	420±20	1480±270
^{241}Am	1240±180	560±230	480±70	900±20
^{85}Sr	6.1±0.8	48±4	4±1	10.0±0.3
^{134}Cs	1430±80	1800±100	570±30	490±2.0
^{137}Cs	1210±60	1570±40	550±30	490±10
^{60}Co	9±2	6.9±8	5±1	11±2

Trench Water: Maxey Flats, disposal site, Trench 27 (MF-157), collected anoxically May 1978

Shale: Maxey Flats, disposal site, Trench 46 (MF-III), unweathered shale at ~ 20 feet

Solution/Soil Ratio: 20 mL/g

Reaction Containers: Screw cap, septum sealed, glass test tubes, Appendix F, Figure F.7

Equilibration Time: 100 hours

Anoxic: Original materials maintained in an argon atmosphere

Oxic: Trench water was exposed to air to precipitate ferric hydroxide. Samples were prepared from the solution after the precipitate was removed by filtration.

[a] K_d is reported as an average ± one standard deviation of the observed results.

In contrast, cesium sorption is sensitive to changes in both water chemistry and soil character for the West Valley and Maxey Flats situations, the later case showing an order of magnitude increase in sorption. Cesium sorption is thought to be controlled by ion exchange equilibria(13,15,16,17,18), and the pattern shown by these experiments is consistent with this idea. Cesium has also been observed to be preferentially sorbed and at least semi-permanently

Table 7.23

Does Soil and Water Composition Variations Affect K_d Results From Maxey Flats, Kentucky, Disposal Site? (See also Table 7.22)

	Comparing K_d Results for:			
	Soil Compositions With		Water Compositions With	
Radionuclide	Anoxic Water	Oxic Water	100-200 Mesh Soil Fraction	Bulk Soil Ultrasonically Disaggregated
^{152}Eu	YES	NO	YES	NO
^{241}Am	YES	YES	YES	YES
^{85}Sr	YES	NO	YES	YES
^{134}Cs	YES	YES	YES	YES
^{137}Cs	YES	YES	YES	YES
^{60}Co	YES	NO	YES	NO

Trench Water: Maxey Flats, disposal site, Trench 27 (MF-157), collected anoxically May 1978

Shale: Maxey Flats, disposal site, Trench 46 (MF-III), unweathered shale at ∿ 20 feet

fixed on specific minerals,(14) most notably illite. In order to determine if this is the case in these experiments, a simple desorption experiment can be performed to determine if the cesium remains fixed in the soil or is readily removed.

A desorption experiment will indicate the extent of passible remobilization of radionuclides. Water regimes are not likely to remain constant over the period of time required for radionuclide decay, resulting in possible migration of previously sorbed radionuclides. Information on this question cannot be derived from consideration of K_d data alone. Similar information about the other radionuclides would be of interest in terms of their longer term retention in the geologic media.

Strontium shows a similar sorption pattern to that for Cs in the Maxey Flats experiments. However, for the West Valley sediments which are high in carbonate, changes in the soil character do not markedly affect the observed sorption under either anoxic or oxic conditions. This suggests that the carbonate in the sediments is exerting a strong influence on strontium behavior. Calcium and strontium in natural waters are controlled by the carbonate-bicarbonate-pH relationships and it is reasonable to assume that similar restraints are operative in these experiments. In order to determine what these restraints are, the carbonate species and calcium in the waters should be analyzed, both before and after the sorption experiment. Cobalt shows the least retention of the radionuclides studied.

Finally, the most striking features of the data are that the combination of anoxic trench water and ultrasonically disaggregated soil produced the least sorption for every radionuclide. Since the combination of unaltered sample materials most closely represents the situation in the disposal trenches, the batch K_d data most relevant to migration close to the trenches must be obtained by measurement with carefully preserved samples.

Earlier batch experiments have shown a time dependency for sorption of some radionuclides, notably cesium. The natural state is a dynamic system rather than the static one represented by batch experiments. Therefore, the results of batch tests may represent upper limits for the sorption of some radionuclides. Column experiments using undisturbed site-specific soil samples and trench waters are needed. Such experiments will give more realistic results for some radionuclides and will compliment the results of batch tests. Such experiments are planned for future work.

7.? 4 Conclusions

At present, the ultimate barrier to migration of radionuclides is the geologic media within which the waste is emplaced. Prediction of potential migration rates for radionuclide bearing groundwaters is a difficult problem involving hydrogeologic as well as physical and chemical parameters. Experimental work described in this section has attempted to examine the sorptive behavior of site specific geological media and trench waters. Experiments were performed to simulate in situ conditions in the trenches, as well as expected variations in environmental conditions likely to be encountered during migration.

Special handling of some sample waters was required which complicated the experimental work. The reducing conditions generated by biological activity in some burial site trenches maintains a considerable amount of ferrous ions in solution. Air exposure of these solutions will precipitate ferric hydroxide and simultaneously coprecipitate other dissolved substances including some of the radionuclides being studied. Anoxic conditions in these samples were attempted with an inert atmosphere (argon or nitrogen).

Ideally the most suitable procedure to obtain K_d results for materials from specific disposal sites is to use TFE Teflon vessels in an inert atmosphere of argon, with no pretreatment of the trench waters or soils. Since oxygen diffuses through TFE Teflon containers, work with anoxic trench water must be performed in an inert atmosphere glove box. Reducing the soil sample to a powder by ultrasonic vibration in the reaction tube, along with the radionuclide spiked trench water, appears to be essential to avoid altering the sample in ways which will affect its sorption capacity.

Glass reaction tubes appear to be only acceptable for relative comparisons and the estimation of the length of time necessary to obtain equilibrium, since glass wall adsorption contributes systematic errors to the isotopic K_d results.

Teflon is generally accepted as a satisfactory container material to advoid wall adsorption. However, the problem of oxygen rapidly diffusing through the Teflon walls will need to be avoided by working in an inert atmosphere glove box.

Generally the K_d coefficient is determined under equilibrium conditions. Establishment of equilibrium of the solution with the soil requires lengthy periods of intimate contact achieved by tumbling the samples ^{241}Am, and ^{137}Cs require mixing periods of greater than 1000 hours. Periodic measurement of the amount of isotope remaining in solution was made by counting the aqueous phase with a Ge(Li) detector. The sorption of the radionuclides ^{241}Am, ^{152}Eu, ^{85}Sr, ^{134}Cs, ^{137}Cs, ^{59}Fe and ^{60}Co was determined. Equilibrium was approached when the concentration of each isotope in solution remained constant.

Experimental results indicate that the observed K_d is a function of both solid and liquid phase compositional variations as well as contact time. In terms of retention and migration prediction, these results have some direct and important implications. Groundwater modeling equations used to predict radionuclide migration involve terms for hydrogeologic parameters, but the sorption term (K_d) is a constant in the equations.(19,20,21,22) It is evident from these experimental results that the sorption is a function of environmental conditions which will vary along the groundwater migration path for any specific situation. Experiments of the type described here can be used to supply possible boundary limits for sorption in any specific field situation.

The observation that the lowest K_d results are observed with anoxic trench waters and ultrasonicated soils points to the need to use site specific materials and experimental conditions which simulate in situ conditions as closely as possible. The observed contact time dependence for some radionuclides indicates the need for K_d determinations using flow through column experiments, which more closely simulate the dynamic conditions operative in the field situation. In order to interface batch and column studies, batch tests using a range of soil/solution ratios need to be performed so that an extrapolation can be made to the soil/solution ratio of a column experiment.

7.3 Future Sorption Tests and Core Analysis

(K. Czyscinski)

7.3.1 Introduction

Sorption tests performed in this program have aimed at supplying relevant K_d numbers for use in the groundwater transport modeling studies of the commercial burial sites. This effort is in cooperation with the U.S. Geological Survey. Order of magnitude approximations are useful in this respect in order to estimate the effects of the sorption term in transport equations. Such general data are sufficient for this narrow application but not for a more general one, such as establishing future site selection criteria based on the results of these sorption studies. This longer range goal is of concern to NRC in terms of its licensing role.

Previous sorption studies involved a phenomenological approach in experimental design. The solid-liquid system of site specific materials was treated essentially as a black box, and K_d results measured for various changes in experimental parameters such as gross water composition and contact time. Results of these experiments are valid only for the exact conditions of the experiment. The experimental results are difficult to interpret because the mechanisms controlling them are not identified, thereby limiting their predictive application. Little of the information obtained can be applied to other geochemical environments, for example, to predict sorption behavior in an area under consideration as a future disposal site. Much more detailed information is required to establish siting criteria based on sorption studies.

Knowledge of mineral-radionuclide associations, which result in effective retention of radionuclides, is required in order to apply the results of these sorption studies to other environments. Reporting the magnitude of sorption alone is inadequate. The combinations of soil minerals, and aqueous phase components, which control the sorption, must be identified. A systems approach to the sorption experiments is required for both batch and column tests.

7.3.2 Batch versus Column Tests

Future sorption experiments will involve some batch experiments, but also flow-through column experiments which more closely simulate the field situation. Batch experiments will be designed to allow comparison with column experiment results, and provide information of a mechanistic nature which will be useful in predictive applications.

By performing both batch and column experiments with identical materials it will be possible to determine which procedure produces more useful information. It may also be possible to establish preferred methods for testing sorptive properties for prospective disposal sites, and obtaining the most useful data for modeling applications.

Batch tests are closed systems, static, and the most frequently used mainly due to their relatively easy execution. Flow-through column tests are dynamic in nature and would probably supply K_d values closest to what would be observed in the field situation. However, column experiments are more difficult technically.

7.3.3 Batch Test

A series of experiments will be designed using the equipment and procedures to maintain anoxic conditions when appropriate. Ultrasonicated soil samples and trench waters will be used. The critical experimental variation will be the soil/solution ratio which will be varied through a specific range for each set of experiments. Any trend in the K_d results, with respect to the ratio, can be extrapolated to the soil/solution ratio of a saturated core of the same material to be used in the column experiment. Differences between batch and column K_d results would then be due to the relative sorption kinetics of the static (batch) versus dynamic (column) experiments. This phase of the work is simply the comparison of results from two experimental methodologies.

In order to extend the amount of information to be gained from a batch test to include information of a mechanistic nature, additional steps are required. Additional steps involve a desorption experiment at the conclusion of the sorption test, and an analysis of the soil material used after the sorption tests. The analysis of the soil will be in terms of its mineral components, with the aim of determining with which components the remaining radionuclides are associated.

Mineral phases which are effective sorbers of specific radionuclides need to be identified, and the ability of the soil to "fix" the radionuclides assessed. Radionuclides may be reversibly sorbed on the soil, in which case relatively small changes in the water regime can result in remobilization, or held in "fixed" positions from which desorption is difficult. Mineral species which fix radionuclides would be useful for selection and design of artificial barriers to radionuclide migration. Changes in the groundwater regime around the trenches are likely to occur with time during the functional lifetime of the disposal site, due to temporal variations in groundwater composition and changes in the leachate composition derived from the waste. Resulting remobilization is not presently considered in the simplistic groundwater transport models presently used.

The final step in the complete batch sorption experiment is the radiochemical analysis of the solids. An analytical procedure is proposed based on separating various mineral fractions for radiochemcial analysis by gamma-ray spectroscopy. Characterization of the soil mineralogy is done on subsamples of the sediment prior to initiating the experiment. The fractionation procedure will be described in more detail in the trench core analysis section (7.3.6).

A schematic plan for the complete batch experiment is given in Figure 7.16. The aqueous phase is analyzed after the completion of the various steps, in addition to its intial characterization. Variables, such as Eh, pH and specific dissolved species, such as carbonate-bicarbonate, can be determined if they are thought to influence the sorption.

7.3.4 Column Experiment

Flow through column experiments will use trench waters and "undisturbed" cores taken from the disposal sites. Due to the extremely low permeabilities of the sediments at West Valley and Maxey Flats, (hydraulic conductivities in the range of 10^{-7}-10^{-9} cm/sec, (9,23)), a column experiment using undisturbed cores from these sites would be technically extremely difficult at best, and very time consuming in any event. Undisturbed cores from Maxey Flats would be very difficult to obtain because the shale is extensively fractured.

Most column experiments described in the literature use columns composed of packed homogenized material. This type of column test is little more than a batch test using a high soil/solution ratio and short contact times. Due to the drastic alterations produced in the solids when they are ground, homogenized and repacked, this type of column experiment is unrealistic in terms of in situ field conditions and will not be done in this study. This leaves little hope for conducting a successful column experiment using cored material from West

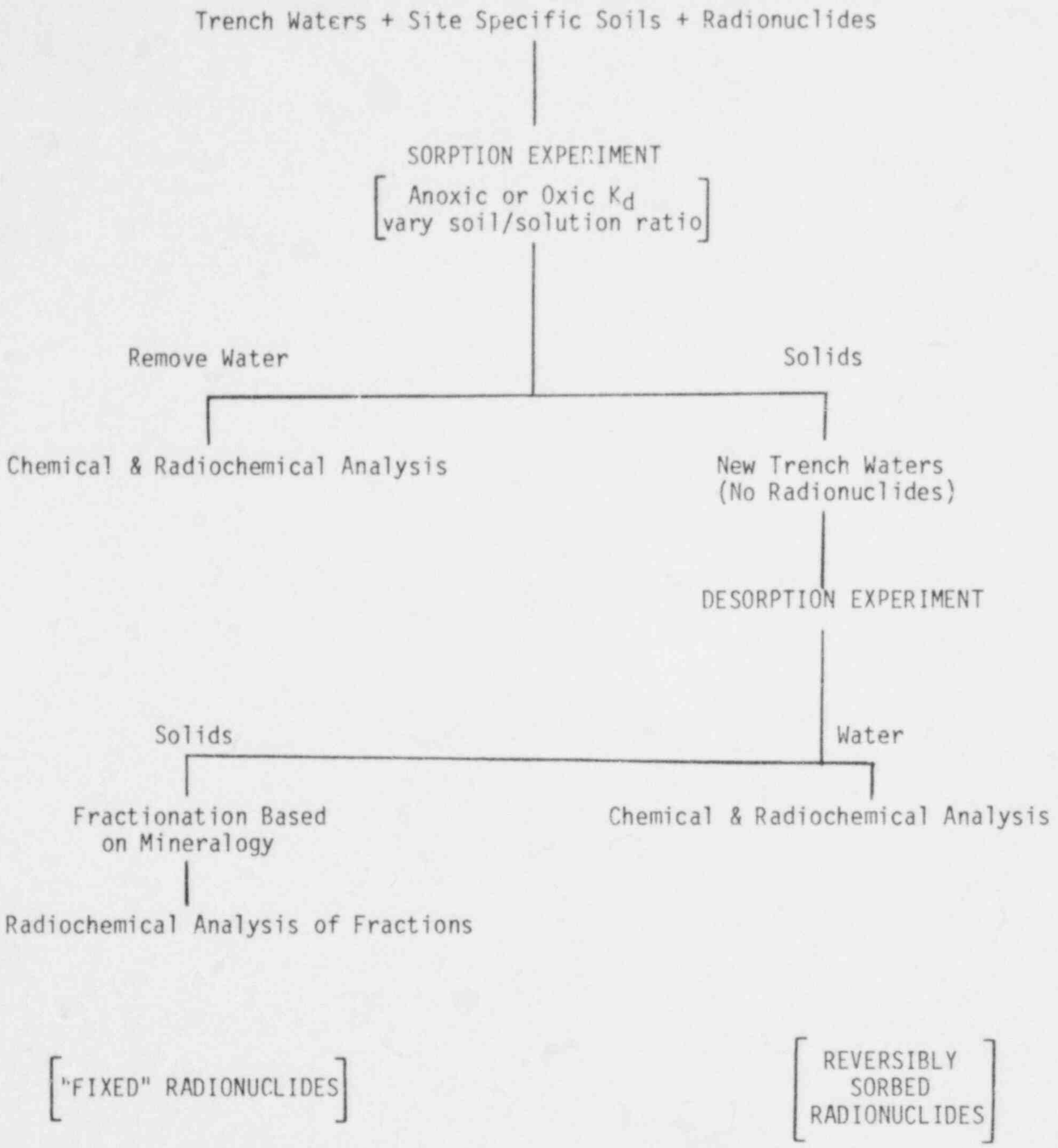

Figure 7.16. Flow chart outline of batch sorption experiment.

Valley and Maxey Flats. Forcing water through the material at high pressure is possible but maintaining anoxic conditions during the process is a formidable task, probably much more difficult than maintaining anoxic conditions during a batch experiment.

A successful column experiment using cored sediments from the Barnwell. South Carolina, disposal facility can be performed comparatively easily. The sediments at this site are composed of unconsolidated sands, silts and clays with hydraulic conductivities in the range of 10^{-5} cm/sec (24). Gravity head is sufficient to maintain adequate flow rates for experiments and the relatively oxic nature of the trench leachates (Section 5.3.4) eliminates the problem of maintaining anoxic conditions during the experiment. In addition, results of column and batch experiments can be related to the results of detailed analysis of cores taken from beneath the disposal trenches at the Barnwell facility. This will allow ideas and information developed as a result of laboratory studies to be compared directly with the field situation. Therefore, priority will be given to batch and column tests using site-specific material from Barnwell, and detailed analysis of the trench cores. For a description of the analysis scheme to be used on the cores see Section 7.3.6.

The proposed column experiment is as follows. A reservoir of trench leachate water collected from the disposal site (Section 5.3.4) will be spiked with radionuclides of interest and percolated through a column consisting of a section of "undisturbed" sediment from the disposal site. Effluent from the core is collected for chemical and radiochemical analysis. The breakthrough time of specific radionuclides into the effluent is determined. After breakthrough, the sorption part of the experiment can be continued until steady-state concentrations of certain radionuclides develop in the effluent. This point represents saturation of the available sites on the soil. Results of batch studies indicate that cobalt would break through rather early, but americium would probably not break through within practical time frames. Therefore, the cut-off time for the column sorption step would be somewhat arbitrary.

Following the initial sorption step, the reservoir of spiked trench water would be replaced with an unspiked trench water and a desorption experiment begun. Again, the effluent would be collected for analysis to qualitatively and quantitatively determine what has been remobilized. Once a steady state situation has been re-established the desorption step is halted. Radionuclides removed were those held in reversibly sorbed positions. Those remaining on the core are in "fixed" positions in the soil. As in the batch experiment, the final step is the fractionation of the sediment based on its mineralogy, and radiochemical analysis of these fractions. This is to determine with which mineral phases the remaining radionuclides are associated. Autoradiography of the split core can be performed to show the spacial distribution of radionuclides before it is processed in the fractionation scheme.

A schematic flow diagram of the column experiment is shown in Figure 7.17. The sequence is virtually identical to that for the batch experiment, allowing direct comparison of results from the various steps.

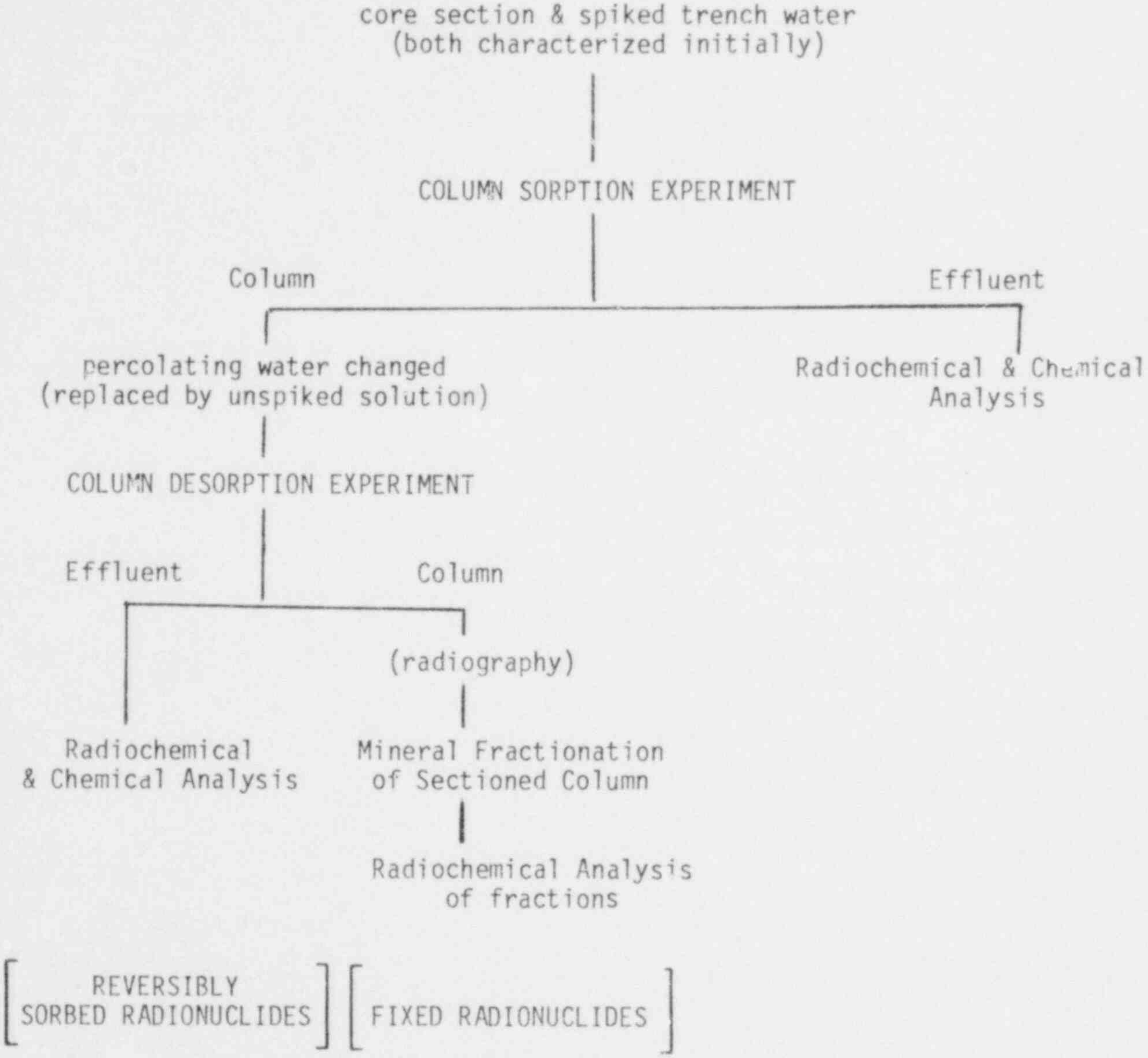

Figure 7.17. Flow chart outline of column sorption experiments.

7.3.5 Selection of Materials

Care must be exercised in the selection of soil materials to be used in these experiments (batch and column). Not only must the materials be sufficiently similar to allow intercomparison; but they must also be sufficiently similar in composition and texture to the material below the trenches to allow direct comparison with field data. Cores from beneath the trenches at Barnwell have been received and their composition and texture will determine what particular soil material will be used for laboratory experiments.

Representative samples of site specific materials from which to select the experiment samples for batch and/or column tests are supplied by U.S. Geologic Survey hydrologists actively involved in studies at these facilities.

Trench waters collected from the site have also been analyzed as described in Chapter 5. Examination of these data will determine which trench water will be used for the liquid phase. Little effort has been made to interpret trench water chemistry in terms of chemical systems. Therefore the selection of a "typical" trench water is somewhat arbitrary. Waters which show extreme values of pH, Eh, or other chemical variables, relative to the range observed in the waters, will be eliminated from consideration. In this way a "typical" water will be selected.

7.3.6 Trench Core Analysis

As part of the cooperative study with the U S. Geological Survey, Brookhaven is performing radiochemical analysis of sediment cores taken from below the trenches at several of the commercial shallow land burial facilities. These cores are important in two respects. First, the efficiency of the geological media in retarding radionuclide migration can be assessed by determining the depth of penetration of radioactive isotopes into these sediments. This information is of interest in site-specific studies, and involves a relatively simple radiochemical analysis of the cores as a function of depth.

The second aspect concerns the interrelation of field and laboratory work. The critical test of information and ideas generated from laboratory work is their confirmation in the field situation. For example, an estimate of radionuclide migration, based on K_d numbers, can be made using the simplistic chromatographic equation:

$$V_W/V_N = R_d = 1 + K_d\ (\rho/\varepsilon) \qquad (1)$$

where V_W = velocityof the water front,
V_N = velocity of the radionuclide front,
R_d = retardation factor,
K_d = radionuclide distribution coefficient,
ρ = bulk density,
ε = porosity.

In a core sample, V_W would represent tritium migration depth (R_d=1), and V_N, penetration depth of specific radionuclides.

More complex equations exist (20-22), however; for a simple one-dimensional flow model through a fracture free core, they reduce to equation (1) above. Predictions of migration can be made using the K_d data generated in laboratory studies once the tritium front is defined. Comparison against actual field results can then be made to test the reliability of these K_d numbers as predictive tools.

Using laboratory sorption data to establish siting criteria involves determining mineral-pore water-radionuclide associations as described previously. Field verification of these associations requires a core analysis scheme more involved than a simple bulk radiochemical analysis as a function of depth.

The trench core material must be radiochemically analyzed based on mineral fractions. An analytical plan for this analysis was designed which allows comparison with results from the various steps in the proposed sorption experiments. Both a bulk radiochemical analysis of the cored material and a further analysis based on mineral fractions will be performed on the trench cores. Figure 7.18 shows the schematic flow chart for these analyses.

The left side of the scheme is a simple bulk radiochemical analysis as a function of depth for the sampled intervals. In the fractionation scheme, the sediment from these depth intervals is processed into various components before radiochemical analysis, in an effort to determine the fate of the nuclides in the geochemical system represented by the core. Radionuclides in the sediment cores are either in the pore water phase, or on the solid material in reversibly sorbed or "fixed" exchange sites.

The following fractions are obtained in the fractionation scheme:

1) water rinse (aqueous fraction) - contains nuclides originally in solution in the pore fluids, and those reversibly sorbed on the solids - the water rinse is analogous to a desorption experiment;

2) extractable "iron" fraction - radionuclides held on freshly precipitated iron (and some aluminum) phases in the sediments;

3) carbonate fraction - nuclides held in carbonate materials;

4) sand, silt, clay fractions - radionuclides held on various minerals in these size fractions.

Radionuclides in steps 2-4 are "fixed"; i.e., not readily mobilized by a change in the pore water regime. The bulk radiochemical analysis cannot distinguish between nuclides in the interstitial waters (pore water), and fixed or reversibly sorbed nuclides. The bulk analysis represents the total content of radionuclides only.

All the trench cores can be analyzed by this procedure, but emphasis will be placed on a complete analysis of the Barnwell material, because both batch and column experiments are scheduled using Barnwell sediments and trench waters. However, bulk radiochemical analysis will be performed on all trench cores as a minimum. As time and resources permit, the fractionation procedure will be done on the other cores.

Data from these core analyses are critical in the total experimental plan. Laboratory results must be verified in the field before applications can be made to siting criteria, predictive modeling, and burial procedures described in the introduction to this chapter.

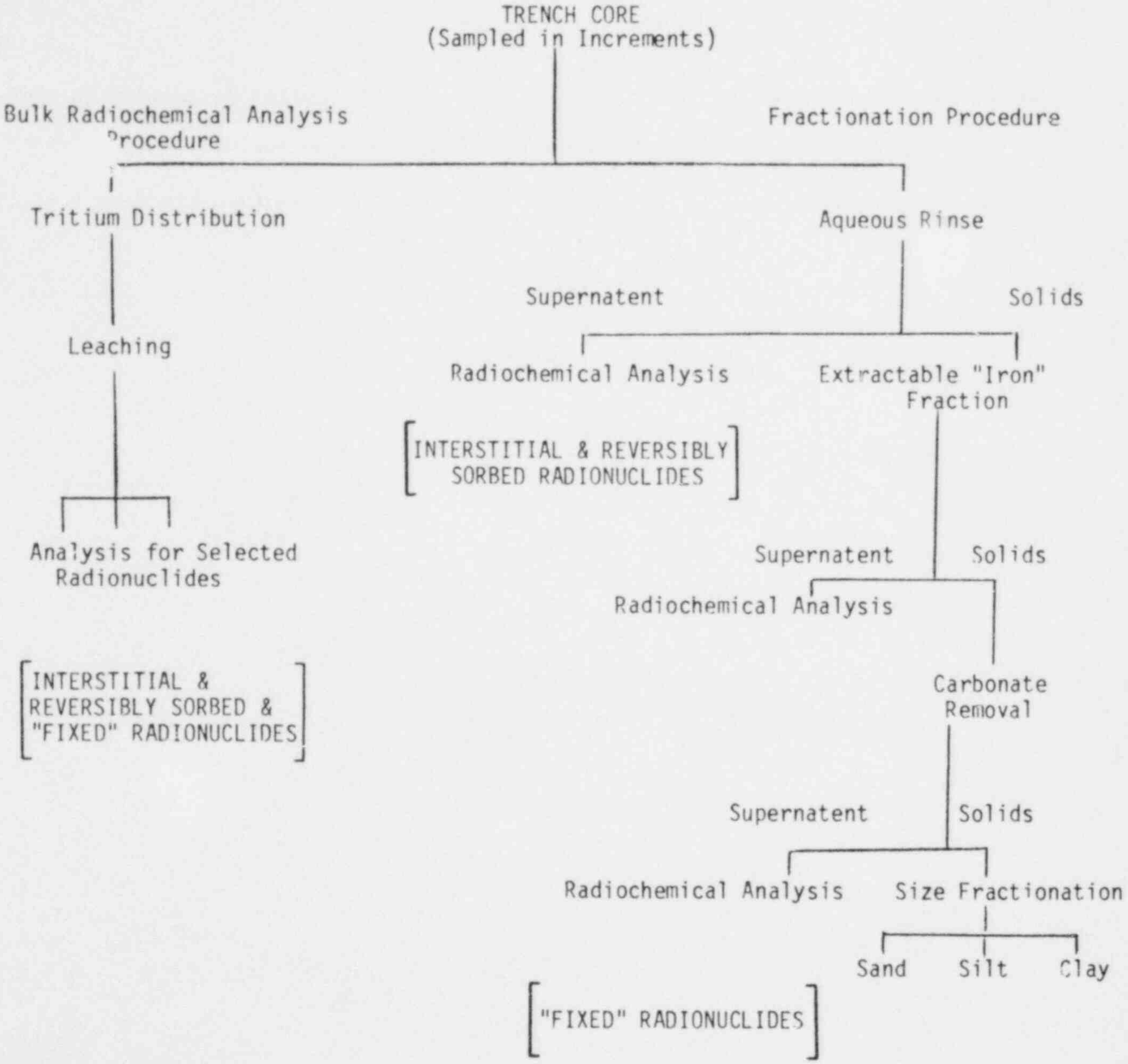

Figure 7.18. Flow chart outline for trench core analysis.

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8 WORK IN PROGRESS AND FUTURE DIRECTIONS

This section will briefly describe some of the work in progress and some of the work presently in the planning stages for future efforts.

- Batch K_d sorption and desorption experiments are in progress using trench waters from Barnwell trenches 6D1 and 25/21-D1 and some site-specific soil material. The soil/solution ratio is varied in these experiments in order to obtain data for extrapolation to expected conditions in the column experiments. Both liquid and solid phases are also to be analyzed at the end of the experiments.

  Determination of batch K_d in an anoxic environment using an improved technique with waters and soils from Maxey Flats and West Valley are in progress. Desorption of radionuclides from the solid phase and chemical analysis of materials after equilibration is also anticipated as outlined in Chapter 7.

- A column K_d experiment is in progress using a water, simulating that from Barnwell trench 6D1 and a sediment core embedded in epoxy resin. The anticipated results will include a radionuclide breakthrough curve, a desorption experiment and analysis of the sediment after the completion of the sorption experiments as outlined in Chapter 7.

- Cores recovered from below several of the disposal trenches at the Barnwell facility and from an evaporation lagoon at West Valley are currently being analyzed according to the scheme described in Chapter 7. Cores from the Beatty, Nevada and Sheffield, Illinois facilities will be analyzed when they are received. A distillation apparatus has been constructed and tritium analyses in pore water from the core sections are in progress. Prior to sectioning, survey gamma scans of the core sections are performed. The remainder of the core analysis procedure will be performed after the tritium distillations are completed.

- Additional radiochemical analyses are planned to survey the concentrations of long lived beta emitting radionuclides present in trench waters.

- Additional radiochemical analyses to measure the concentrations of alpha emitting radionuclides in trench waters (e.g. radium, uranium, and thorium isotopes) leached from source materials buried in the trenches will also be performed.

- Selected trench waters from Maxey Flats, West Valley, and Barnwell will be analyzed for the presence of specific organic complexing agents, as well as their concentrations.

- To study the effects of small concentrations of organic complexing agents on the sorptive behavior of the trench water-soil system, a series of batch K_d experiments are to be initiated.

The liquid phase for these expeirments will consist of trench waters from Maxey Flats spiked with various organic complexing reagents (EDTA, oxalic acid, MIBK, etc.) at several concentrations. Site-specific soil materials will be used for the solid phases. Additional experiments will use generic soil forming minerals such as illite, kaolinite, limonite, etc. to determine the effect of organic material on these mineral-trench water systems. Common soil forming minerals that do not show a decrease in K_d in the presence of organic complexing agents may be useful as trench lining materials to decrease the migration potential of radionuclides in trench waters where organic complexing agents are present.

- Waters recovered from the interceptor trench adjacent to trench 27 at Maxey Flats will be analyzed for radionuclide content, dissolved organic carbon, and selected inorganic constituents.
- Background levels for tritium in waters collected around the Barnwell disposal site will be measured.
- Analysis of waters from wells which border the chemical disposal ground at the Sheffield, Illinois disposal facility are in the planning stages.

APPENDIX A

PROCEDURE FOR SURVEY STUDY OF COMMERCIAL LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITES

(A.J. Weiss)

The following procedure for conducting the survey study of water samples from commercial low-level radioactive waste disposal sites was adopted by the U.S. Geological Survey (USGS) and Brookhaven National Laboratory (BNL) at Reston, Virginia, March 29, 1977. Water samples will be collected by USGS personnel conducting hydrogeological studies at the disposal sites, who will be responsible for measuring the temperature, pH, and conductivity of the samples. BNL will be responsible for measuring dissolved organic carbon (DOC), gross alpha, gross beta, tritium, and gamma radioactivity in the samples.

A.1 Equipment and Supplies

The equipment needed for sampling consists of items supplied by BNL and USGS.

A.1.1 Items Supplied by BNL

Polyethylene bottles (500-mL)*
DOC bottles from USGS Central Labs, Denver, Colorado
Glass bottles (1-liter)*
pH paper (range pH 1-2.5)
Plastic bags (water tight)
Masking tape
Insulated ice chest
Metal cans
Aluminum foil
Scotch tape
Hose clamps
Plastic squeeze bottles

A.1.2 Items Supplied by USGS

Peristaltic pump
Tygon tubing, laboratory grade R3603**, 5/8" x 3/8" and 3/8" x 1/4" sizes
Bailer
Nitric acid (HNO_3), reagent grade (conc)
Pipette or graduated cylinder
Radiation survey meter
Protective clothing (disposable gloves, shoe covering, etc.)

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*All items cleaned at BNL. Do not make substitutions.

**Tygon tubing R3603 is available in various sizes compatable with the peristaltic pump available at the burial site.

A.1.2 Items Supplied by USGS (Cont'd)

Marking pen
pH meter and electrodes
Conductivity meter and cell
Thermometer
Ice
Shipping crate
Absorbent material, e.g., vermiculite
In-line stainless steel filter assembly with 3-way valve
Silver membrane filters; 47-mm-diam, 0.45-μm thick.
Acetone
Distilled water

A.2 Collection Procedure

All trenches and wells from which water can be obtained should be sampled. A radiochemical sample and an organic sample will be collected from each sampling location.

A.2.1 Trench Sampling

1. Prior to collecting a trench sample, purge with trench water to clean the lines. NEW TYGON TUBING SHOULD BE USED FOR EACH TRENCH TO AVOID CROSS CONTAMINATING THE SAMPLES.

2. Rinse a 1-liter glass bottle with some trench water prior to collecting approximately one liter of water sample. A hose clamp can be used to regulate the flow rate.

3. Record the sample source and collection date on each bottle used. Cover all written labels with transparent tape to protect the label from water.

A.2.1.1 Radiochemical Sample

1. Dispense 5 mL of reagent grade concentrated nitric acid into a 500-mL polyethylene bottle followed by 100 mL of trench water (from A.2.1 step 2), 30 mL of concentrated nitric acid, and trench water (from A.2.1 step 2) to approximately four hundred mL (total volume). Shake the contents of the glass bottle before pouring into the polyethylene bottle.

2. Shake the contents of the polyethylene bottle and test the acidified sample with pH paper supplied. If the color is not red (pH < 1) add an additional 5 mL of concentrated nitric acid, shake and test again. A maximum of 100 mL of nitric acid should be added.

3. Fill the polyethylene bottle to the neck with trench water.

4. Do not cap the acidified sample bottle until all effervescence has ceased.

5. Record the total amount of nitric acid added to the sample on the bottle label.

A.2.1.2 Organic Sample

1. Prior to collecting the organic sample, the in-line filtration assembly must be carefully cleaned by washing with detergent and brush, rinsing with water, rinsing with acetone (use a squeeze bottle), rinsing with water, and finally rinsing with distilled water. IT IS IMPERATIVE THAT CAREFUL ATTENTION BE GIVEN TO RINSING THE FILTER ASSEMBLY WITH SUFFICIENT WATER TO REMOVE ALL TRACES OF DETERGENT AND ACETONE. Any residue will adversely affect the DOC measurement.

2. Attach the stainless steel filter assembly containing a new silver membrane filter by clamping a short piece of 3/8" x 1/4" Tygon tubing into the 5/8" x 3/8" tubing attached to the peristaltic pump and connecting to the inlet port of the filter.

3. Set the three-way valve on the filter assembly to bypass the silver membrane filter and purge some trench water to waste.

4. Set the three-way valve to allow flow through the silver membrane filter and filter some trench water to waste.

5. Remove the cap of the DOC bottle and carefully peel back the aluminum foil cover. Place the cap and aluminum foil cover on a piece of clean aluminum foil to avoid contaminating the cover.

6. Place the discharge tube of the filter assembly (3/8" x 1/4" Tygon tubing) in the bottom of the DOC bottle and filter trench water through the silver membrane filter to the shoulder of the bottle.

7. Seal the bottle with the aluminum foil cover and cap.

8. Secure the DOC bottle in a plastic bag by folding the top of the bag several times and bending over the tabs. Remove as much air as possible before sealing the bag.

9. This sample must be kept on ice and in the dark until it is analyzed for DOC at BNL.

10. The temperature, pH, and conductivity of the remainder of the sample in the glass bottle are measured in the field. Temperature is to be measured immediately after collection.

11. Waste water from pumping the trenches and wells should be collected in suitable containers and disposed of in a manner approved by site managers.

12. Discard the remainder of the trench water, bottle, and Tygon tubing as prescribed by the site managers.

A.2.2 Water Well Sampling

1. Wells should be developed if possible, before sampling.

2. A bailer is used to raise the water sample if the water level is too low for a peristaltic pump. A separate bailer should be used for each well to eliminate the possibility of cross contaminating well samples.

3. The bailer should be bounced in the well to mix the standing water and to obtain a water sample containing bottom sediment.

4. Rinse a 1-liter glass bottle with some well water prior to collecting approximately one liter of water sample.

5. Labels for well samples should indicate the kind of well casing, the kind of bailer used, and the duration of time water sat in the well before sampling.

A.2.2.1 Radiochemical Sample

Shake the contents of the well sample in the 1-liter glass bottle and take an aliquot for radiochemical sample as in A.2.1.1 steps 1-5.

A.2.2.2 Organic Sample

1. Allow the remaining well sample in the 1-liter glass bottle to settle for approximately fifteen minutes.

2. Connect the in-line filter assembly to a short length of Tygon tubing and attach to the peristaltic pump.

3. Filter the settled well water into a DOC bottle as in A.2.1.2 steps 1-12.

A.2.3 Stream Sampling

Stream samples should be collected and processed similar to well samples.

A.3 Packaging Procec

A.3.1 Radiochemical Sample

1. Seal the 500-mL polyethylene bottle containing acidified sample in a plastic bag using the twist ties supplied.

2. Place each bagged 500-mL plastic bottle into a metal can and fill the void space with absorbent material, such as vermiculite, prior to sealing.

3. Each can must have a radioactivity label which includes sample identification and radiation level at the surface of the can.

4. The sealed cans may be packed in any convenient shipping carton.

5. The radioactivity at the surface of the shipping carton must be less than 0.5 mr/hr, as required by Department of Transportation regulations.

6. No refrigeration is required for the acidified samples in the 500-mL plastic bottles.

A.3.2 Organic Sample

1. Place each bagged DOC bottle into a metal can and fill the void space with ice prior to sealing.

2. Label each can as in A.3.1 step 3.

3. The sealed cans must be stored in an insulated chest filled with ice to maintain ∿ 4°C until they arrive at BNL.

4. The ice chest may be packed in any convenient shipping carton.

APPENDIX B

ANOXIC COLLECTION AND FILTRATION PROCEDURES
(J. Clinton, G. G. Galdi, R. F. Pietrzak, and A. J. Weiss)

B.1 Introduction

A proper study of water from waste disposal trenches requires that the trench water be collected and maintained under conditions that prevent the occurrence of significant alterations in the states of the various components of the collected solution. Removal of a water sample from the anoxic environment of a trench, under conditions which allowed its exposure to air, resulted in the formation of a reddish-brown precipitate that contained iron and other substances, which had been in the dissolved state under ambient trench conditions. To prevent formation of this precipitate, procedures were devised that exclude air from the sample during collection, storage, and removal of aliquots. These anoxic procedures allow samples to be stored for months without visible signs of iron precipitation. The apparatus and procedures used for anoxic sample collection, storage and filtration of trench water samples are presented here.

B.2 The Collection System

B.2.1 General Aspects

The system and procedures developed for obtaining water samples from a burial trench allow (i) collection and storage of the sample in an anoxic state, such as exists within the trench, (ii) continuous in-line measurements of a number of water quality parameters throughout the period of sample collection, (iii) total containment of all radioactive water removed from the trench, and (iv) return to the trench of all water not included in the sample. Figure B.1 gives a schematic diagram of the collection system. A peristaltic pump draws trench water into the collection system through Tygon tubing that is lowered into the trench through an established well or riser pipe. At the surface, a series of valves controls the flow of water into one or more of three Tygon lines connected to (i) a waste receptacle, (ii) one or more collection bottles, (arranged in tandem order if more than one is used), and (iii) a manifold (Figure B.2) that holds probes for detecting pH, redox potential (Eh), dissolved oxygen, temperature, and specific conductance. Other sample lines, such as the one for microbiological sampling shown in Figure B.1, can be added as desired. Since the water stream passing through the probe manifold and from the exit port of the collection bottle is ultimately deposited in the waste receptacle, the system is essentially closed. After the collection bottles are filled and sealed, the water in the waste container is pumped back into the trench.

Anoxia during sample collection results from a number of factors. The collection bottles are made anoxic by flushing and filling them with an inert gas (e.g. nitrogen or argon) prior to departure from the laboratory. After the manifold is assembled in the field, air is removed from it by purging with the inert gas from a gas cylinder incorporated as part of the system (Figure B.1). Once the pumping operation begins all gases within the system are displaced by

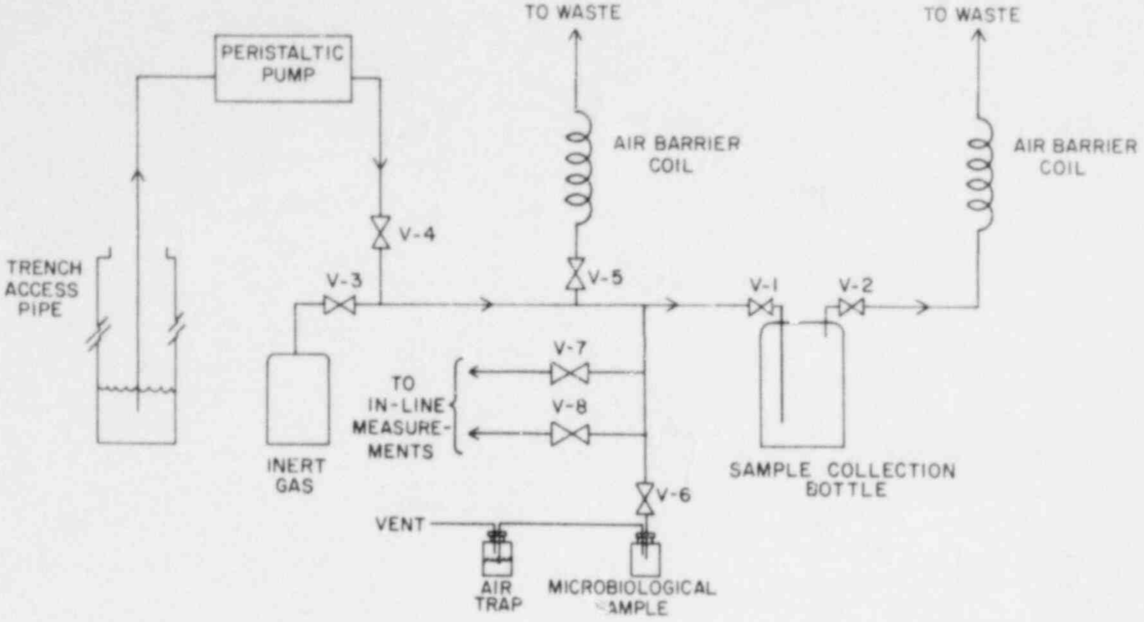


Figure B.1. Schematic diagram of the system for anoxic collection of water.

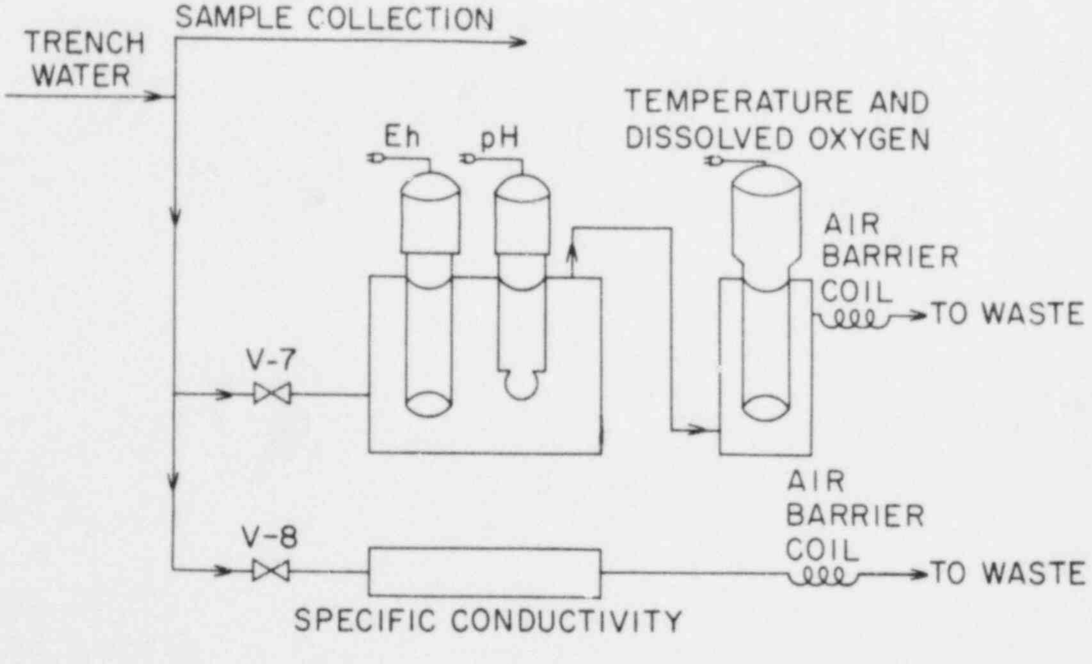


Figure B.2. Schematic diagram depicting the arrangement of probes for in-line measurements.

trench water. Since the first several liters of water removed from a trench come from within, or from the immediate vicinity of, the riser pipe, and may have been affected by oxygen in the ambient air in the pipe, the actual sample is collected only after the in-line measurements show that freshly recharged, anoxic, raw trench waters are present. Air-barrier coils remain filled with water whenever water flow is stopped and serve to prevent air from re-entering the system through the waste container. At the same time these coils allow the pressure in the collection bottles to come to near atmospheric level before the valves on bottles are closed.

The collection system is assembled in the field for each day's sampling session. A photograph of a field set-up is shown in Figure B.3. After each trench is sampled, all tubing except that connected to the waste container is replaced.

Full collection bottles are enclosed in plastic bags and stored in ice-filled coolers until they are returned to the laboratory, where they are transferred to refrigerators and stored for analyses.

Figure B.3. Portable anoxic collection system used to sample trench water from low-level radioactive waste disposal sites.

The collection procedure and apparatus are both readily modified to deal with a special problem such as is presented by a trench that is known or suspected to contain only a limited volume of water. In such a case, the usual practice is to retain the normal configuration of the sampling apparatus, but to reduce the volume of water diverted to waste before beginning to fill the collection bottles. Another useful strategy is to fill the bottles separately rather than in tandem, and to thereby assure that, if the water supply is depleted before all bottles are filled, only the one being filled at the time of depletion is exposed to air. Branches for filling bottles separately can be added to either the normal sample line or to the normal waste line. Separate filling of collection bottles also allows one to vary the duration of the interval between times when samples are taken from the same trench during the same pumping operation. If the volume of water obtained from a trench is extremely small, one can also take a sample from the water in the waste receptacle.

B.2.2 Equipment List

peristaltic pump
cylinder of an inert gas (e.g., nitrogen or argon) with appropriate regulator and pressure gauge
borosilicate glass collection bottles -- flushed and filled with the inert gas prior to use
monitoring probes and meters for measurement of pH, redox potential, specific conductance, dissolved oxygen and temperature -- meters should be capable of battery operation
monitoring probe holders
special in-line combination valve
waste receptable (i.e., 30 gallon drum)
Tygon tubing (Labroatory Grade, R-3603)
borosilicate glass tees
hosecock clamps
hose clamps
plexiglas board upon which valves, probe holders, and the gas cylinder are mounted
ice-chest for transport and cold storage of collected samples
gasoline operated generator or electric power cord depending upon extant field conditions.

B.2.3 Sample Collection Bottle

A special bottle designed for anoxic collection and storage of trench water, as well as for subsequent anoxic removal of aliquots of water for analysis, was produced at BNL. This container, which is shown in Figure B.4, is a modified 4-liter borosilicate glass bottle having two high-vacuum-type stopcock valves attached as input and output ports. The valve stems are made of Teflon and have o-rings for gas-tight sealing against the valve barrel.

B.2.4 Combination Valve

The combination valve pictured in Figure B.5 includes valves V-3 and V-4, as well as the outlets to both the collection bottle(s) and the direct line to

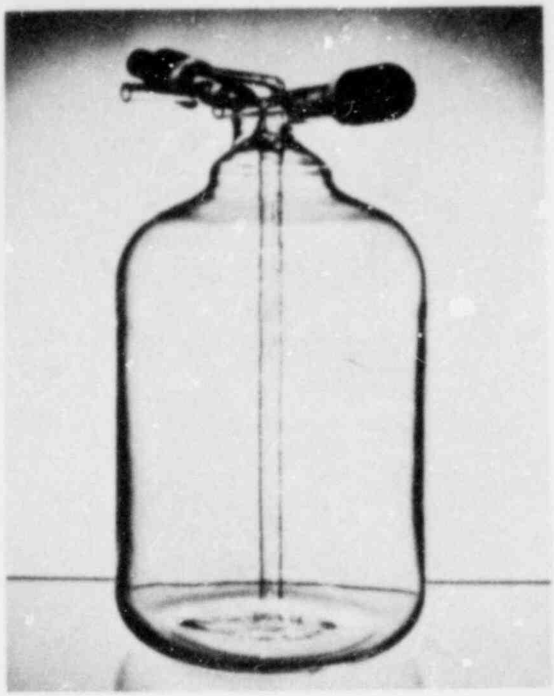


Figure B.4. Sample Collection Bottle

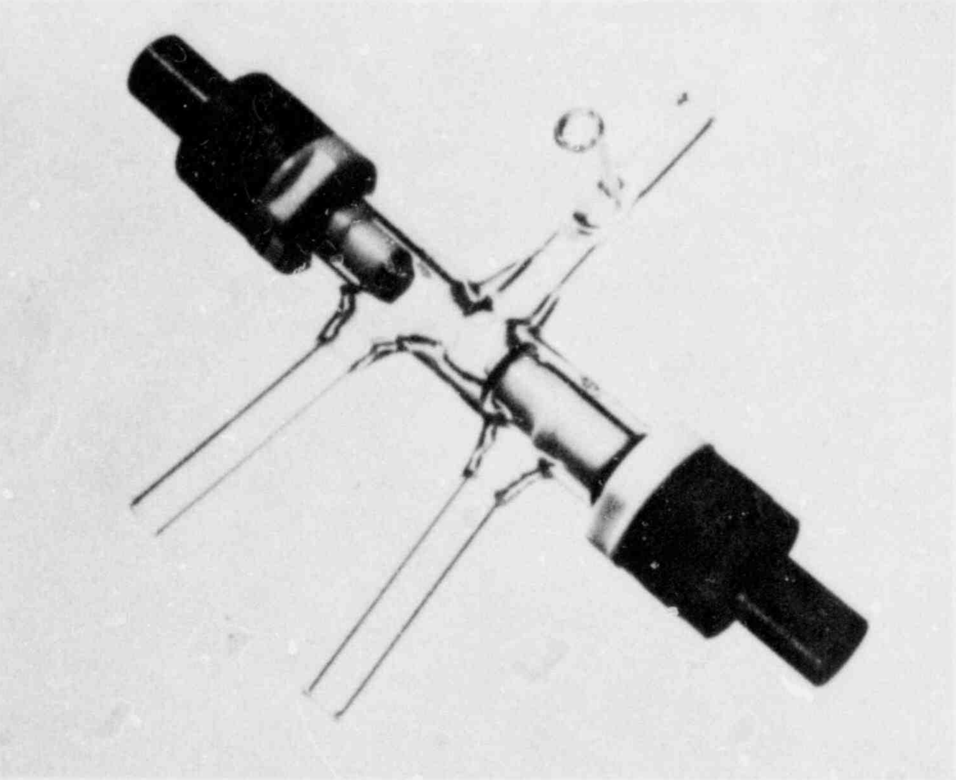


Figure B.5. Combination Valve

the waste receptacle. This valve uses two high-vacuum-type stopcocks identical to those on the collection bottle. The stopcock on the left is shown in the open position to illustrate the non-restrictive flow design necessary to allow passage of particulate material contained in trench water. The valve on the right illustrates the sealing action of the o-rings against the glass.

B.2.5 In-Line Measurements

B.2.5.1 Introduction

The temperature, pH, redox potential (Eh), dissolved oxygen and specific conductance of trench waters are monitored and measured throughout the sample collection operation. To accommodate these measurements without contaminating the sample with substances released from the detector probes, the probes are contained in a manifold on a line separate from that carrying water to the collection bottles. The probes are sealed in the manifold (made of Lucite) with pressure-flattened o-rings. A schematic diagram of the probe manifold is shown in Figure B.2.

B.2.5.2. pH

The pH is measured with an Orion 407A specific ion meter in conjunction with a porous-plug combination glass and silver/silver chloride reference electrode.

B.2.5.3 Redox Potential (Eh)

Redox is measured with an Orion 407A specific ion meter in conjunction with an Orion 96-78 combination platinum redox and reference electrode. The electrode system is calibrated with Zobell solution as described by Wood(1). Redox potentials of trench waters, measured in the field relative to the reference incorporated in the Orion probe, are reported relative to the normal hydrogen electrode (NHE).

The redox potential for a solution provides a measure of the relative oxidizing or reducing characteristics of the system. Higher values are indicative of conditions more favorable to oxidation and lower values of conditions favoring reduction. Since many reactions contribute to the overall redox potential of a complex solution system such as trench water, and since some of these reactions, especially those involving oxygen, occur at very slow rates, a redox potential measured in the field may not represent a true equilibrium condition. Consequently, any such value should be considered as only a qualitative or semi-quantitative tool for evaluating such a system. Redox potentials are important, in that calculations based upon such measurements, help to set limits to the processes which might be expected to occur.

B.2.5.4 Temperature and Dissolved Oxygen

These parameters are measured with a YSI Model 57 dissolved oxygen meter and a YSI 5739 dissolved oxygen probe. The probe is a polarographic-type whereby the current produced and measured is directly proportional to the absolute pressure of oxygen outside the thin Teflon membrane separating the sample from the sensor element. An internal thermocouple provides temperature compensation, and the probe is pressure compensated as well. It is calibrated against atmospheric air in a humid environment before each sample session.

B.2.5.5 Specific Conductance

Specific conductance, a measure of ionized substances in solution, gives an indication of the concentration of dissolved solids in trench water. It is measured with a Markson Model 10 portable conductivity meter and a Markson 1100 flow-through conductivity cell. The cell contains an internal thermocouple for automatic temperature compensation and specific conductance at 25°C is read directly from the meter.

B.2.6 Calibration

Prior to collection of each series of samples, the operation of all probes and meters is checked, and they are calibrated against appropriate standards.

B.2.6 Detailed Collection Procedure

Refer to Figure B.1 and Figure B.2 for locations of valves and parts named in this section.

- Flush the assembly with an inert gas (e.g. nitrogen or argon)

  1. Close valve V-4
  2. Open valve V-3 and adjust the pressure at the gas regulator to 3 psi
  3. Adjust valves V-5, V-7 and V-8 to assure that gas flushes all portions of the assembly

- Direct the first portion of pumped water into the waste receptacle, activate the monitoring system, and flush the collection system with water

  4. Close or leave closed valves V-1, V-2, V-3, V-6, V-7, V-8
  5. Open valves V-4 and V-5
  6. Turn the pump on
  7. Open valves V-7 and V-8 and use these and V-5 to adjust the flow through the monitoring subsystem
  8. Activate the monitoring meters and start readings

- When meter readings have reached a near steady state, initiate sample collection

  9. Open valves V-2 and V-1 (in the order indicated)
  10. Close valve V-5
  11. If necessary readjust water flow through the monitoring subsystem
  12. Flush four or five volumes of water through the collection bottles

- Collect the microbiology sample (this may be done before or during collection of trench water)

13. Open valve V-6 and flush lines by running several milliliters into a waste container
14. Close valve V-6
15. Place a sterile syringe needle on the Leur-loc tip at valve V-6, and insert it through the rubber diaphragm that seals an inert-gas-filled, sterile collection bottle
16. Prior to collection prepare an air trap bottle which is 1/2 to 2/3 full of water and, similar to the microbiology sample collection bottle, sealed with a rubber diaphragm. To collect the microbiology sample, insert a sterile syringe needle through the diaphragm to serve as a vent; being careful not to submerse the tip into the water. Next, take a sterile piece of plastic tubing with sterile needles at both ends and insert one needle through the diaphragm on the air-trap so that its tip is submersed in the water
17. Open valve V-6 and, as soon as liquid enters the collection bottle, insert the sterile needle at the other end of the piece of plastic tubing (from step 16) through the diaphragm on the collection bottle
18. Fill the collection bottle to the desired level
19. Close valve V-6
20. Break the tubing connection between the collection bottle and the air-trap bottle by removing the needle (from step 17) from the collection bottle
21. Remove the collection bottle from the needle at valve V-6 and store in ice

- Terminate sample collection

22. Turn the pump off
23. Close valves V-7 and V-8
24. Open valve V-3 and, with the gas regulator set no higher than 3 psi, bubble inert gas through the collection bottles
25. Close valves V-1 and V-2 (in that order)
26. Open valves V-7 and V-8, and use the inert gas to move water contained in the probe lines into the waste receptacle
27. Close valves V-3, V-7 and V-8

- Return water from the waste receptacle to the trench

28. Reverse the direction of the tubing in the peristaltic pump
29. Open valve V-5
30. Start the pump to return waste water to the trench
31. After waste water is returned, turn off the pump, carefully detach hoses connected to the sample bottles, and as each hose is removed wipe any water trapped in the nipples by which these hoses were attached to the input or output ports. Label sample bottle, place into a double plastic bag, and store in ice in an insulated chest

B.3 Anoxic Filtration Procedure

Along with development of procedures for collecting samples anoxically, methods were also devised by which aliquots of such samples could be withdrawn anoxically from a collection bottle and, if desired, filtered anoxically. In this way water can be retained under anoxic conditions until it is withdrawn for chemical analysis. Furthermore, anoxic aliquots can be obtained by collecting filtered water samples in sealed bottles which had been previously purged with an inert gas. In this section the apparatus and methods used to withdraw and filter samples anoxically will be described. A schematic diagram and photograph of the system are shown in Figure B.6 and Figure B.7.

B.3.1 Equipment

Collection bottles
Cylinder of inert gas (nitrogen or argon)
Millipore stainless steel sanitary sterilizing filter holder, 147 mm
0.45 μm Millipore filter, 147 mm
0.45 μm silver membrane filter, 147 mm
glass by-pass valve
Tygon tubing (Laboratory Grade, R-3603)
Glass tees
Hosecock clamps
Hose clamps
Lucite board upon which are mounted the hose-cock clamps used as valves
Narrow-mouthed bottles for air-barrier traps
Plastic bucket to contain collection bottles and air-barrier traps during filtration
Various bottles to receive filtered samples
Petri-dishes in which to store used filters

B.3.2 Operation

A clean filtering apparatus containing a tared 0.45 μm Millipore filter membrane is assembled for each filtration performed. During filtration operations, bottles that are to receive filtrates and that are not to be acidified are kept on ice. Those to be acidified are kept at ambient temperature. Due to the presence of very fine particulates, most filtrations, even of apparently clear samples, proceed slowly. The detailed procedure for filtration is given below. See Figure B.6 for the locations of valves or parts named in this section.

- Purge the system with an inert gas to replace air

    1. Close or leave closed valves V-1, V-2, V-7 and V-8
    2. Open valves V-3, V-5 and V-6
    3. Open valve V-4 and, with the gas regulator set at 3 psi, purge the system with the inert gas
    4. Open valves V-7 and V-8, and close valve V-6 to purge the interior of the filter holder

- Initiate filtration

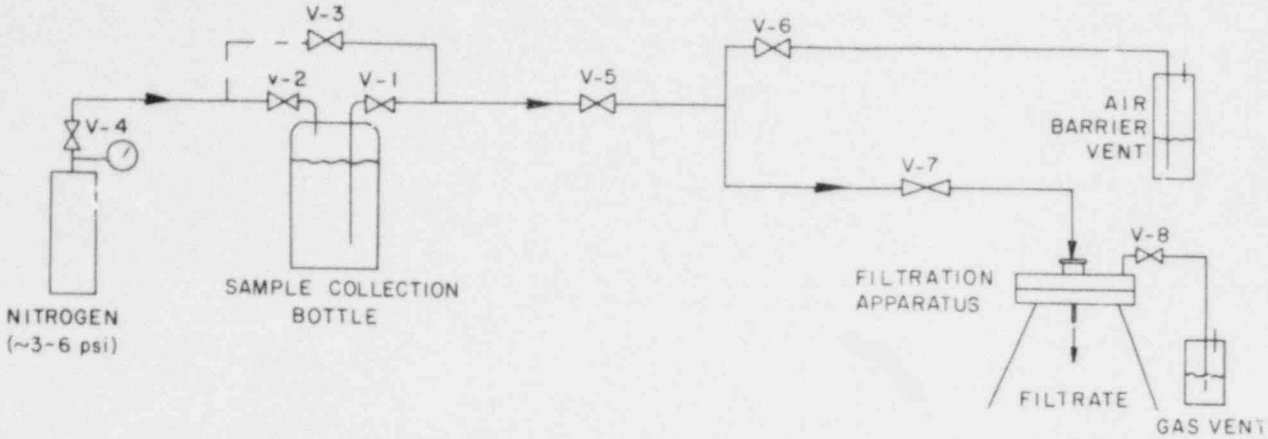


Figure B.6. Schematic diagram depicting the apparatus for anoxic filtration of water.

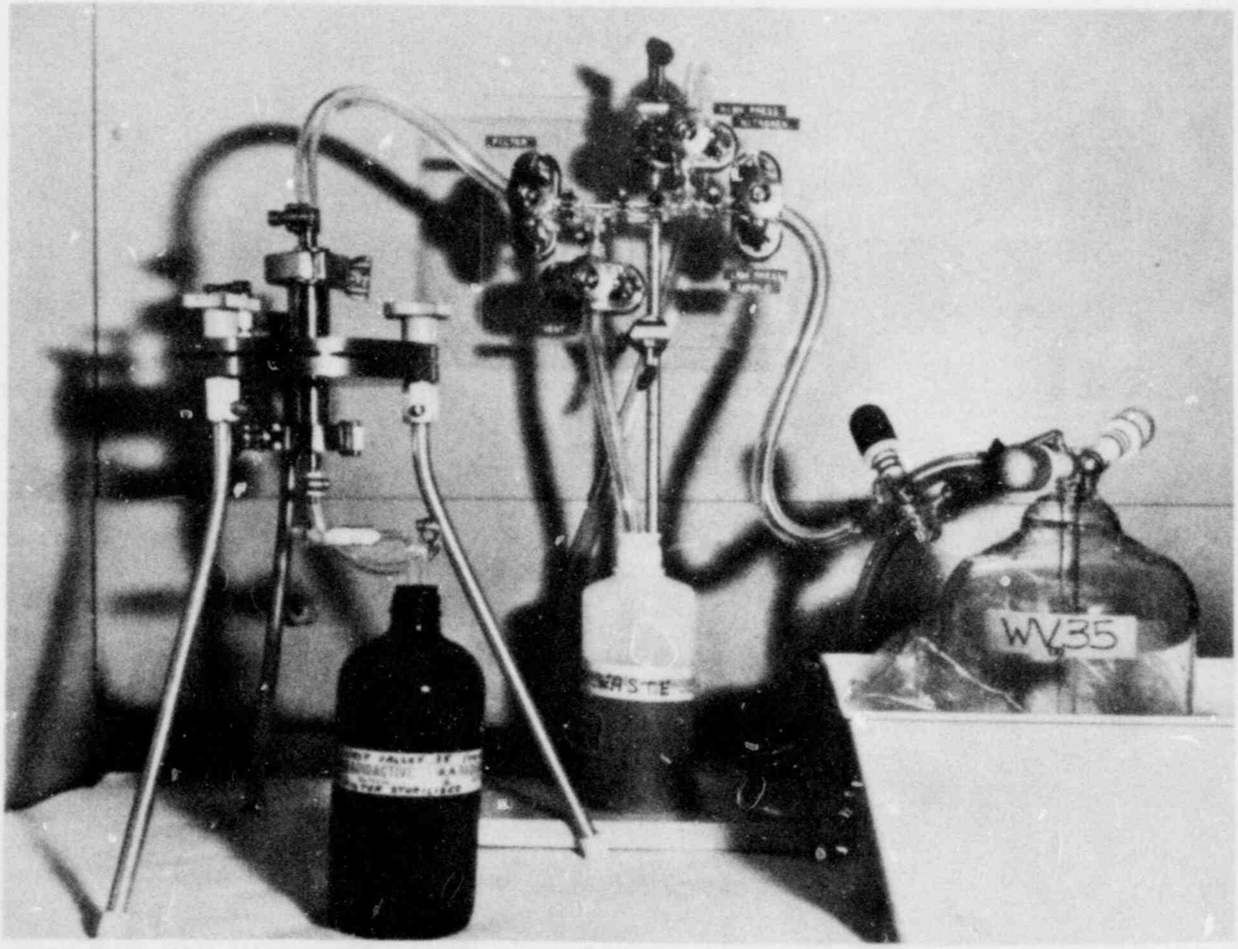


Figure B.7. Apparatus for anoxic filtration of water.

5. Close valve V-3
6. Open valves V-2 and V-1, in that order. This will start movement of liquid from the collection bottle to the filter holder
7. When the liquid reaches the filter holder, close valve V-8
8. Continue filtration at gas pressures ranging between 3 and 6 psi

- To change a filter membrane if one should become clogged

9. Close valve V-4
10. Open valve V-6
11. Close valves V-1, V-2 and V-7
12. Open valve V-8
13. Open valves V-4 and V-3, and use gas to purge water out of the tubing and into the air-barrier vent bottle
14. Close valves V-4, V-3 and V-5
15. Disassemble the filter holder, replace the clogged membrane with a new weighed membrane, reassemble the filter holder, and proceed as indicated in steps 1-8 above

- To terminate filtration

16. Close valves V-1 and V-2
17. Open valve V-3
18. Close valve V-7
19. Open valve V-6 and purge water from the filter lines into the air-barrier vent bottle
20. Close valves V-4 and V-3, in that order
21. Momentarily open valves V-1 and V-2 to allow pressure in the collection bottle to come to near atmospheric level
22. Carefully disassemble the filtration apparatus and save the filter in a labelled Petri-dish.

B.3.3 Filtration of Water for Analysis of Organic Constituents

Water that is to be analyzed for its organic constituents is filtered through a 0.45 µm silver metal membrane (from Selas Flotronics) to achieve initial filter-sterilization and, due to the bacteriostatic action of silver, to inhibit bacterial regrowth in the filtrate. In this way post-filtration changes in the organic composition of the filtrate due to bacterial metabolism are precluded. The filtration apparatus and method described above are usually used for these filtrations. However, a cylindrical stainless steel filter-holder, having a capacity of approximately 200 milliliters and containing a 47-mm-diameter silver filter membrane, is also used.

B.4 Reference

1. W. W. Wood, "Guidelines for Collection and Field Analyses of Ground-Water Samples for Selected Unstable Constituents," in Techniques of Water-Resources Investigations of the United States Geological Survey, Book 1, Collection of Water DAta by Direct Measurement, Chapter D2, Stock Number 024-001-02878-4, 1976. Available for purchase from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

APPENDIX C

METHODS FOR THE DETERMINATION OF INORGANIC CONSTITUENTS IN TRENCH LEACHATES FROM SHALLOW LAND RADIOACTIVE WASTE DISPOSAL SITES

(S.L. Garber)

The methods described in this manual are derived from established procedures frequently involving modifications of parameters due to the unique case at hand. No claim for strict originality is made for these procedures. The value of this manual is that all the recommended techniques have been tested on samples of chemically complex radioactive waste waters and therefore are applicable to a varied range of aqueous samples having different matrices.

Although specifically written as a guide for the inorganic analyses of low-level radioactive waste waters, the methods described are also applicable to waste waters derived from land fills, waste disposal plants and sewers.

It is the intention of the author that the procedures described will be useable by any competent analyst. In several methods, reagents or equipment are cited by proprietary name. This is not intended as an endorsement and equivalent products may be substituted.

NON-METALS

Preparation and Storage of Samples

Samples received in our laboratory are stored prior to filtration at 4°C in anoxic glass collection bottles. The samples are analyzed for dissolved ammonia immediately after anoxic filtration. Analysis of other nutrients such as phosphate, nitrate, nitrite and sulfate are completed within 48 hours. The samples are stored at 4°C in tightly capped polyproplene bottles or, more recently, in sterile nitrogen purged glass serum bottles.

AMMONIA (By Probe)

1. Application

This method is applicable to dissolved ammonia in a homogeneous liquid solution.

2. Summary of Method

The ammonia electrode uses a hydrophobic gas-permeable membrane which permits dissolved ammonia to diffuse through until the partial pressure of ammonia is the same on both sides. The partial pressure of ammonia will then be proportional to the concentration as determined by Henry's Law.

$$K_h = \frac{[NH_3]}{P_{NH_3}} \cong 56 \text{ moles/liter-atom } (25°C)$$

Standards and samples should contain about the same concentration level of dissolved species at a given temperature. The method of standard additions is preferred over direct reading methods.

3. Interferences

Volatile amines interfere with measurements. Mercury, silver, copper, gold, nickel, cobalt, cadmium, and zinc form complexes with ammonia. Most of these metal interferences can be removed by hydroxide precipitation or complex formation. Mercury interference can be eliminated by the addition of iodide.

Water vapor can move across the membrane and change the concentration of the filling solution thus causing an electrode drift. Water vapor transport is not a problem when electrode and sample temperatures are the same and the osmotic strength of the solution is below 1 molar. The following procedure is used most often in our laboratory.

(1) dilute samples with high osmotic strength, high ammonia concentration

(2) add 10 molar NaOH to samples of low osmotic strength

(3) add 4.25 g solid $NaNO_3$ to each 100 mL of filling solution to samples of high osmotic strength (above 1 molar) and low ammonium levels (below 10^{-5} molar).

Surfactants wet the membrane and the liquid solution can then penetrate. The probe must then be placed in a closed system where the electrode can respond to ammonia in the gas phase.

4. Apparatus

A 407A specific ion meter with an Orion ammonia electrode model 95-10.

5. Reagents

DISTILLED OR DEIONIZED WATER

Preparation: Pass distilled or deionized water through an ion-exchange column containing a strongly acidic cation exchange resin, such as Dowex 50W-X8.

10 M NaOH

Sodium Hydroxide	40 g
Distilled Water	100 mL

Preparation: To prepare 10 M NaOH, add 40 g reagent-grade NaOH to 80 mL distilled water in a 100-mL volumetric flask, dissolve, and dilute to volume with distilled water, or dilute 80 mL of commercially available 50% NaOH to 100 mL with distilled water.

STANDARDS

STOCK STANDARD, 100 mg N/L

Ammonium Chloride (NH_4Cl)	0.382 g
Distilled Water	1000 mL

Preparation: Dissolve 0.315 g of ammonium chloride in distilled water and dilute to 1 liter.

STANDARD SOLUTION

0.1 M ammonium chloride standard, Orion Cat. No. 95-10-06,
or 1000 mg N/L as nitrogen standard, Orion Cat. No. 95-10-07.

Preparation: To prepare a 0.1 M ammonium chloride standard from laboratory supplies, add 0.535 g reagent-grade NH_4Cl to 50 mL distilled water in a 100-mL volumetric flask, stir to dissolve, and dilute to volume with distilled water. To prepare a 1000 mg/L as N standard from laboratory supplies, add 0.382 g reagent-grade NH_4Cl to 50 mL distilled water in a 100-mL volumetric flask. Stir to dissolve and dilute to volume with distilled water.

INTERNAL FILLING SOLUTION

Orion Cat. No. 95-10-02.

6. Procedure

Obtain a rough concentration range by direct measurement. Then adjust the concentration of sample and standards for the method of standard additions. To measure ammonia in samples containing surfactants adjust the sample pH to 12 with 10 M NaOH. Alizarin yellow b is a good indicator for this. Immediately transfer the solution to a 125-mL Erlenmeyer flask fitted with a rubber stopper with a hole large enough to hold the electrode.

Direct measurement using 407A specific ion meter-ppm

(1) Prepare 100 and 10 mg N/L standards by serial dilution of the 1000 mg N/L standard.

(2) Place electrode in the 10 mg N/L standard. Add 1 mL 10 M NaOH to each 100 mL of standard. Turn the function switch to X^-. Adjust the meter needle to "1" (center scale) on the red logarithmic scale with the calibration control. Use magnetic stirring throughout the procedure.

(3) Rinse electrode and place in the 100 m/L standard. Add 1 mL 10 M NaOH to each 100 mL of standard. Stir thoroughly. Turn the temperature compensator knob until the meter needle reads "10" (full-scale right) on the red logarithmic scale.

(4) Rinse electrode and place in sample. Add 1 mL 10 M NaOH to each 100 mL of sample. Stir thoroughly. Multiply the meter reading on the red logarithmic scale by 10 to determine sample concentration in mg/L of nitrogen.

Standard addition using 407A specific ion meter

(1) Prepare a standard solution about a hundred times as concentrated as the sample concentration by diluting the 0.1 M or 1000 mg N/L standard.

(2) Add 1 mL 10 M NaOH to each 100 mL sample. Place the electrode in the solution. When checking a direct measurement, leave the electrode in 100 mL of the same sample used for direct measurement. Use magnetic stirring throughout the known addition procedure.

(3) Turn the function switch to $\bar{X}$. Turn the slope indicator and dial to the percent slope of the electrode as determined in the daily electrode check. Turn the temperature compensator knob until the white arrow points to the solution temperature. Adjust the calibration control knob to set the needle to "∞" on the green increment scale.

(4) Pipet 1 mL standard solution into 100 mL sample. Stir thoroughly. Record the reading, Q, from the green increment scale.

7. Calculations

(1) To determine the total sample concentration, use the following equation:

$$C_o = (Q/100)C_s$$

where:

C_o = total sample concentration
Q = reading from green increment scale
C_s = concentration of added standard

(2) To check a direct measurement, compare results of the two methods. If they agree within ±4%, the measurements are probably good. If the known standard addition result is much larger than the direct measurement, the sample may contain complexing agents, and measurements should be confirmed by another method of analysis.

8. References

1. Orion Research Instruction Manual for the Ammonia Electrode 95-10 Orion Research Incorporated Form 1M95-10/679, 1976. Available from Orion Research, 380 Putnam Avenue, Cambridge, Mass. 02139.

AMMONIA (Colorimetric)

1. Application

This automated procedure for the determination of ammonia is applicable in the range 0-10 mg/L of ammonia in filtered liquid samples. Approximately sixty samples per hour can be analyzed.

2. Summary of Method

The Berthelot reaction involves the formation of a green compound believed to be related to indophenol when a solution of an ammonium salt is added to sodium phenoxide followed by the addition of sodium hypochlorite. A solution of potassium sodium tartrate is added to the sample stream to eliminate the precipitation of the heavy metals.

3. Interferences

Air must be scrubbed through acid to remove ammonia before introduction into the system.

In some instances a high salt concentration may interfere. The previously described probe procedure is then the method of choice.

In samples of high ammonia concentration, dilution of sample eliminates refractive index interferences.

In other complex matrices the method of standard additions may be used by spiking successive sample cups containing the same volume with increasing amounts of a concentrated standard.

4. Apparatus

Technicon auto analyzer equipped with manifold #116-D186-01.

5. Reagents

ALKALINE PHENOL (Technicon No. T01-0115)

Sodium Hydroxide ($NaOH$)	200	g
Liquified Phenol, 88% (C_6H_5OH)	276	mL
Distilled Water, q.s.	1000	mL
Brij-35 Wetting Agent (Technicon No. T21-0010-01)	0.5	mL

Preparation: Dissolve 200 g of sodium hydroxide to approximately 600 mL of distilled water contained in a vessel surrounded by circulating cold water. Slowly add while cooling 276 mL liquified phenol (88%) stirring continuously. Dilute to 1 liter with distilled water and store in a brown bottle. Add 0.5 mL of Brij-35 per liter.

SODIUM HYPOCHLORITE (Technicon No. T01-0114)
Household bleach having 5.25% available chlorine may be used.

POTASSIUM SODIUM TARTRATE

Potassium Sodium Tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$)	150	g
Distilled Water	1000	mL
Brij-35	0.5	mL

Preparation: Dissolve 150 g of potassium sodium tartrate in 850 mL distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 per liter.

STANDARDS
STOCK STANDARD, 100 mg N/L

Ammonium Chloride (NH_4Cl)	0.382	g
Distilled Water	1000	mL

Preparation: Dissolve 0.382 g of ammonium chloride in distilled water and dilute to 1 liter.

6. Procedure

Samples and wash water should be adjusted to a pH of 6.5 - 7.0 using 0.1 N HCl. Arrange ammonia standards in decreasing concentrations of ammonia and alternate each sample and standard with a wash cup of ultrapure pH adjusted water. Ultrapure water may be obtained by additional treatment of laboratory grade water by a Millipore "Milli-Q" or similar system.

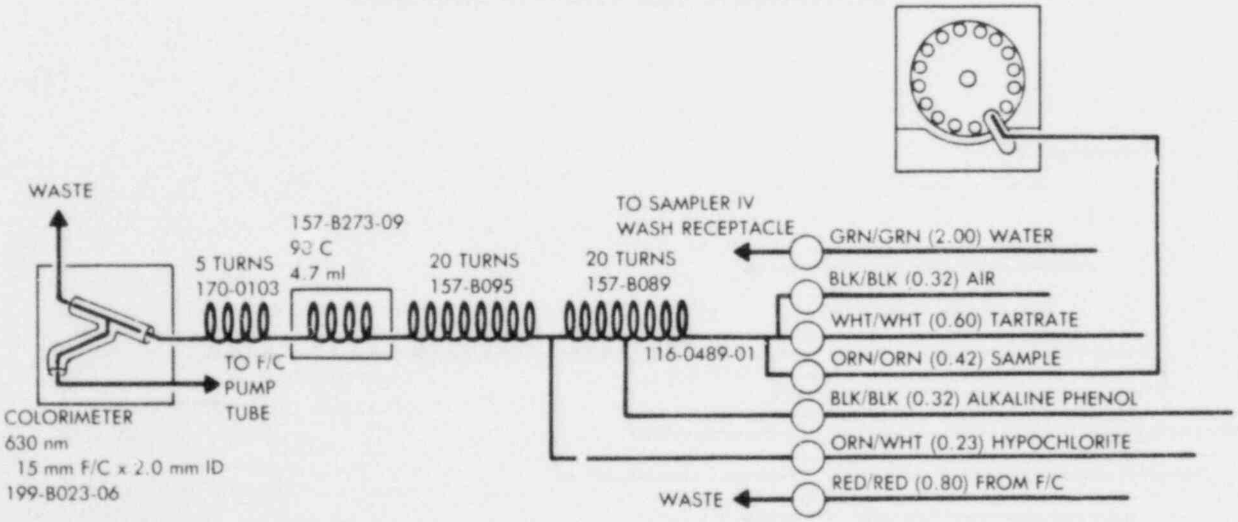
7. Calculations

Prepare appropriate curve and determine concentration value of samples directly. This then is compared to values obtained using the ammonia probe.

8. References

1. D.D. Van Slyke and A.J. Hiller, J. Bio. Chem., Vol. 2, 1933, p. 499.
2. J. Fiore and J.E. O'Brien, "Ammonia Determination by Automatic Analysis", Wastes Engineering 33, 352 (1962). Available in public technical libraries.

AMMONIA IN WATER AND WASTEWATER



NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN.

Technicon Manifold No. 116-D186-01

CHLORIDE

1. Application

This automated method is applicable to filtered waters in the ranges of 0.2-10 mg/L and 2-100 mg/L. Approximately forty samples per hour can be analyzed.

2. Summary of Method

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of non-ionic but soluble mercuric chloride. In the presence of ferric ion the liberated thiocyanate forms a highly colored ferric thiocyanate complex, the colour intensity being proportional to the original chloride concentration.

3. Interferences

Filtration just prior to analysis is desirable. In our laboratory the samples are injected into the sample cups utilizing a Millipore millex sterile 0.45 µm filter.

4. Apparatus

Technicon Auto Analyzer Manifold No. 116-D051-01

5. Reagents

MERCURIC THIOCYANATE (STOCK)

Mercuric Thiocyanate ($Hg(SCN)_2$)	4.17 g
Methanol, (CH_3OH)	1000 mL

Preparation: Transfer 500 mL of methanol into a 1-liter volumetric flask containing 4.17 g of mercuric thiocyanate and dissolve. Dilute to volume with methanol, mix and filter through filter paper.

FERRIC NITRATE, 20.2% (Stock) (Technicon No. T01-0028)

Ferric Nitrate ($Fe(NO_3)_3 \cdot 9H_2O$)	202 g
Nitric Acid, Concentrated (HNO_3)	31.5 mL
Distilled Water	1000 mL

Preparation: Place the ferric nitrate in a 1 liter volumetric flask, and add approximately 500 mL of distilled water. Shake until all the ferric nitrate is dissolved. Carefully add the concentrated nitric acid to the flask, and mix, bring to volume with distilled water. Filter through an analytical grade of filter paper and store in a sealed amber reagent bottle.

CHLORIDE COLOR REAGENT (Technicon No. T01-0352)

Mercuric Thiocyanate (Stock)	150 mL
Ferric Nitrate 20.2% (Stock) (Technicon No. T01-0028)	150 mL
Distilled Water	1000 mL
Brij-35, 30% Solution (Technicon No. T21-0110)	1.0 mL

Preparation: Place 150 mL of mercuric thiocyanate into a 1-liter volumetric flask. Add 150 mL of 20.2% ferric nitrate, and mix. Dilute to volume with distilled water. Add 1 mL of Brij-35 per liter.

DILUENT WATER, 10 mL/L Brij-35 (.2-10 mg/L Range)

Distilled Water	1000	mL
Brij-35, 30% solution	10	mL

Preparation: Add 10 mL of Brij-35, 30% solution, to 1 liter of distilled water and mix thoroughly.

DILUENT WATER, 1 mL/L Brij-35 (2-100 mg/L Range)

Distilled water	1000	mL
Brij-35, 30% solution	1	mL

Preparation: Add 1 mL of Brij-35, 30% solution, to 1 liter of distilled water and mix thoroughly.

STANDARDS

STOCK SODIUM CHLORIDE STANDARD SOLUTIONS

Stock A, 1000 mg/L Cl (for 2-100 mg/L Range)

Stock B, 100 mg/L Cl (for 0.2-10 mg/L Range)

STOCK SOLUTION A, 1000 mg/L Cl

Sodium Chloride (NaCl)	1.648	g
Distilled Water	1000	mL

Preparation: Dissolve 1.648 g of sodium chloride in about 600 mL of distilled water. Dilute to 1 liter with distilled water and mix thoroughly.

STOCK SOLUTION B, 100 mg/L Cl

Sodium Choride	0.165	g
Distilled Water	1000	mL

Preparation: Dissolve 0.165 g of sodium chloride in about 600 mL of distilled water. Dilute to 1 liter with distilled water and mix thoroughly.

6. Procedure

A series of standards corresponding to the anticipated concentration range of the samples are analyzed. Technicon advises that the range of analysis for this manifold is 0.2-100 mg/L. However, because this chemistry does not conform to Beer's law and produces several predictable slope changes, it is found to be more practical to analyze in concentration ranges of 0.2-10 mg/L and 2-100 mg/L. These concentration ranges approximately correspond to the linear portions of the curve. At all times the sample is "bracketed" by standards, i.e., a standard with a concentration above and below that of the sample is analyzed on the same sampler tray. Water blanks of the diluent water are also run routinely.

Ideally the standards would be prepared having the same chemical matrix as the samples. However, due to the complexity of the samples received, duplicating the chemical composition is difficult. We have found a hundred-fold dilution and analyses at the lower concentration range to be quite satisfactory.

7. Calculations

Compute concentration of samples by comparing with standard curve.

8. References

1. J.E. O'Brien, "Automatic Analysis of Chlorides in Sewage", Wastes Engineering 33, 670-672 (December 1962).[a]

2. D.M. Zall, D. Fisher, and M.D. Garner, Anal. Chem. 28 (1956).[a]

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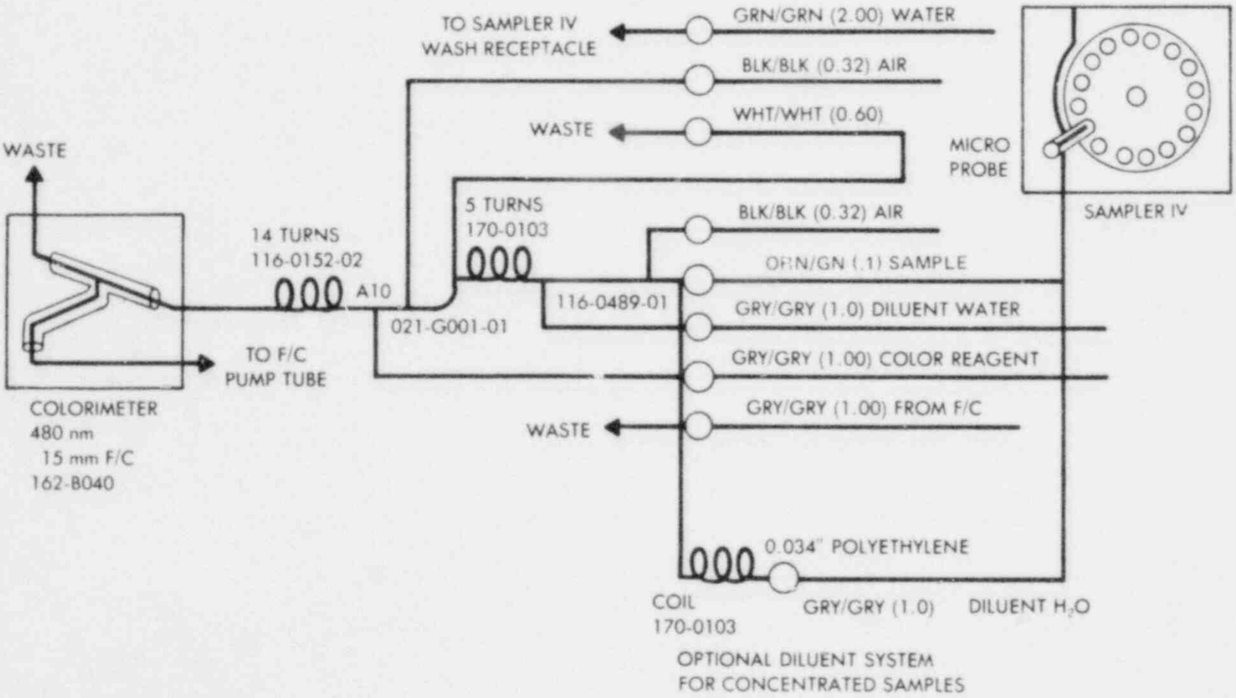
[a] Available in public technical libraries.

CHLORIDE IN WATER AND WASTEWATER



NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN.

Manifold Adapted From
Technicon Auto Analyzer
Manifold No. 116-D051-01

FLUORIDE

1. Application

This method is applicable to fluoride in a homogenous liquid solution which does not contain highly polar solvents.

2. Summary of Method

Fluoride is determined with a specific ion electrode consisting of a single-crystal lanthanum fluoride membrane and an internal reference. The crystal is an ionic conductor in which only fluoride ions are mobile. The potential developed across the membrane in the Orion 94-09 probe is proportional to the fluoride ions in solution and is measured against an external reference with the Orion 407A specific ion meter.

3. Interferences

Fluoride forms complexes with aluminum, silicon, iron (+3) and other polyvalent cations. The extent of complexation depends on the concentration of the above cations, the total fluoride concentration, the pH of the solution and the total ionic strength of the solution.

Addition of TISAB to fluoride standards and samples buffers the pH between 5.0 and 5.5 to avoid hydroxide interferences or the formation of hydrogen complexes of fluoride. It is advisable to check the pH of the buffered samples prior to analysis.

4. Apparatus

A 407A specific ion meter with an Orion fluoride electrode.

5. Reagents

TOTAL IONIC STRENGTH ADJUSTOR (TISAB III Orion Cat. No. 94-09-11)

Sodium Fluoride (NaF)	0.221 g
Distilled Water	100 mL

Preparation: Dissolve 0.221 g of sodium fluoride in distilled water and dilute to 100 mL.

6. Procedure

Obtain a rough concentration range by direct measurement. Then, adjust the concentration of sample and standards for the method of standard additions. Direct measurement using 407A specific ion meter is as follows:

(1) Prepare a 10 mg/L fluoride as F^- standard by serial dilution of the 100 mg/L standard. Place 50 mL of 10 mg/L standard and 50 mL of 100 mg/L standard into separate 250-mL beakers. Add 50 mL TISAB II or IV, or 5 mL TISAB III, to each 50 mL standard. Use the nominal values of the standards in calibrating

the electrodes; e.g., if a 100 mg/L standard is diluted with TISAB, the reading obtained is still designated "100 mg/L".

(2) Place electrodes in the 10 mg/L standard. Turn Function Switch to X^-. Stir thoroughly. Adjust the meter needle to "1" (center scale) on the red logarithmic scale with the Calibration Control.

(3) Rinse electrodes, blot dry, and place in the 100 mg/L standard. Stir thoroughly. Turn the Temperature Compensator knob until the meter needle reads "10" (full-scale right) on the red logarithmic scale.

(4) Transfer 50 to 100 mL of sample to a 150-mL plastic beaker. Add 50 mL TISAB II or IV, or 5 mL TISAB III, to each 50 mL sample.

(5) Rinse electrodes, blot dry, and place in sample. Stir thoroughly. Multiply the meter reading on the red logarithmic scale by 10 to determine the sample concentration in mg/L.

(6) Recalibrate every 1 or 2 hours. If the ambient temperature has not changed, repeat step 2. If the temperature has changed, repeat steps 2 and 3.

Known Addition

Known addition is convenient for measuring occasional samples because no calibration is needed. Since an accurate measurement requires that the concentration double as a result of the addition, sample concentration must be known within a factor of three. Total concentration of fluoride can be measured in the absence of complexing agents down to 2×10^{-5} M fluoride or in the presence of a large excess (50 to 100 times) of complexing agent if there is a high level of fluoride (over 10^{-2} M) in solution. Known addition is a convenient check on the results of direct measurement.

Using the 407A Specific Ion Meter

(1) When measuring an occasional sample, add 50 mL TISAB II or IV to 50 mL sample, or add 5 mL TISAB III to 50 mL sample. Place the electrodes in the solution. When checking a direct measurement, leave the electrodes in 100 mL of the same sample used for direct measurement. Use magnetic stirring throughout the known addition procedure.

(2) Prepare a standard solution about a hundred times as concentrated as the sample concentration by diluting the 0.1 M or 100 mg/L standard. Add 50 mL TISAB II or IV, or 5 mL TISAB III, to each 50 mL standard. Use the nominal value of the standard in calculating results; e.g., if a 100 mg/L standard is diluted with TISAB, the standard is still designated "100 mg/L".

(3) Set the Function Switch to X^-. Turn the Slope Indicator dial to the percent slope of the electrode as determined in the daily electrode check. Turn the Temperature Compensator knob until the white arrow points to the solution temperature. Adjust the Calibration Control knob to set the needle to "∞" on the green increment scale.

(4) Pipet 1 mL standard solution into 100 mL sample. Stir thoroughly. Record the reading, Q, from the green increment scale.

7. Calculations

To determine the total sample concentration, use the following equation:

$$C_o = (Q/100)C_s$$

where:

C_o = total sample concentration
Q = reading from green increment scale
C_s = concentration of added standard before addition of TISAB

To check a direct measurement, compare results of the two methods. If they agree within ±4%, the measurements are probably good. If the known addition result is much larger than the direct measurement, the sample probably contains complexing agents.

For example, suppose that the meter reading, Q, after the addition of 100 mg/L standard, was 3.5. Sample concentration then is:

$$\begin{aligned} C_o &= (Q/100)C_s \\ &= (3.5/100) \times 100 \\ &= 3.5 \text{ mg/L} \end{aligned}$$

If a result of previous direct measurement had been in the range 3.4 to 3.6 mg/L, the result is probably good.

8. References

1. Orion, "Fluoride Electrode", U.S. Patent No. 3, 431, 182, March 4, 1969. Information available from Orion, 380 Putnam Avenue, Cambridge, Mass. 02139.

NITRATE AND NITRITE

1. Application

This method may be used to determine nitrite alone or the sum of nitrite plus nitrate nitrogen in the 0-2 mg/L range.

2. Summary of Method

The nitrate is reduced to nitrite by a copper-cadmium column. The nitrite ion is then treated with sulfanilamide under acidic conditions to yield a diazo compound which couples with N-(1-napthyl)-ethylenediamine dihydrochloride to form a red colored compound.

3. Interferences

Large concentrations of metal ions particularly divalent copper and mercury will form a colored complex having absorption bands in the 520 nm region. This may be compensated for only by spiking the standard with the determined concentration of these ions. Hence, standards must be prepared for each individual sample matrix.

Highly turbid samples are pre-treated off-line with zinc sulfate and then filtered using an in-line filter cartridge, such as millipore millex filters, just prior to analysis.

In most trench water smaples it is necessary to add EDTA to eliminate the interference from iron.

Samples that contain large amounts of organic are extracted with chloroform to facilitate good hydrolysis through the column.

All samples must be pH adjusted to 6-8 prior to analysis as acid will destroy the cadmium column.

4. Apparatus

A Technicon Auto Analyzer with manifold No. 116-D049-01. The manifold has a three way valve in line to permit the column to be by-passed for nitrite analysis.

Preparation of column:

A purple/purple Auto Analyzer I pump tube is used for the reductor column. Before filling the column prepare the cadmium.

Cadmium powder is obtained from E. M. Laboratories, Elmsford, NY 10523, (40-60 mesh). It is then ground and carefully sieved. The fraction which passes through a 20 mesh sieve but is retained on a 40 mesh sieve is used. All ferrous metal is removed by a magnet.

The powder is then degreased with acetone and air dried. The cadmium is then placed in a small beaker and covered with water. Add conc. HNO_3 dropwise until nitrogen dioxide is evolved. This addition pits the surface of the powder. Next rinse thoroughly (10 times) with distilled water then treat the cleaned cadmium repeatedly with 50 mL portions of 2% w/v copper sulfate until the blue color does not fade. Rinse thoroughly with 1% NH_4Cl to remove all collodial cadmium.

The cadmium is then packed in the column using a large disposable syringe fitted with a tygon sleeve. This permits back-flushing.

5. Reagents

GRANULATED CADMIUM (E. M. Laboratories)
STANDARDS
STOCK STANDARD A, 100 mg N/L

Potassium Nitrate (KNO_3) (Technicon No. T13-5074)	0.722	g
Distilled Water	1000	mL
Chloroform ($CHCl_3$)	1	mL

Preparation: Dissolve 0.722 g of potassium nitrate in distilled water and dilute to 1 liter. Store in a dark bottle. Add 1 mL of chloroform as a preservative.

STANDARDS

NITRITE NITROGEN STANDARD, 100 mg N/L

Sodium Nitrite ($NaNO_2$)	0.493	g
Distilled Water	1000	mL

Preparation: Dissolve 0.493 g of sodium nitrite in distilled water and dilute to 1 liter. Store in a dark bottle. Add 1 mL of chloroform.

COLOR REAGENT

Sulfanilamide ($C_6H_8N_2O_2S$)	20	g
Concentrated Phosphoric Acid (H_3PO_4)	200	mL
N-1-Naphthylethylenediamine Dihydrochloride ($C_{12}H_{14}N_2 \cdot 2HCl$)	1	g
Distilled Water	2000	mL
Brij-35 (Technicon No. T21-0110)	1.0	mL

Preparation: To approximately 1500 mL of distilled water add 200 mL of concentrated phosphoric acid and 20 g of sulfanilamide. Dissolve completely. Heat, if necessary. Add 1 g of N-1-naphthylethylenediamine dihydrochloride and dissolve. Dilute to 2 liters. Add 1.0 mL of Brij-35. Store in a brown bottle, preferably flushed with nitrogen and keep in refrigerator.

AMMONIUM CHLORIDE - EDTA SOLUTION

Ammonium Chloride	10	g
Disodium ethylendiamine tetracetate	1.7	g
Distilled Water	1000	mL

Preparation: Dissolve 10 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 mL of distilled water. Adjust the pH to 8.5 with conc ammonium hydroxide, add 0.5 mL Brij-35, dilute to 1 liter, use for analysis when Fe is present.

ZINC SULFATE SOLUTION

Zinc Sulfate $ZnSO_4 \cdot 7H_2O$	100	g
Distilled Water	1000	mL

Preparation: Dissolve 100 g $ZnSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.

SODIUM HYDROXIDE SOLUTION, 6N

Sodium Hydroxide NaOH	240	g
Distilled Water	1000	mL

Preparation: Dissolve 240 g NaOH in approximately six hundred mL distilled water, cool and dilute to 1 liter.

DILUTE HYDROCHLORIC ACID, 6N		
Conc. Hydrochloric Acid	50	mL
Distilled Water	100	mL

Preparation: Dilute 50 mL of conc. HCl to 100 mL with distilled water.

COPPER SULFATE SOLUTION, 2%		
Copper Sulfate $CuSO_4 \cdot 5H_2O$	20	g

Preparation: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 mL of distilled water and dilute to 1 liter.

6. Procedure

Ideally samples are analyzed immediately after filtering or refrigerated at 4°C.

Sample Pre-Treatment

Turbidity removal

Add the zinc sulfate solution, 1 mL for each mL of sample and mix thoroughly. Add sufficient sodium hydroxide solution to obtain a pH of 10.5, let sample stand and filter through a glass fiber filter.

Organic extraction

Extract the organics from the agueous solution using two 10 mL portions of chloroform for each 20 mL sample portion.

pH adjustment

Using conc. HCl or conc. NaOH, the pH is adusted off-line to between 6 and 8.

A series of standards corresponding to the 0.01 - 2.0 mg N/L concentration range are analyzed. The samples are loaded with a mid-range standard every five samples and an ultrapure water blank after each group of ten.

7. Calculations

Compute concentration of samples by comparing with standard curve.

8. References

1. L.J. Kamphake, S.A. Hannah, and J.M. Cohen, Automated Analyses for Nitrate by Hydrazine Reduction, Water Research 1, 206 (1967).[a]

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[a] Available in public technical libraries.

2. J. Fiore and J.E. O'Brien, "Automation in Sanitary Chemistry - parts 1 and 2, Determination of Nitrates and Nitrites", Wastes Engineering 33, 128 and 238 (1962).[a]

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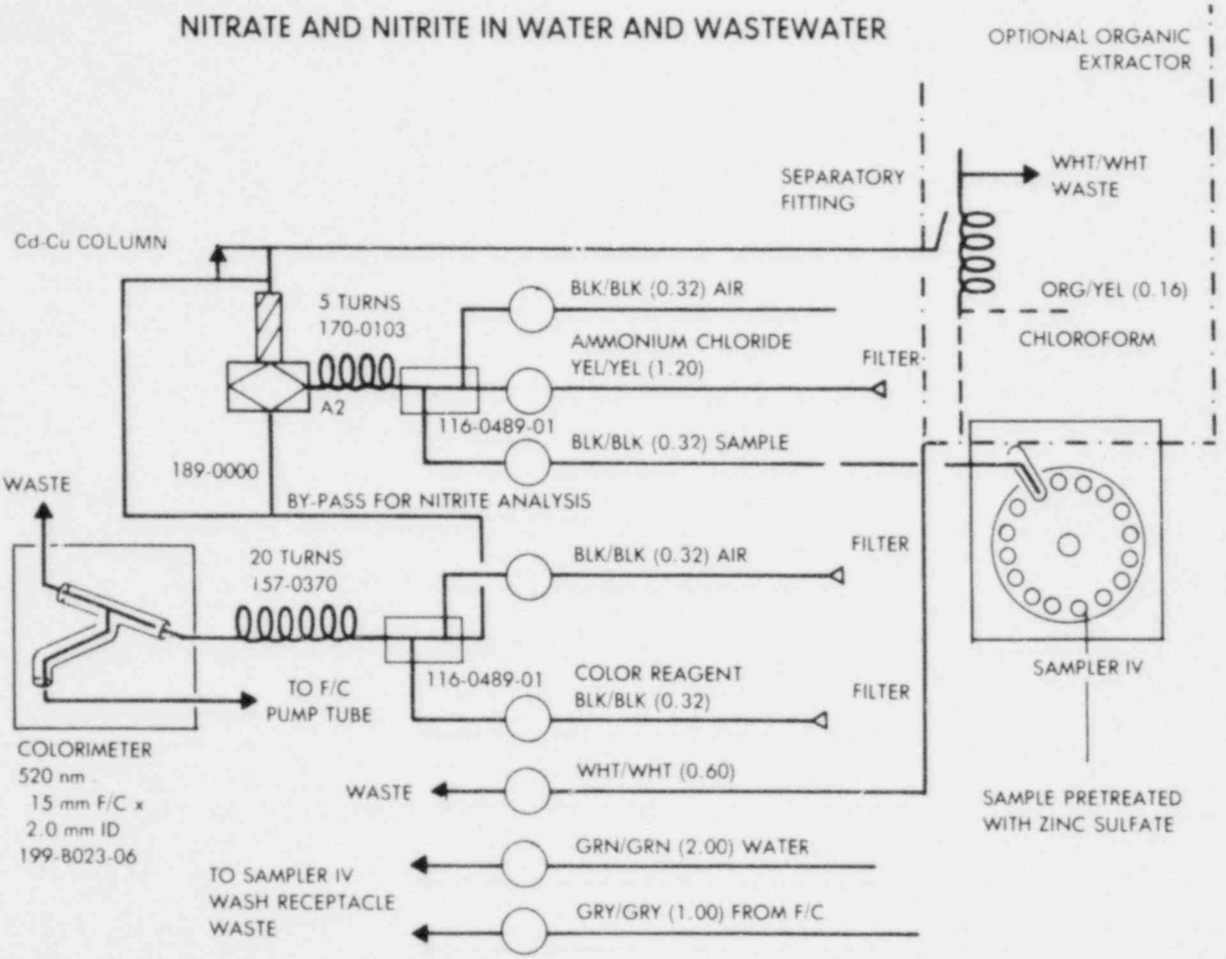
[a] Available in public technical libraries.

NITRATE AND NITRITE IN WATER AND WASTEWATER



NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN.
*0.034 POLYETHYLENE

Manifold Adapted From
Technicon Auto Analyzer
Manifold No. 116-D049-01

PHOSPHATE

1. Application

This method is applicable to dissolved ortho-phosphate in the range 0.2-10 mg/L in water.

2. Summary of Method

The determination of ortho-phosphate depends on the formation of a molybdophosphoric acid which is reduced to a molybdenum blue complex by reaction with ascorbic acid.

3. Interferences

An excess of dissolved silica interferes, but the magnitude of this interference can be estimated by analyzing for dissolved SiO_2 and PO_4 simultaneously. Interference from nitrite or sulfide ions can be minimized by adding an excess of saturated potassium permanganate solution.

Interference from sample color, turbidity, etc., is determined by running sample color blanks; that is, repeating the analysis using 0.1 N H_2SO_4 rather than the ammonium molybdate reagent.

Iron above 50 mg/L can cause an erroneously positive value.

4. Apparatus

Technicon auto analyzer equipped with manifold No. 116-D186-01.

5. Reagents

ASCROBIC ACID REAGENT

Ascorbic Acid, U.S.P. ($C_6H_8O_6$)	17.6	g
Acetone (CH_3COCH_3)	50	mL
Distilled Water	1000	mL
Levor IV (technicon No. T21-0332)	0.5	mL

Preparation: Dissolve 17.6 g of U.S.P. quality ascorbic acid in approximately 600 mL of distilled water containing 50 mL of acetone. Mix and dilute to 1 liter with distilled water. Add 0.5 mL of Levor IV per liter of reagent.

AMMONIUM MOLYBDATE REAGENT

Ammonium Molybdate $(NH_4)_6\ Mo_7\ O_{24} \cdot 4H_2O$	10	g
Sulfuric Acid 2.2N	1000	mL

Preparation: Dissolve 10 g of ammonium molybdate in 1 liter of 2.2N sulfuric acid (62 mL of concentrated sulfuric acid, sp.gr. 1.84). Filter and store in an amber bottle. Discard if discolored.

STANDARD

STOCK STANDARD, 100 mg/L PO_4

Anhydrous Potassium Dihydrogen Phosphate (Kh_2PO_4)	0.143	g
Concentrated Sulfuric Acid	1	mL
Distilled Water	1000	mL

Preparation: Dissolve the anhydrous potassium dihydrogen phosphate in approximately 600 mL of distilled water. Add 1 mL of sulfuric acid and dilute to 1 liter with distilled water.

6. Procedure

All glassware should be well rinsed and care exercised in the use of detergents which frequently contain phosphates. If a manifold employing Brij-35 was used prior to phosphate analysis, it is recommended that the flow cell of the colorimeter be flushed with a solution of 5 mL of Levor IV/liter of water.

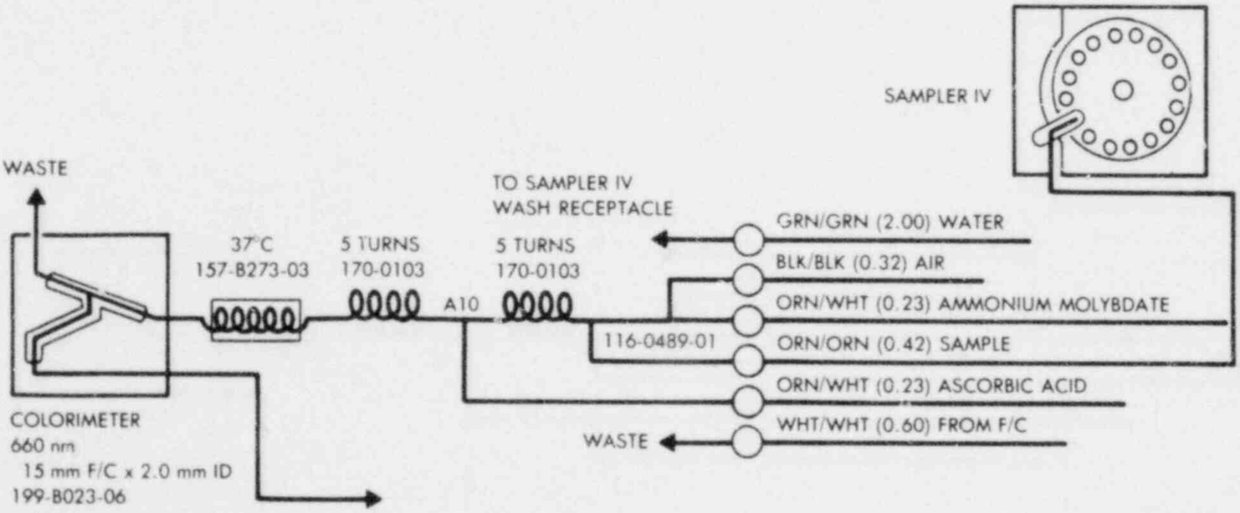
7. Calculations

The concentration of samples is read by comparing with a standard curve. Subtract any sample color value determined.

8. References

1. ASTM "water", 1978 Annual Book of ASTM Standards, part 31, R.P. Lukens, Ed. (American Society for Testing and Materials, Pa. 1978). Available from the ASTM, 1916 Race Street, Philadelphia, Pa. 19103.

ORTHO PHOSPHATE IN WATER AND WASTEWATER



NOTE: FIGURES IN PARENTHESES
SIGNIFY FLOW RATES
IN ML/MIN.

SILICATE

1. Application

This method is applicable to the determination of monomeric reactive silica in the 0.2-10 mg/L range.

2. Summary of Method

Ammonium molybdate reacts with dissolved silica in acid medium to form a silcomolybdate complex. This is reduced to molybdenum blue by ascorbic acid.

3. Interferences

Phosphate also reacts with ammonium molybdate to form molybdophosphoric acid. This complex is destroyed with oxalic acid. Tannin, large amounts of iron color, turbidity and sulfide interfere. Sulfide may be removed by boiling the acidified sample prior to analysis. Turbidity and color are corrected for by running sample color blanks; that is, repeating the analysis using 0.1 N H_2SO_4 rather than the ammonium molybdate reagent. Tannin interference is controlled by the addition of oxalic acid. The method of standard additions is suggested for dealing with iron interferences.

4. Apparatus

Technicon auto analyzer equipped with manifold #116-0056-01.

5. Reagents

AMMONIUM MOLYBDATE REAGENT (Technicon No. T01-5050)

Ammonium Molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	10	g
Sulfuric Acid, 0.1 N	1000	mL

Preparation: Dissolve 10 g of ammonium molybdate in 1 liter of 0.1 N sulfuric acid (2.8 ml concentrated sulfuric acid, sp. gr. - 1.84/L). Filter and store in an amber plastic container.

OXALIC ACID

Oxalic Acid ($H_2C_2O_4$) (Technicon No. T11-5051)	50	g
Distilled Water	1000	mL

Preparation: Dissolve 50 g of oxalic acid in 900 mL of distilled water and dilute to 1 liter.

ASCORBIC ACID REAGENT

Ascorbic Acid, U.S.P. ($C_6H_8O_6$) (Technicon No. T11-5070)	17.6	g
Acetone (CH_3COCH_3) (Technicon No. T21-5071)	50	mL

Distilled Water, q.s.	1000 mL
Levor IV (Technicon No. T21-0332)	0.5 mL

Preparation: Dissolve 17.6 g of U.S.P. quality ascorbic acid in 500 mL of distilled water containing 50 mL of acetone. Mix and dilute to 1 liter with distilled water. Add 0.5 mL of Levor IV per liter of reagent.

STANDARDS

STOCK STANDARD, 100 mg/L SiO_2

Sodium Metasilicate Nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) (Technicon No. T13-5080)	0.473 g
Distilled Water	1000 mL

Preparation: Dissolve 0.473 g of sodium metasilicate nonahydrate in 1 liter of recently boiled and cooled distilled water. Store this stock solution in a tightly stoppered plastic bottle.

6. Procedure

The use of glassware should be avoided. A dilution of sample is usually necessary. This is accomplished in line by adding an injection of polished water after the sampler and decreasing the size of the sampler tubing. An orange-green sampler tube and gray water tube have been most satisfactory. Standards are then made to be 10 times more concentrated.

The method of standard additions may be used by spiking successive sample cups containing the same volume with increasing amounts of a concentrated standard. However, we have found the off-line preparation of samples for standard addition to be more accurate.

7. Calculations

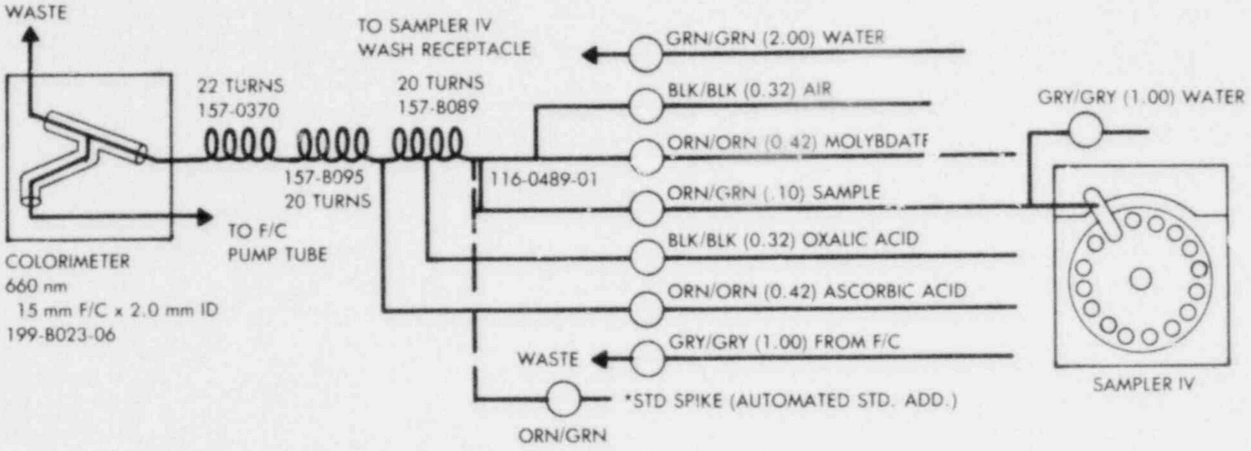
The concentration of samples is initially determined by comparing with a standard curve. Subtract any sample color value contribution determined.

The concentration of sample as determined by standard addition is calculated by extrapolation thru the origin and that value multipled by any dilution factors.

8. References

1. APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Waste Water, 13th edition, 303-306 (1971). Available in public technical libraries.

SILICATES IN WATER AND WASTEWATER



*For automated std addition, the sample is run using
(1) H_2O
(2) a std soln equal to the initial concentration of the sample
(3) a std soln equal to 2 × the initial conc. of the sample.

NOTE: FIGURES IN PARENTHESES
SIGNIFY FLOW RATES IN
ML/MIN.

Manifold Adapted From
Technicon Auto Analyzer
Manifold No. 116-D056-01

SULFATE

1. Application

This automated method is applicable to filtered waters in the range of 10 to 300 mg SO_4/L. Approximately fifteen samples per hour can be analyzed.

2. Summary of Method

Sulfate is reacted with barium chloride at a pH of 2.5-3.0 to form barium sulfate. Excess barium then reacts with methylthymol blue to form a blue-colored chelate at a pH of 12.5-13.0. Initially the reagents are prepared to be equimolar in barium chloride and methylthymol blue, thus the amount of uncomplexed grey methylthymol blue, measured at 460 nm, is equal to the sulfate present.

3. Interferences

Cations such as calcium, aluminum and iron interfere by complexing the methylthymol blue. These ions are removed by passage through an ion-exchange column of Dowex-50W-X8. In most instances, a length of resin-filled .018-ID-tubing may be put in line. For samples of unusual ionic concentration pretreatment utilizing a standard ion exchange column is recommended.

As $BaSO_4$ is appreciably more soluble in acids than water, precipitations of $BaSO_4$ should be made from solutions that are only slightly acidic. It is therefore advisable to adjust the pH of samples prior to analysis. In samples displaying unusual buffering action, an off-line pH check of the sample/reagent combination is necessary to assure a pH of 2.5-3.0. An in line addition of a citrate buffer is suggested in those instances where voluminous quantities of samples display a wide variation in pH. The buffer addition is accomplished by means of an injection fitting prior to the mixing coil on the commercially available manifold.

4. Apparatus

Technicon auto analyzer equipped with MTB manifold No. 116-D096-01 and 460 nm filters. Additional p/p pump tubing or .018-I.D.-glass tubing and injection fitting No. 116-0489-01.

5. Reagents

STANDARD STOCK SOLUTION

Preparation: Dissolve 1.47 g of sodium sulfate in water, dilute to 1 liter.

BARIUM CHLORIDE SOLUTION

Barium Chloride Dihydrate ($BaCl_2 \cdot 2H_2O$)	1.526	g
Reagent Grade Water	1000	mL

Preparation: Dissolve 1.526 g of barium chloride dihydrate in approximately 600 mL of water. Dilute to 1000 mL. Store in a brown polyethylene bottle.

METHYLTHYMOL BLUE REAGENT

Methylthymol Blue	0.1182	g
Barium Chloride Solution	25	mL
Hydrochloric Acid (1.0 N HCl)	4	mL
Reagent Grade Water	71	mL
Ethanol	500	mL

Preparation: Dissolve 0.1182 g of methylthymol blue in 25 mL of barium chloride solution. Add 4 mL of 1.0 N HCl. Add 71 mL of water and dilute to 500 mL with ethanol. Check pH of solution to be 2.6. Store in an amber glass bottle and prepare fresh daily.

BUFFER pH 10.5 ± 0.5

NH_4Cl	6.75	g
NH_4OH Concentrated (28M)	57	mL
Reagent Water	1000	mL

Preparation: Dissolve 6.75 g of NH_4Cl in 500 mL of water. Add 57 of concentrated NH_4OH and dilute to 1 liter with water. Store in a brown polyethylene bottle.

BUFFERED EDTA

Tetrasodium EDTA	40	g
Buffer pH 10.5	1000	mL

Preparation: Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer and q.s. to 1 liter with buffer.

SODIUM HYDROXIDE 0.18 N

Sodium Hydroxide	7.2	g
Reagent Water	1000	mL

Preparation: Dissolve 72 g of sodium hydroxide in 800 mL distilled water. Allow to cool and dilute to volume with water.

Ion Exchange Column

The in-line column consists of "purple/purple AAI" pump tubing (2.0-mm-I.D.) or a length of glass tubing 3.6-mm-I.D. no larger than 2.0-mm-I.D. (available from Gamma, Mt. Vernon, N.Y. 10550). The Bio-Rex 70 resin is freed from fines by backflushing. A large quantity may be processed by backflushing a 17-mm by 315-mm column or burette. The ends of the purple/purple tube are plugged with glass wool, care should be taken that air is not trapped within the column and that excess glass wool does not cause back pressure.

6. Procedure

A series of standards corresponding to the anticipated concentration range of the samples are analyzed. Technicon advises that the range of analysis for this manifold is 10-300 mg/L. However, because this chemistry does not conform to Beer's law and produces several predictable slope changes; it is found to be more practical to analyze in concentration ranges of 1-50, 20-150, 100-300. These ranges roughly correspond to the linear portions of the absorbance/concentration curve. The observed changes in slope are commonly attributed to precipitation phenomenon. At all times the sample is "bracketed" by standards, i.e., a standard with a concentration above and below that of the sample analyzed on the same sampler tray. Water blanks of the diluent water are also run routinely

Ideally, the standards would be prepared in the same chemical matrix as the samples. However, due to the complexity of the samples received, duplicating the chemical composition is impossible. It is desirable to dilute the sample and analyze at a lower concentration range whenever possible. Then the matrix of the sample closely approximates that of the water used in the preparation of the standards.

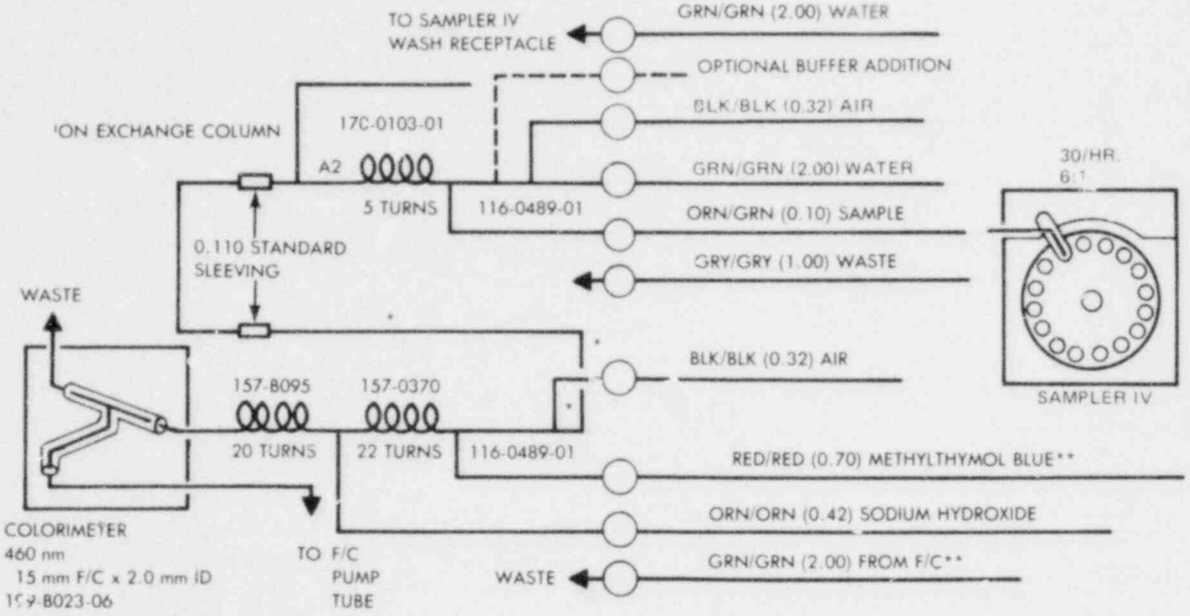
Dilution alone is not sufficient to remove suspected interferences. This is particularly true if the sample contains appreciable colloidial material or substances which pass thru a filter but interfere with the hydraulics of the manifold and flow cell. The method of additions is then recommended; determinations are verified by adding a known amount of standard to aliquots of the sample and all aliquots diluted to the same final volume. Additions of standard are made to be approximately the same concentrations as that anticipated for the diluted sample solutions.

In samples that are intensely turbid or in some manner contribute to the gray color of the uncomplexed methylthymol blue, the color value of the samples must be determined. All reagents and standards are prepared as described except no MTB is added to the MTB reagent. The pH of the solutions individually and combined is adjusted to be consistent with the methodology. The absorbance reading subsequently obtained approximates the absorbance value contributed to the system by the individual sample.

8. References

1. M.E. Gales, W.H. Kaylor, Jr., and J.E. Longbottom, "Determination of Sulfate by Automatic Colorimetric Analysis", Analyst, 93, 97 (1968). Available in public technical libraries.

SULFATE IN WATER AND WASTEWATER



NOTE: FIGURES IN PARENTHESES
SIGNIFY FLOW RATES IN
ML/MIN.

*0.034 POLYETHYLENE
**SILICONE RUBBER

Manifold Adapted From
Technicon Auto Analyzer
Manifold No. 116-D096-01

METALS

(Atomic Absorption, Flame Emission Methods)

General discussion as applicable in our studies:

1. Application

These methods are applicable to cation analysis on homogeneous liquid samples.

2. Summary of Method

Atomic absorption spectrometry and flame emission are closely related analytical techniques for the quantitative determination at the part per million range or less. In both methods, a homogeneous liquid sample is aspirated into a chemical flame, where thermal and chemical reactions cause the sample to break into free atoms. These free atoms can then be observed to emit or absorb light of a specific wavelength, characteristic of the element being determined.

Flame photometry measures the amount of light emitted, whereas in atomic absorption a light beam is directed through the flame into a monochromator and onto a detector. The atoms in the flame absorb the light and re-emit it equally in all directions, hence the monochromator measures only a percentage of the original light source, those photons not scattered in the flame.

A major difference between flame emission and atomic absorption is the comparative analytical sensitivities for elements whose excited states lie about and below 3500 A. If the principle spectral line of an element is below 3500 A, then flame emission is the method of choice; above 3500 A atomic absorption provides more sensitivity.

Copper is particularly useful in that its principle absorption is 3247 A, hence it is only slightly more sensitive by absorption than by emission. This dual sensitivity makes copper standards applicable in both modes, thus providing a convenient cross-reference.

3. Interferences

Chemical interferences occur when a chemical compound is formed between the element of interest and some other material present in the sample. If the compound formed is refractory and resists atomization, the free atom concentration in the flame is lowered. Most multivalent cations and multivalent anions such as sulfate, silicate, phosphate, etc., exhibit chemical interferences. A releasing agent such as lanthanum is added as standard practice for the analysis of any Group II element and sometimes for the transition metals. Generally, chemical interferences are not significant with Group I elements, but ionization of the species depopulates both the state and excited state causing reduction in both the emission and scatter signals. To suppress this ionization effect, a surplus of a readily ionized element is added to both samples and standards.

By using the higher temperature nitrous oxide flame as the oxidant, some elements which form refractory oxides can be atomized more readily. However, the increased temperature can cause excessive ionization, necessitating the use of an ionization suppressant if the element of interest has a low ionization potential.

4. Apparatus

Perkin-Elmer atomic absorption spectrophotometer equipped with vent containing an absolute filter (Figure C.1).

A Platinum-rhodium nebulizer is recommended. Earlier analysis utilizing a corrosion resistant (Kel-F) nebulizer indicated that preferential adhesion occurred on the nebulizer surface.

5. Reagents

Standards: All standards are obtained as prepared concentrates or from a precisely weighed primary standard dissolved in an appropriate acid or base. The acid or base employed for dissolution should contain only monovalent cations and anions. In most cases the standard stock containing 1000 mg/L is adjusted with acid to a pH between 1 and 2.

Glass containers are not considered operable for the storage of standards primarily because glass surfaces are very efficient ion exchangers and will exchange polyvalent cations in the solutions for monovalent cations present in the glass. In addition, elements subject to hydrolysis will plate out. Wide capped bottles made of linear polyethylene are the containers of choice.

Standards below 1 mg/L must be prepared fresh daily. All standards should be kept in the bottle in which samples of the same concentration of the same element have been stored.

Occasionally a polyethylene bottle is blow molded in air that was too hot and some oxidation occurred at the inner surface resulting in the formation of hydroxyl or acetate groups on the surface of the plastic. These act as ion exchangers and cause an initial loss of material from a standard. Thus re-use of the same bottles for the same concentration of species conditions the container.

6. Procedure

Ideally the standards would be prepared in the same chemical and physical matrix as the samples, then any interferences that may occur in the sample will be compensated for in the standards. One commonly used method of insuring similarity of matrix is the method of Standard Additions. In this procedure known amounts of standard are added to aliquots of the sample and all samples diluted to the same final volume. The signals from the samples are plotted vs concentration of standard added, (at least three points must be linear) and the line is extrapolated beyond the origin. The concentration of the diluted sample is read at the intersection with the axis.

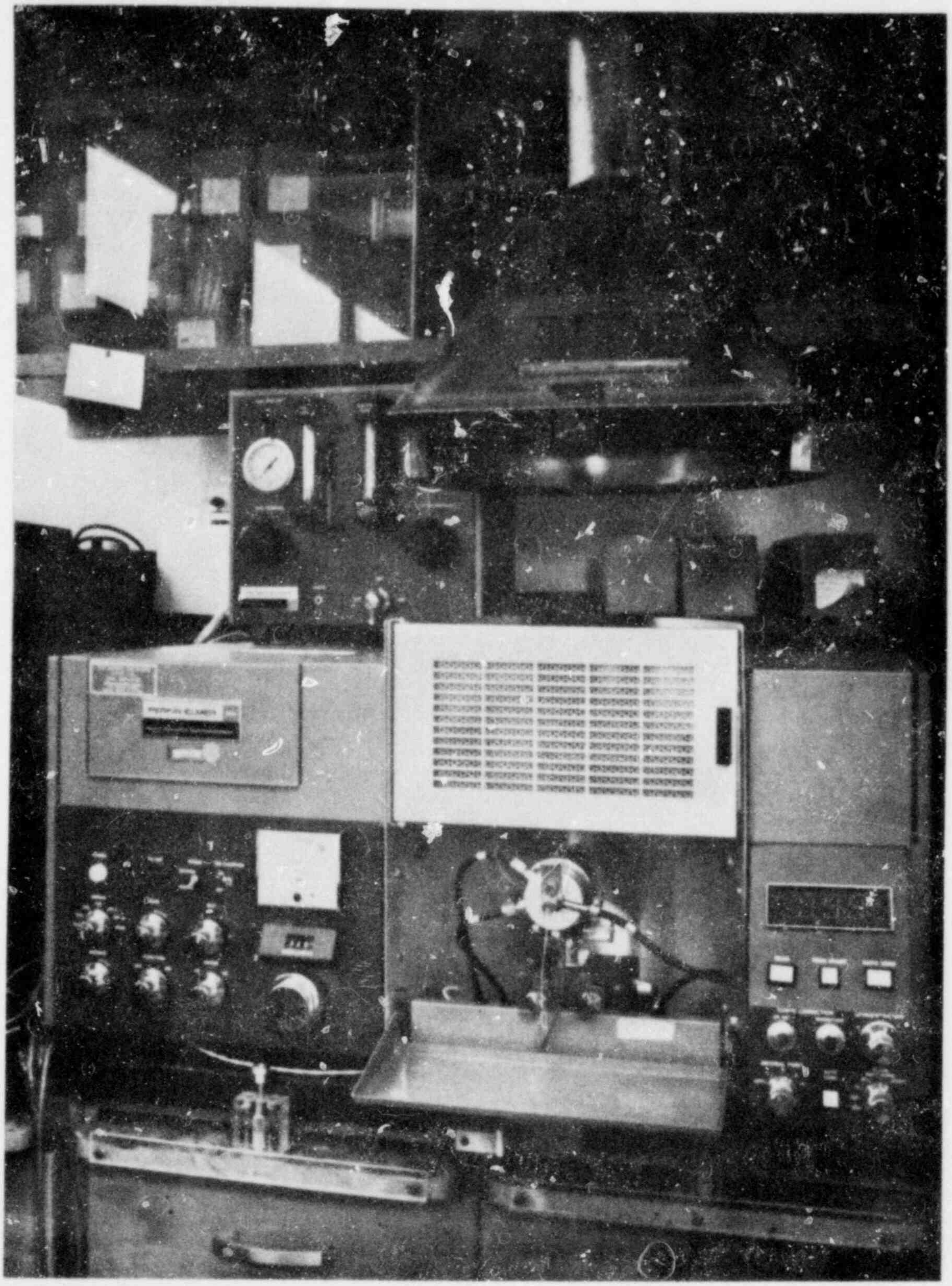


Figure C.1. Atomic absorbtion apparatus vented to hood and absolute filter.

Secondary standardization is another technique, useful for a larger number of similar samples. One sample is analyzed by the method of standard additions and then those solutions are used as standards for the remainder of the analysis, thus the standards are closely matched in physical and chemical properties.

7. Calculations

Waste water samples which frequently contain high solids, high acid concentrations, organic solvents or matrices which may cause light scatter or molecular absorption will require the use of background correction. This is determined by obtaining a reading at a nearby non-absorbing wavelength, or by installing a deuterum arc background corrector.

Sensitivity is defined as that concentration of an element that will produce a 1% absorption.

Detection limit is that concentration of standard that will produce a signal that is twice the mean variation in the baseline measurement.

8. References

1. H.L. Kahn, "Principles and Practice of Atomic Absorption - Trace Inorganics in Water", Advances in Chemistry Series Number 73, American Chemical Society, 1968. Available from the American Chemical Society, Washington, D.C.

2. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Conn., 1973.[a]

3. M.J. Fisman, "The Use of Atomic Absorption for Analysis of Natural Waters," Atomic Absorption Newsletter, Vol. 5, No. 5, September-October, 1966.[a]

4. R.A. Isaac and J.D. Kerber, "Atomic Absorption and Flame Photometry: Techniques and Uses in Soil, Plant and Water Analysis", Instrumental Methods for Analysis of Soils and Plant Tissue, SSSA, Wisconsin 1971. Available from SSSA, 677 South Segoe Road, Madison, Wisc. 53711.

5. E.E. Pickett and S.R. Kovityohann, "Emission Flame Photometry - A New Look at an Old Method", Analytical Chemistry 41, No. 14, 28-42 (December 1969).[b]

7. P.W. West, P. Folse, and D. Montgomery, "Application of Flame Spectrophotometry to Water Analysis, Determinatin of Sodium, Potassium and Calcium", Anal. Chem. 22, 667 (1950).[b]

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[a] Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.
[b] Available from public technical libraries.

CALCIUM

1. Application

Under standard conditions, the working range for calcium is linear up to 7 mg/L in aqueous solution.

2. Summary of Method

Atomic absorption, utilizing a hollow cathode lamp at 422.7 nm-visible in an acetylene/nitrous oxide flame.

The most sensitive emission wavelength is 422.7 nm. However, there is a definite emission interference in the nitrous oxide/acetylene flame at calcium concentrations greater than 4.0 mg/L.

3. Interferences

The air-acetylene flame is more stable at high calcium concentrations, but has more chemical interferences and lower sensitivity. The addition of $LaCl_3$ is suggested to suppress these interferences.

Generally the dilution of the sample to a concentration of approximately two mg/L and the use of nitrous oxide/acetylene is the method of choice. The addition of an alkali salt is necessary to suppress ionization.

Welders acetylene which contains acetone depresses the calcium absorption. We have found Matheson lab grade acetylene satisfactory as a fuel.

Most organic matrices cause a molecular absorption in the flame. This may be eliminated by using a strongly oxidizing flame at optimum adjustment.

4. Apparatus

High quality two stage regulators.

5. Reagents

CALCIUM STOCK STANDARD	1000 mg/L

Preparation: Markson Catalog #U 5114 or dissolve 2.4973 g calcium carbonite, $CaCO_3$, with dropwise addition in a minimum volume of HCl and dilute to 1 liter with water.

POTASSIUM SOLUTION	1500 mg/L

Preparation: Dissolve 3.787 g of KNO_3 in water and dilute to 1 liter.

6. Procedure

Since the absorption of Ca is dependent on the fuel to air ratio and height of the light beam the following adjustments should be made:

(1) High quality two stage regulators should be used on the gas line.

(2) Purified acetylene should be used.

(3) The flame should be ignited and water aspirated at least 15 min before analysis.

(4) Maximum hollow cathode current should be used to overcome the flame emission of calcium in nitrous oxide/acetylene flame.

(5) The flame is further optimized while aspirating a 4 mg/L standard until maximum sensitivity is reached (about 40% absorption). In making this adjustment the potassium blank solution is frequently re-zeroed so the absorption readings represent the difference between the blank and 4 mg/L calcium. Water is aspirated between standard and blank adjustments to clear the nebulizer and maintain thermal equilibrium of the burner head.

(6) Rotation of the burner head is not recommended since calcium is very emissive at high concentrations.

(7) The nebulizer uptake is adjusted to a reduced level. This is accomplished by aspirating a solution and turning the knurled end cap of the nebulizer counter clockwise until air bubbles back into the solution. Then the end cap is turned clockwise and the locking ring turned until it rests against the nebulizer end cap. Readings of standards and samples are taken by utilizing the longest instrument intergration available and averaging at least three reported values.

Although the working range for calcium is linear up to 7 mg/L it is desirable to dilute all samples to a final concentration between 1-2 mg/L.

The method of additions utilizing incremental 1 mg/L increases is desirable. (The method of additions is described in Metals, Section No. 6.)

In this analysis it is important to match the pH of samples and standards. An initial 1 to 100 dilution of sample utilizing the potassium solution is recommended, but in some instances this is insufficient to adjust the pH to that of the standard matrix. It is then necessary to alter the pH of the standards using 0.1 N HCl or 0.1 N NaOH.

7. Calculations

Blank correction is always necessary. Standard additions is the method of choice.

The sensitivity for calcium is 0.08 mg/L for absorption. The lower limit of detection is 0.02 mg/L units.

Concentration may be read directly or calculated from a plot of absorbance vs standard concentrations.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.

2. P.W. West, P. Folse, and D. Montgomery, "Application of Flame Spectrophotometry to Water Analysis, Determination of Sodium, Potassium and Calcium", Anal. Chem. 22 667 (1950). Available in public technical libraries.

CESIUM

1. Application

This method is applicable to homogenous solutions up to 15 mg/L.

2. Summary of Method

Atomic absorption utilizing an arc discharge lamp at 852.2 nm-visible, a slit setting of 4.0 nm and an air-acetylene flame.

The most sensitive emission wavelength is 852.2 nm using an air/acetylene flame.

3. Interferences

Cesium has a lower ionization potential than any other metal so alkali salts must be added. Solutions containing 1500 mg/L sodium ion are preferable. Potassium salts, while effective ionizers, tend to produce high blank values.

4. Apparatus

A second order red filter is necessary.

A continium lamp or background correction using the 848.0 nm line is utilized for emission analysis.

5. Reagents

CESIUM STOCK STANDARD 1000 mg/L

Preparation: Markson Catalog #J 5115 or dissolve 1.267 g of cesium chloride, CsCl, in 1 liter of purified water.

SODIUM SOLUTION 1500 mg/L

Preparation: Dissolve 5.6 g of $NaNO_3$ in 1 liter of water. Store in plastic.

6. Procedure

Emission analysis was the method of choice in our laboratory. The absorption method uses a discharge lamp and considerable self-reversal occurs with this source. Occasionally metal will condense on the portion of the lamp that is in the optical beam thus causing the light to be obstructed. If this occurs, it is suggested to run the lamp for 10 minutes at a higher current (1.1 amps).

7. Calculations

Background corrections are necessary with emission.

Blank corrections for the alkali addition are necessary.

Concentrations are determined from a concentration of standards vs absorbance plot.

For the conditions described the sensitivity is 0.3 mg/L for 1% absorption.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.
2. E.E. Pickett and S.R. Kovityohann, "Emission Flame Photometry - A New Look at an Old Method", Analytical Chemistry 41, No. 14, 28-42 (December 1969). Available in public technical libraries.

IRON

1. Application

Ideally this method is used on anoxically filtered samples which were immediately acidified after filtration to a pH of 2.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at a 248.3 nm uv line with a lean air/acetylene flame.

The most sensitive emission wavelength for iron is 372.0 nm using a nitrous/oxide flame.

3. Interferences

A reduction in sensitivity occurs when samples containing nickel are acidified with nitric acid.

Multi-element lamps containing cobalt demonstrate interference with the 248.3 nm line; the 372 nm uv line is recommended.

4. Apparatus

A continium lamp, or background correction using the 247.5 nm non-absorbing Fe line, is usually necessary for low Fe concentrations in the high solids matrices.

An oxidizing flame is optimum.

Best precision and accuracy is obtained if the burner is pre-ignited and the samples aspirated in such a manner as to maintain thermal stability at the burner slot.

5. Reagents

IRON STOCK STANDARD 1000 mg/L

Preparation: Markson Catalog #J 5120 or dissolve 1.000 g of iron wire in 50 mL of conc HNO_3 and dilute to 1 liter with purified water.

6. Procedure

Sampling, Storage, Re-dissolution, Aliquoting.

Iron in the ferrous state is relatively soluble in waters but upon exposure to air the iron is oxidized to the ferric state and may hydrolyze to form a hydrated ferric oxide. Also, "iron bacteria" are considered capable of withdrawing iron and depositing it in the form of hydrated ferric hydroxide in their secretions. Samples received in the laboratory may contain iron in true solution, as a colloid, as a suspension, or as a complex. Thus, withdrawing a representative aliquot and assuring a homogenous solution that will not clog the nebulizer then becomes of chief concern.

Determination of Dissolved Metals

(1) Samples collected and filtered anoxically with HNO_3 added immediately.

Dilution of samples is accomplished using an Eppendort pipette and volumetric flask. All glassware is acid washed with 1:1 HCl then rinsed with polished water.*

Concentration of Samples

Samples containing below 30 ppm Fe should be concentrated for analysis. This is accomplished by gently evaporating an HNO_3 acidified sample until

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*Polished water in our laboratory is obtained using reagent grade water and a milii-Q system.

a light colored quiscient residue remains. The initial volume reduction is done using a hot plate stirrer, but the last stage evaporation is accomplished utilizing an overhead heat lamp. The walls and sides of the beaker are then washed thoroughly with 1:1 HCl and the residue re-dissolved and quantitatively transferred to a volumetric flask.

(2) Samples not collected anoxically.

(a) Those with a pH 2 or below

In samples not collected anoxically, but sufficiently acidified for the ferric hydroxide to be in solution, a simple aliquot may be withdrawn and analyzed. However, it is anticipated that the reported value, while representative of the concentration in the sample vial, will be lower than that observed in the source well or trench.

(b) Samples with a pH above 2

Samples collected non-anoxically and sent to our laboratory unacidified frequently exhibit color, turbidity and visible precipitation. For routine comparative analysis the observed precipitate is dissolved using known amounts of acid and the standards adjusted accordingly. It is necessary in these instances to repeatedly police the sides of the container and to stir the now acidified samples for several hours until the sample appears clear. Subsequent analysis of the container even after two days of acid dissolution indicates that some iron does remain imbedded in the plastic walls, thus this method of sampling produces a somewhat lowered iron value.

In those studies where it is desirable to analyze only the supernate, the sample is stirred using a teflon stir bar. An aliquot is withdrawn via a disposable syringe and then filtered just prior to analysis or dilution using a Millipore "millex" disposable filter unit.

(3) Determinations of suspended Fe.

The 0.45 µm membrane filter is digested using HNO_3. The sample is then evaporated gently and additional HNO_3 added until the residue is clear. The residue is then dissolved in 3 mL 1:1 HCl and diluted to a known volume usually 10 mL with polished water. Appropriate dilutions are then made for analysis and the standards prepared in a similar HCl matrix.

7. Calculations

As discussed, sampling can lower the amount of Fe available for analysis. For the conditions described the sensitivity is 0.12 mg/L Fe for 1% absorption.

The method of standard additions as described in Metals, Section No. 6, is suggested.

Concentrations may also be determined directly.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.

LITHIUM

1. Application

For the described standard conditions the working range for Li is linear up to concentration of approximately 2 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 670.8 nm visible line with an oxidizing air/acetylene flame.

The most sensitive emission wavelength is 670.8 nm with a nitrous oxide/acetylene flame.

3. Interferences

Like its sister elements in Group 1, Li is partially ionized in an air/acetylene flame. This is controlled by the addition of 1500 mg/L alkali.

4. Apparatus

A red second order interference filter is necessary to mask out the neon line emitted at the secondary 335.4 nm wavelength.

5. Reagents

LITHIUM STOCK STANDARD	1000 mg/L

Preparation: Markson Catalog #J 5122 or dissolve 5.324 g of lithium carbonate, Li_2CO_3, in a minimum volume of 1:1 HCl and dilute to 1 liter with water.

SODIUM STOCK SOLUTION	150 g/L

Preparation: Dissolve 554.3 g of $NaNO_3$ in 1 liter of water, use 100 microliters for each 10 milliliter of sample aliquot.

6. Procedure

Because of the low Li concentrations usually found in waste waters, little dilution of the sample is necessary. The alkali spike is added in microliter amounts to adjust the total alkali concentration to 1500 mg/L.

Only high purity sodium salts should be used for the spike and a blank sodium ion solution value substracted from the absorbance or concentration reading.

Background correction is not normally necessary for the determination of lithium but blank correction for lithium contamination in reagents is an important consideration.

7. Calculations

The sensitivity for Li under the conditions described is 0.035 mg/L Li for 1% absorption. The lower limit of detection under ideal conditions is 0.001 mg/L.

Concentration values are usually read directly from the instrument display.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.

MAGNESIUM

1. Application

Under standard conditions the working range for Mg is linear up to concentrations of approximately 0.5 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 285.2 nm - uv, [illegible] slit setting of 0.7 nm and an oxidizing acetylene/nitrous oxide flame.

The most sensitive emission wavelength is 285.2 nm with a nitrous oxide/acetylene flame.

3. Interferences

Silcon and aluminum depress magnesium absorption in an air/acetylene flame, but 1% lanthanum may remove this interference. Studies comparing lanthanum spiked samples in air/acetylene and non-spiked samples in the recommended N_2O/acetylene indicates that the N_2O/acetylene flame is hot enough to remove these interferences.

4. Apparatus

The analytical range may be extended by rotation of the burner head.

5. Reagent

Magnesium STOCK STANDARD 1000 mg/L

Preparation: Markson Catalog #J 5123 or dissolve 1.854 g of Ultrex Magnesium Gluconate Dehydrate and dilute to 100 mL.

6. Procedure

The recommended dilution for trench water samples is one to five hundred. This is usually sufficient to remove any matrix effects and facilitates direct reading of sample concentrations bracketed by standards.

7. Calculations

Background correction is not normally necessary for Mg and concentration values can be determined directly from the instrument display.

The sensitivity for Mg is about 0.007 mg/L Mg for 1% absorption. The lower limit of detection is 0.005 mg/L.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.

MANGANESE

1. Application

Ideally this method is used on anoxically filtered samples which are acidified or analyzed immediately. Under standard conditions, the working range for manganese is linear up to 3 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 279.5 nm-UV, a slit width of 0.2 nm and an oxidizing air/acetylene flame.

The most sensitive emission wavelength is at 403.1 nm, but a nitrous oxide/acetylene flame is necessary.

3. Interferences

There appears to be little chemical or spectral interference in this method. The low concentration of manganese present in waste water does not permit dilution so consequent clogging of the burner head and nebulizer with accumulated salts is frequently a problem. It is therefore necessary to constantly aspirate purified water and check the zero reading.

4. Apparatus

A continuum lamp or background correction using the 282.5 nm non-absorbing line is usually necessary in these complex, high solid matrices.

An oxidizing flame is optimum.

5. Reagents

MANGANESE STOCK STANDARD	1000 mg/L

Preparation: Markson Catalog #J 5148 or dissolve 1.000 g of Mn metal in a minimum volume of 8M HNO_3 and dilute to 1 liter with 1% v/v HCl.

POTASSIUM SOLUTION	1500 mg/L

Preparation: Dissolve 3.787 g of KNO_3 in water and dilute to 1 liter.

6. Procedure

Sampling, Storage, Redissolution, Concentrating, Extracting, and Aliquoting.

Manganese collected anoxically is generally present in the soluble divalent ionic form. When exposed to air it steadily oxidizes and precipitates from solution or becomes adsorbed on the walls of the container.

Determination of Dissolved Metals

Anoxic filtration and immediate acidification are most desirable. In those samples exposed to air without prior acidification, attempts at recovering the Mn from the container walls by acid digestion and ultra sonic cleaning have met with only limted success.

Concentration

EPA recommends that all samples below 25 mg/L be concentrated. This is consistent with the operational lower limit of detection experienced in our laboratory. Manganese may be concentrated by extraction at a pH 5-10 with APDC/MIBK. However, the presence of unusual organics and/or chealating agents in these trench waters occasionally results in an emulsion like interface between the aqueous and organic layers. Aspiration of this third interface layer with the Mn-MIBK layer results in definite matrix problems. Discarding the interface results in lowered Mn concentration values. Continuous back extraction yields an increased volume negating attempts at concentration.

Concentration by evaporation is then the method of preference. Gently evaporate 50 mL of an HNO_3 acidified sample on a Corning hot plate stirrer. The simultaneous use of an overhead heat lamp speeds the evaporation and hinders bumping. The residue is then dissolved in ∿ two mL of 1:1 HCl and quantitatively transferred to a 10 mL-volumetric flask. The sample is now concentrated five times.

On occasion, the salt content is too high for the residue to be dissolved in 10 mL and a 25 mL volumetric is used, the sample is then concentrated two times.

Filtrating just prior to aspirating using a 0.45 µm membrane filter is frequently necessary in concentrated samples.

Alkali Spiking of Sample

It is recommended that all Mn analysis be done in a 1500 mg/L alkali salt solution to suppress ionization. However, studies done in our laboratory have indicated no difference in concentration value obtained between potassium spiked and unspiked samples. On occasion, attempts to add a potassium spike to a concentrated sample have resulted in the formation of salts indicating a super saturated solution. The sample and salts must then be re-dissolved and diluted to a higher volume.

7. Calculations

As discussed, sampling can lower the amount of manganese available for analysis. For the conditions described the sensitivity is 0.055 mg/L Mn for 1% absorption.

Concentration may be read directly from the instrument display.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.

2. W.B. Barnett, "Acid interferences in Atomic Absorption Spectrometry", Analytical Chemistry 44, 695-698 (April 1972). Available in public technical libraries.

POTASSIUM

1. Application

For atomic absorption operating parameters, the working range for potassium is linear up to concentrations of approximately 2 mg/L in filtered aqueous solution. Potassium is seventh in order of abundance and appears to exist in greater than trace amounts in the samples received in our laboratory. The recommended dilution is one to fifty. The optimum range 0.5 - 1.0 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 766.5 nm-visible line with a lean air/acetylene flame.

The most sensitive emission wavelength for potassium is 766.5 nm, although a much better signal to noise ratio is reported at the secondary line of 404.4 nm using an air/hydrogen flame.

3. Interferences

The red filter which absorbs radiation shorter than 650 nm should be used for this determination.

The effects of ionization may be substantially overcome by the use of diluent water containing 1500 mg Na/L.

4. Apparatus

A second order filter is necessary for this determination.

5. Reagents

POTASSIUM STOCK STANDARD	1000 mg/L

Preparation: Markson Catalog #J 5128 or dissolve 1.907 g of potassium chloride (KCl) in 1 liter of water.

SODIUM SOLUTION	1500 mg/L

Preparation: Dissolve 5.6 g of $NaNO_3$ in 1 liter of water. Store in plastic.

All dilutions of standards are to be made to contain 1500 mg/L sodium.

6. Procedure

Dilution of samples are made one to fifty using the sodium spiked water.

A standard curve is obtained in the 0.05 to 1.0 mg/L range.

Because of the large salt concentration care should be taken to flush the nebulizer assembly, scrape the burner head and ream the nebulizer tube between each analysis. Frequent replacement of the nebulizer tube is necessary and there is a tendency for it to develop internal grooves and ridges. A platinum nebulizer is suggested as it is capable of withstanding the chemical and mechanical abuse incurred in this analysis. Periodic microscopic examination of the nebulizer is necessary to insure its integrity.

7. Calculations

A blank correction of the sodium solution is necessary.

Report and Precision

The sensitivity for the described conditions to 0.04 mg/L K for 1% absorption. The detection limit is 0.005 mg/L.

Concentration values are most frequently determined from a concentration vs absorbance plot.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.

2. P.W. West, P. Folse, and D. Montgomery, "Application of Flame Spectrophotometry to Water Analysis, Determination of Sodium, Potassium and Calcium", Anal. Chem. 22, 667 (1950). Available in public technical libraries.

SODIUM

1. Application

Under standard conditions the working range for sodium is linear up to concentrations of approximately 1 mg/L. As sodium is the sixth most abundant element and is commonly present in waste waters in appreciable quantities, dilution is usually necessary.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 589.0 nm visible line with an oxidizing flame. Because of the concentrated nature of the samples an initial thousand-fold dilution is recommended. In addition the analytical range may be extended by rotation of the burner head. To overcome the effects of ionization, 1500 mg K/L as KNO_3 is added to standards and samples.

The most sensitive emission wavelength for sodium is at 589.0 nm, the 330.2 nm line is less sensitive; (3 mg/L sodium for 1% absorption) and provides a convenient way to avoid further dilutions. An air/acetylene flame is suggested. There is usually good agreement between absorption and emission data using the described methods.

3. Interferences

Because of the large dilution necessary for analysis we have observed little interference in our laboratory. Comparisons between direct reading and standard addition values indicate there is negligible matrix effect. For the determination of low concentrations and all dilutions care should be taken that the standards and samples are not stored in glass.

4. Apparatus

A second order filter is necessary for flame emission determinations of sodium.

5. Reagents

SODIUM STOCK STANDARD 1000 mg/L

Preparation: Markson Catalog #J 5131 or dissolve 2.5421 g of Sodium Chloride, (NaCl), in 1 liter of water.

POTASSIUM SOLUTION 1500 mg/L

Preparation: Dissolve 3.787 g of KNO_3 in water and dilute to 1 liter.

6. Procedure

Dilution of samples are made 1 to 1000 using a 1500 mg/L potassium solution.

A standard curve is obtained in the .05 to 1.0 mg/L range, all standards being made from dilutions of a stock standard with 1500 mg/L potassium spiked water.

7. Calculations

Background correction does not appear necessary at the 589.0 nm wavelength and concentration values can be read directly from the machine display.

The sensitivity is about 0.015 mg/L for Na for 1% absorption.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.

2. P.W. West, P. Folse, and D. Montgomery, "Application of Flame Spectrophotometry to Water Analysis, Determination of Sodium, Potassium and Calcium", Anal. Chem. 22, 667 (1950). Available in public technical libraries.

STRONTIUM (TOTAL)

1. Application

This method is applicable to homogenous solutions up to 10 mg/L although under standard operation, the working range is linear only up to concentrations of 5 mg/L.

2. Summary of Method

Atomic absorption utilizing a hollow cathode lamp at 460.7 nm visible, a slit setting of 0.4 nm and either a reducing air/acetylene or nitrous oxide/acetylene flame.

The most sensitive emission wavelength is at 460.7 nm with a nitrous oxide/acetylene flame.

3. Interferences

Nitric acid, used to acidify samples after filtration reduces the absorption of a strontium solution. Care should be taken to have standards and samples equal in HNO_3 concentration.

Silicon, aluminum, and phosphorous depress the absorption in the air/acetylene flame. 1% lanthanum solution is suggested to control this interference. The use of a nitrous oxide/acetylene flame is another method. To control ionization, potassium is preferred as a spike because it has the highest ionization potential of the available alkali salts.

Analysts have reported varying levels of success with the aforementioned methods. Some manufacturers insist on the addition of 1% lanthanum, others prefer N_2O/acetylene flame, alkali spiked. To date in our laboratory, the use of N_2O/acetylene flame with potassium spiked standards and samples has been the method of choice. It affords a ready cross check of absorption and emission methods and has presented the least nebulizer problems.

4. Apparatus

The analytical ranges may be extended by rotation of the burner head.

5. Reagents

STRONTIUM STOCK STANDARD 1000 mg/L

Preparation: Markson Catalog #J 5132 or dissolve 2.415 g of strontium nitrate, $Sr(NO_3)_2$ in 1 liter of 1% v/v HNO_3.

POTASSIUM SOLUTION 1500 mg/L

Preparation: Dissolve 3.787 g of KNO_3 in 1 liter of water.

6. Procedure

The method of standard additions is preferred. The initial concentration range is determined by direct reading of a potassium spike sample using N_2O/acetylene flame. Dilutions if necessary are made to obtain a final concentration of approximately 1 mg/L Sr. A second aliquot of the sample is then combined with standards to yield a final concentration of unknown plus 1 mg/L Sr. A third aliquot is then taken to yield a final concentration of unknown plus 2 mg/L Sr. All samples contain 1500 mg/L of potassium.

Sr may be extracted with 0.2 molar thenoyltrifluoroacetone and MIBK at pH 10-12, but this has met with little success in our laboratory.

7. Calculations

The method of additions as described in Metals, Section No. 6.

For the conditions described the sensitivity for a HNO_3 acidified standard is 0.12 mg/L Sr for 1% absorption. The sensitivity as observed in trench waters is usually lower.

8. References

1. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry Perkin-Elmer, Connecticut, 1973. Available from Perkin-Elmer, Main Avenue, Norwalk, Conn. 06856.

2. V.J. Luciano, "Atomic Absorption", Pittsburgh Conference, 1975. Available for purchase from Fisher Scientific, Analytical Instrument Division Pittsburgh, Pa.

APPENDIX D

ORGANIC ANALYSIS

(A.J. Francis, B. Nine, C.R. Iden*, and C. Chang*)

D.1 Procedure

Water samples collected anoxically from trenches and wells at low-level radioactive waste disposal sites were filtered through a 0.45 µm silver membrane filter under anoxic conditions and refrigerated until further analysis.

The total carbon and inorganic carbon content of the filtered water samples were determined using a Beckman Model 915 Total Carbon Analyzer.(1) The difference between the total carbon and the inorganic carbon measurements is the dissolved organic carbon (DOC) content of the water samples.

A liquid extraction technique,(2) used to isolate acidic, neutral, and basic organic components from the trench water samples is shown schematically in Figure D.1. Approximately two hundred to three hundred milliliters of filtered water sample was acidified to pH 2 with HCl and extracted three times with 30 mL methylene chloride (Burdick & Jackson Laboratories, Inc., Muskegon, MI). The extracts were combined and back-extracted three times with 30 mL-5% w/v NaOH, to remove acidic components, leaving only neutral compounds in the first organic extract. The basic fractions were combined, acidified to pH 2, and extracted with methylene chloride as before. This second organic extract contains acidic compounds. The original water sample was then brought to pH 11 with 5% w/v NaOH and extracted three times with 30 mL of methylene chloride. The third extract contains basic organic components. Each extract was dried over Na_2SO_4 and concentrated to 1 mL using Kuderna-Danish and Micro-Snyder column evaporators. The extract containing the acid components was divided in half. One portion was reacted with N,O-bis-(trimethylsilyl)-trifluoroacetamide (Pierce Chemical Co., Rockford, IL) for approximately one hour at room temperature in order to form the trimethylsilyl (TMS) derivatives.

The extracts and derivatized extracts of water samples and control blank samples were analyzed by gas-liquid chromatograph (GLC) using a Perkin Elmer Model 900 Gas Chromatograph. A 1.8-m x 2.1-mm-i.d. stainless steel column packed with 10% SE-30 on Chromosorb-W (80/100 mesh) was used for all analyses. Helium was used for the carrier gas at a flow rate of 35 mL/min. The column temperature initially was held constant at 60°C for 4 min and then programmed to 240°C at 4°C/min. The upper temperature was maintained until the analysis was terminated. The GLC instrument was equipped with a flame ionization detector. For quantitative analysis a known quantity of an internal standard, usually diethyl phthalate, was added to the sample. The ratio of the area of the GLC-peak of interest to the area of the internal standard peak was converted to a concentration with a calibrated standard curve specific for the compound undergoing analysis.

The water extracts were further analyzed by gas chromatography-mass spectrometry (GC/MS). A Hewlett Packard 5983 Mass Spectrometer system coupled to a

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*SUNY at Stony Brook, N.Y. 11794

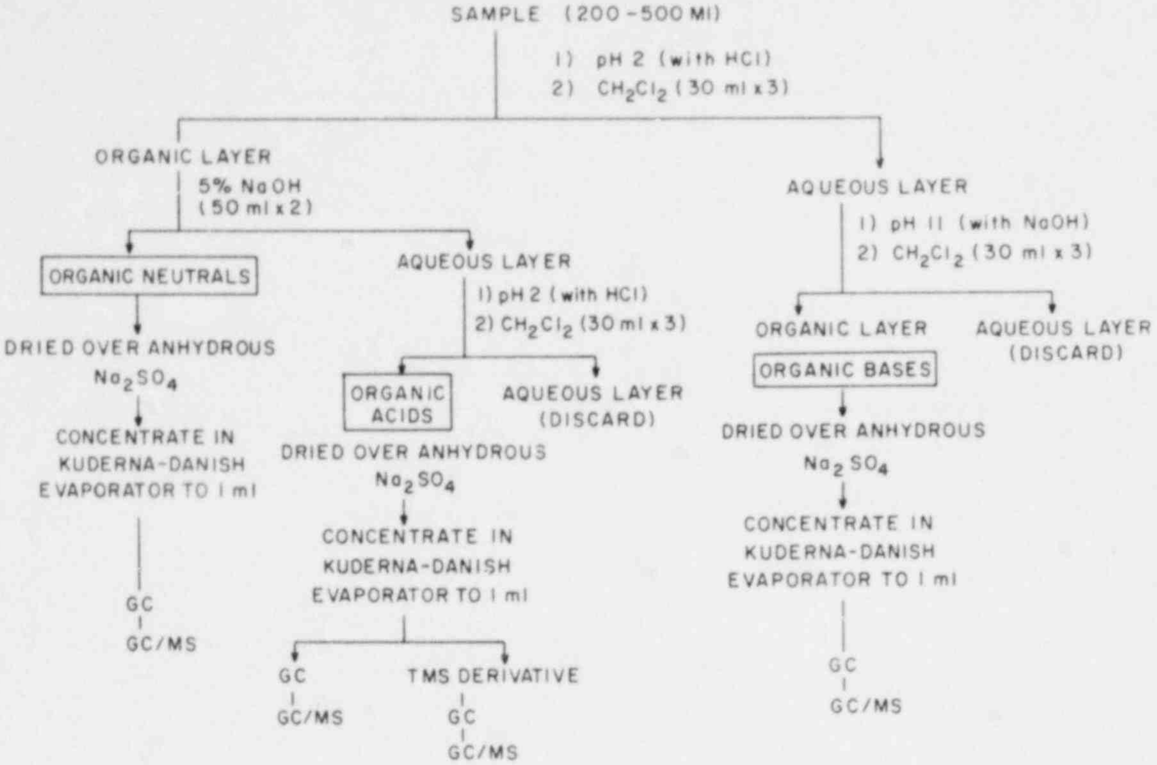

Figure D.1. Extraction and fractionation scheme for organic analysis of trench water samples.

Hewlett Packard 5700 Gas Chromatograph and a 5933 Data System was used. The gas chromatograph and mass spectrometer are interfaced by a heated glass jet separator. Gas chromatographic conditions were the same as listed above, except that a 2-mm-i.d. glass column was used. Mass spectral identification was facilitated by use of the mass spectral search capabilities of the 5933 Data System. For this purpose, both the HP Contributed Libraries and the EPA-NIH Library were available on disc. Furthermore, the mass spectral search facilities of the CIS Project were accessible through a separate terminal. In some cases, known standards were purchased commercially and run on the GC/MS instrument in order to verify identifications. It should be noted that not all organic compounds can be extracted by methylene chloride, and that many other organic compounds may be present in the leachates.

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APPENDIX E

ANALYTICAL METHODS FOR SEDIMENT CHARACTERIZATION

Representative samples of the site specific materials used in the sorption experiments were used for characterization studies. Bulk samples were disaggregated by ultrasonic agitation. Analytical methods are summarized in the accompanying table.

Table E.1

Sediment Characterization - Analytical Procedures

Parameter	Procedure	Modifications
Particle Size Distribution	Sieving & Pipette Analysis(1)	
Surface Area	Organic Liquid	
	Ethylene Glycol (EG)(2)	No Sample Pre-Treatment
	Ethylene Glycol Monoethyl Ether (EGME)(3)	
	Gas	
	N_2 Adsorption (BET)(4)	Freeze Dried Samples of Consolidated Materials used after Initial Disaggregation
Mineralogy	Standard Techniques of X-ray and Petrographic Analysis	
Extractable Iron	Dithionite Extraction(5)	
Organic Carbon	Oxidation with Dichromatic (Walkley-Black method)(6)	
Carbonate Material	Gravimetrically by Loss of CO_2(7)	Ultrasonic Disaggregation of Consolidated Material
Cation Exchange Capacity		
Total Cation Exch. Cap.	Na Displacement pH 8.2(8)	Standard Technique for CEC_T
pH dependent cation Exchange Capacity (ΔpH)	Na Displacement pH 4.5(9)	Na^+ Used as Index Cation Rather than Ba^{+2}
Sr Cation Exch. Cap.	Same Procedure as Total Cation Exch.	Uses Sr as Displacing Ion Rather than NH_4^+
Cs Cation Exch. Cap.	(10)	To be Completed

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[a] Available from public technical information libraries.

APPENDIX F

PREPARATION PROCEDURE FOR THE DETERMINATION OF K_D SORPTION COEFFICIENTS

(R.F. Pietrzak, G.G. Galdi, and A.J. Weiss)

F.1. Summary

Samples for the determination of K_d were prepared from waste burial site trench waters (15 mL) and soils (0.75 g) in reaction containers of glass and Teflon. Gamma emitting radionuclides of ^{241}Am, ^{85}Sr, ^{134}Cs, ^{137}Cs, ^{59}Fe, ^{60}Co and ^{152}Eu were added to filtered trench water before mixing with the soil. Control samples without any soil were reserved to determine the initial activity of a solution for any isotope. The sorption coefficient K_d was calculated using the following equation

$K_d = A_s/A_\ell$

$A_s = (A_r - A_i)/W_s$ = radionuclide concentration in soil

$A_\ell = A_i/V_\ell$ = radionuclide concentration in solution

A_r = activity of the original solution

A_i = sample solution activity

W_s = solid weight

V_ℓ = liquid volume

Special precautions to preserve reducing conditions were taken only with samples that are described as "anoxic". This was accomplished by use of a nitrogen or argon atmosphere during preparation and equilibration of the samples.

F.2. Materials

F.2.1 Mixed Tracer Solution

A carrier-free solution containing approximately one mCi/mL each of commercially obtained ^{85}Sr, ^{134,137}Cs, and ^{60}Co in 0.5 M HCl was used to spike the filtered trench water. A 0.02-mL aliquot of tracer solution was used with 100 mL of trench water.

F.2.2 ^{241}Am Tracer Solution

A carrier-free solution containing approximately one mCi/mL of commercially obtained ^{241}Am in 8 M HNO_3. A 0.02-mL aliquot of tracer solution was used with 100 mL of trench water.

F.2.3 ^{152}Eu Tracer Solution

A commercially obtained solution of ^{152}Eu, approximately one mCi/mL, in 0.5 M HCl which contains 0.19 mg Eu/mL. A 0.02 mL aliquot of tracer solution was used with 100 mL of trench water.

F.3. Equipment

F.3.1 Filtration System

Trench water samples were filtered anoxically. A schematic diagram of the filtration system is shown in Figure F.1, and a breakdown of the filter unit is shown in Figure F.2. Trench water was transferred from the collection bottle to the filter unit through 3/8"-i.d. Tygon tubing, and filtered through a 142-mm-diameter, 0.1-μm-cellulose membrane. All filter body surfaces that come in contact with the trench water were coated with Teflon.

F.3.2 Sample Preparation Manifold

The primary function of the sample preparation manifold was to prepare the filtered trench water for the K_d experiment and to transfer measured amounts of the water to reaction vessels containing soil. A schematic diagram of the manifold is shown in Figure F.3. The valve operations to perform various manifold manipulations are indicated in the diagram. Three types of valves on the manifold were used to route the trench water: (a) two-position/double function valves (PCV, RVV), (b) two-position/triple function valves (SV, FV, SIV), and (c) a six-position/single function valve (DV). All tubing and valve surfaces of the sample preparation manifold shown in Figure F.4 are Teflon. The total system is shown in Figure F.5.

The manipulations required to prepare a sample for a K_d measurement are described in Tables F.1 and F.2. Table F.1 gives sequential operations for replacing air with nitrogen in various sections of the apparatus, and Table F.2 shows the positions of controls on the manifold for manipulating the filtered trench water. These manipulations include: (a) diverting water to the probe chamber shown in Figure F.6 where pH, Eh, and temperature are measured, (b) filling the mixing reservoirs where pH adjustments, dilutions, and tracer radionuclide additions are made, and (c) transferring 14.6 mL of water from a mixing reservoir to a reaction vessel containing 0.75 g of soil.

F.3.3 Reaction Vessels

F.3.3.1 Glass Tubes

Commercially available 20-mL glass tubes (Bellco 2047-16125) that were sealed with screw cap septa (Figure F.7) were used in some K_d experiments. Approximately 2% of the original radioactivity in the solution was adsorbed onto the container wall, and in approximately 10% of the experiments the tubes failed to maintain an anoxic condition. Failure to maintain an anoxic condition is easily seen by the presence of a red $Fe(OH)_3$ precipitate. The systematic error due to glass wall adsorption needs to be evaluated.

F.3.3.2 Teflon Containers

Teflon containers were machined from TFE Teflon rod and crimp-sealed with aluminum cap and septa (Figure F.8). These bottles were found to adsorb less than 0.1% of the radioactivity and are ideally suited for K_d experiments, especially where the K_d is large and little of the initial activity remains in solution. The failure rate for maintaining anoxic conditions was high.

F.3.3.3 Septum and O-ring Sealed Teflon Bottles

An attempt to resolve the problem of maintaining trench waters in an anoxic condition was made by constructing Teflon bottles with both septum and o-ring seals (Figure F.9) and working in an inert atmosphere glove box. The single seal Teflon bottles could be used in K_d experiments where anoxic conditions were not required and where the problem of wall adsorption was to be avoided.

F.3.4 Sample Mixing Tumbler

The samples were mixed by tumbling the reaction vessels on a ball-mill roller. A plastic chamber designed to maintain an inert atmosphere around the sample bottles during the equilibration process is shown in Figure F.10. Inert gas was passed through the chamber to insure an anoxic environment in the reaction vessel in the event of an improper seal in the reaction vessel. When anoxic conditions were not required, mixing was effected by packing the reaction vessels in an appropriate container and tumbling on a ball-mill roller.

F.3.5 Counting Shield

After equilibration, the liquid phase was separated from the solid phase by centrifugation at 3,000 rpm for 20 minutes and analyzed with a Ge(Li) counting system. The reaction vessel was counted in a collimated lead shield shown in Figure F.8, where the soil in the bottom of the vessel was below the circular window facing the detector. Thus, approximately three inches of lead was between the soil and the detector, and as such, the detector saw the gamma radiation from the liquid phase with an insignificant contribution from the soil. This counting configuration eliminated opening the reaction vessel to separate the liquid from the soil and enabled repeated shaking and counting of the same sample to determine the optimum mixing time to approach equilibrium.

The small fraction of radiation from the soil that penetrates the shield becomes significant when the K_d is very large. In this case, the centrifuged samples were opened in an inert-atmosphere glove box to separate the liquid from the soil before counting. An aliquot of the filtered liquid phase was counted.

F.4. Procedure

Soil samples were added to the reaction vessels which were crimp sealed and connected to the K_d manifold. Air in the manifold, filtration unit, probe chamber, and vessels was replaced with inert gas by alternately evacuating and refilling with inert gas at least six times. This prevented iron hydroxide from precipitating during the equilibration period. The procedure is summarized in the operation sequence chart shown in Table F.1. The chart is read from left to right and from top line down. The filtration apparatus was purged with inert gas prior to purging the manifold. Filtered trench water was passed through the probe chamber where pH, Eh, and temperature were measured. The filtrate was then collected in four of the mixing reservoirs which may contain radionuclide spike, acid, base, or deionized water. Measured volumes of a modified trench water were transferred to an empty control vessel and to each of two reaction vessels containing soil. The transfer lines were then washed with water from the fifth mixing reservoir. Thus, four variations of a single trench water could be studied in one run. The manipulations to accomplish these tasks are shown in Table F.2. The reaction vessels containing soil and trench water were removed from the manifold and mixed in the tumbling apparatus for a known length of time. After centrifugation, the samples were analyzed by gamma-ray spectroscopy using a Ge(Li) detector. The lead shield used to prevent radiation from the soil from reaching the Ge(Li) detector is shown in Figure F.11. Samples were counted long enough to accumulate 10,000 counts in each gamma-ray peak, or for 1,000 minutes, whichever was reached first. After counting was completed, the final pH and Eh of the water were measured in an inert atmosphere glove box.

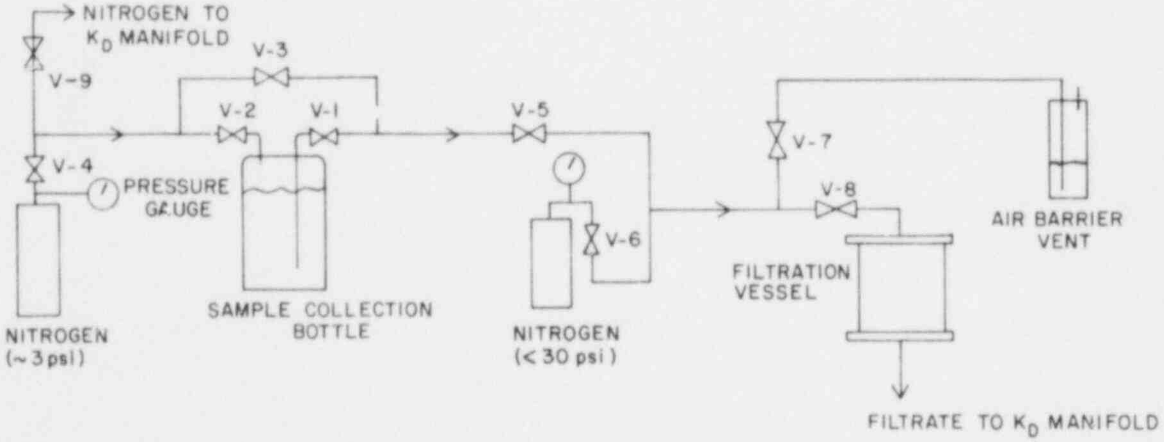

Figure F.1. Schematic diagram of the filtration system for K_d manifold.

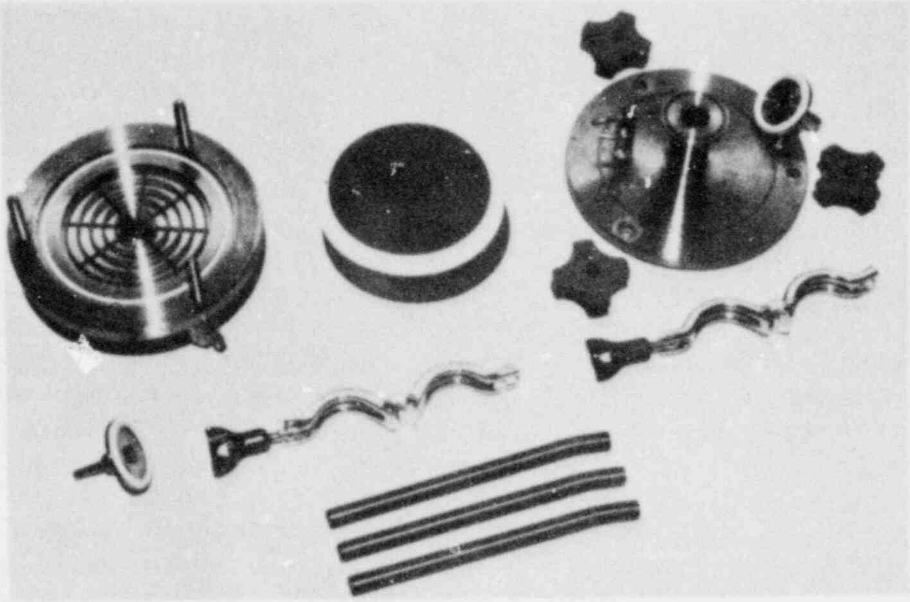

Figure F.2. Breakdown of the filtration unit used in K_d experiments.

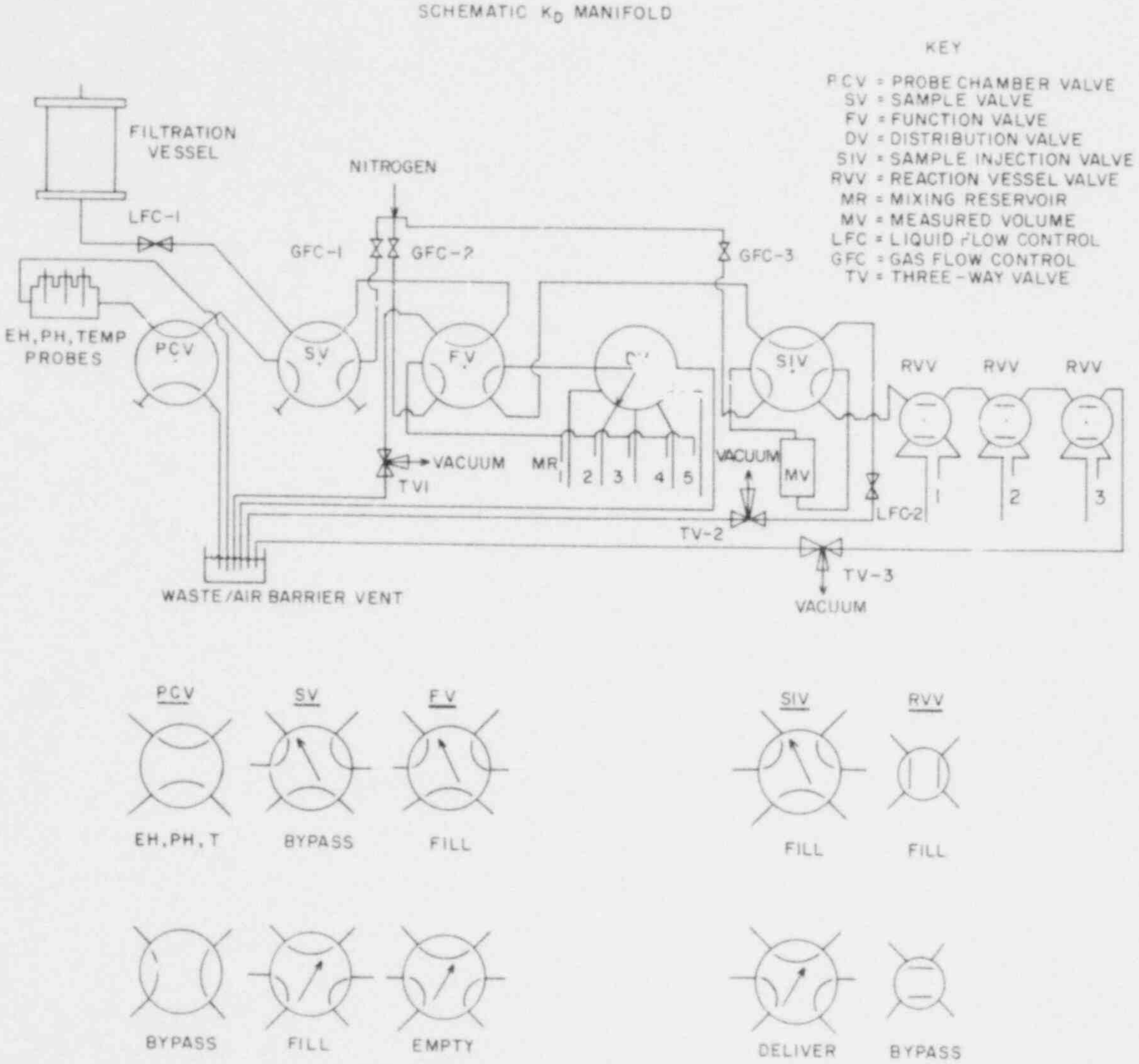

Figure F.3. Schematic diagram of the sample preparation manifold for anoxic K_d experiments.

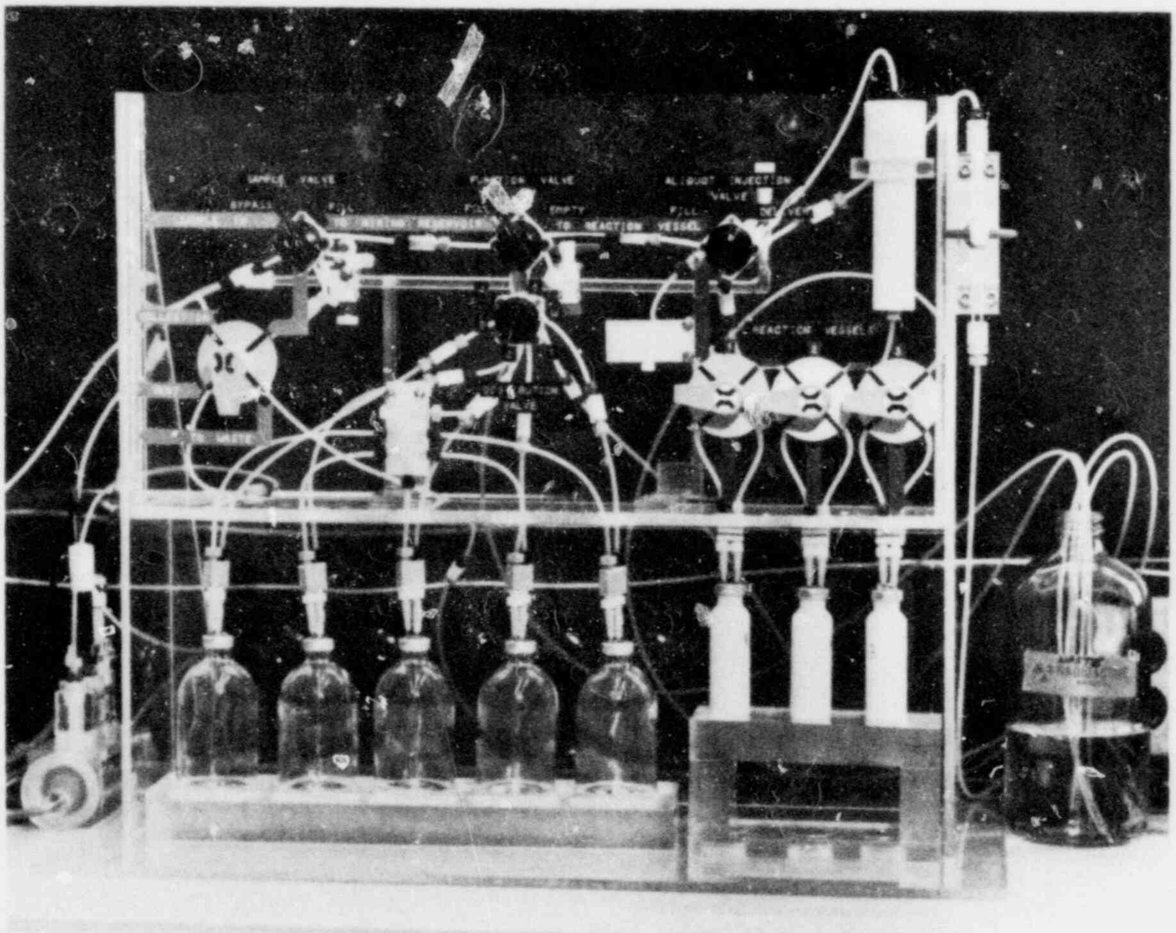

Figure F.4. Sample preparation manifold.

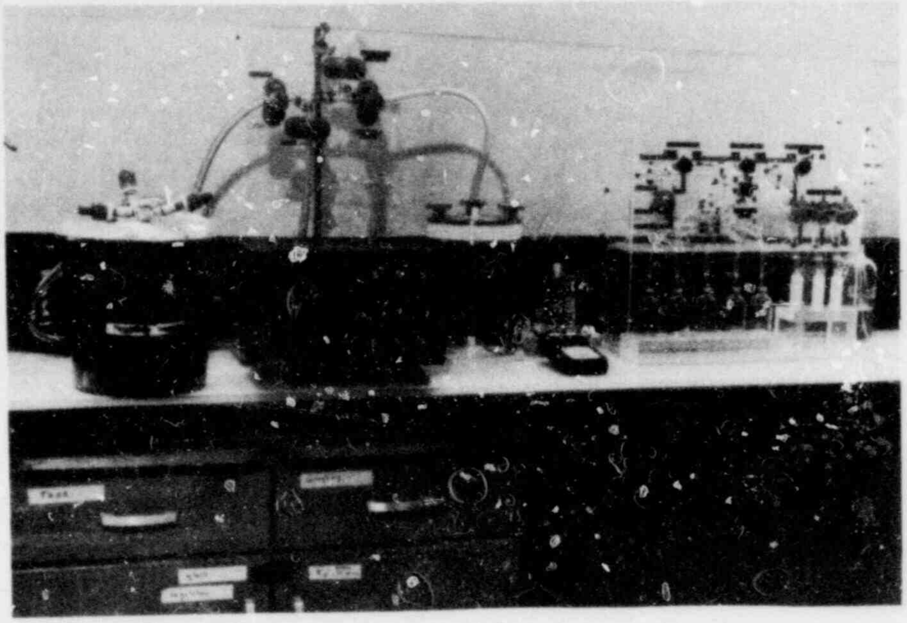

Figure F.5. Equipment for anoxic K_d experiment.

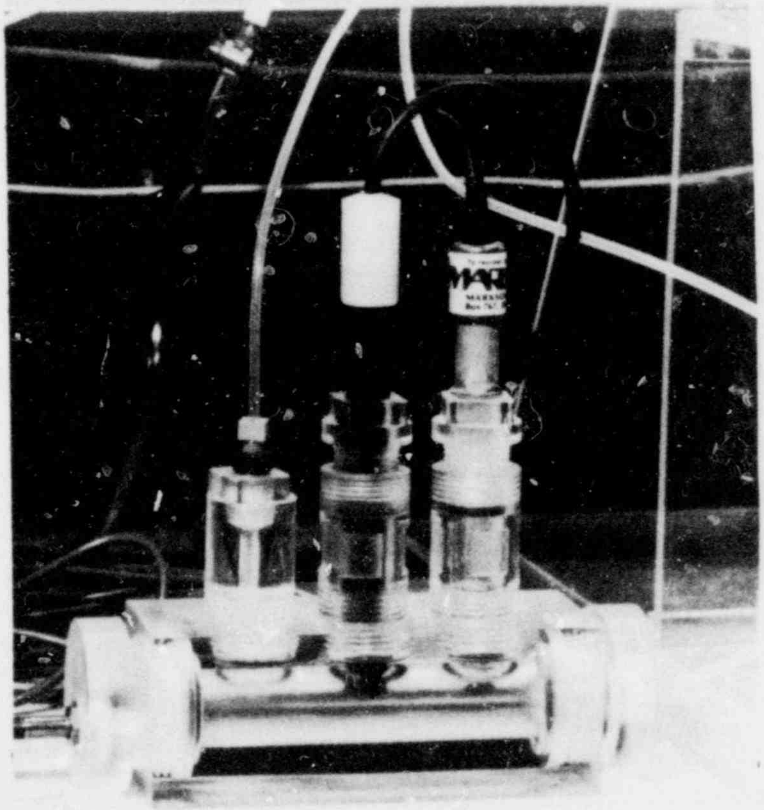

Figure F.6. Probe chamber for measuring pH, Eh, and temperature.

Table F.1

Operations Sequence to Replace Air in the K_d Manifold with Nitrogen

OBJECTIVE	OPERATIONS SEQUENCE									
A. Preliminary Purge of All Lines Including Filtration Unit, K_d Manifold, and Probe Chamber with Nitrogen	TURN VALVES THROUGH ALL OPERATING MODES									
B.1 Evacuate Reaction Vessels	GFC-1 Close	GFC-2 Close	GFC-3 Close	SV Bypass	SIV Fill	RVV-1 Fill	RVV-2 Fill	RVV-3 Fill	TV-3 W Cell VAC	Apply Vacuum
B.2 Purge Reaction Vessels with Nitrogen			GFC-3 Open First						TV-3 W← Cell VAC	N_2 Flush
C.1 Evacuate Measured Volume Chamber	GFC-1 Close	GFC-2 Close	GFC-3 Close	SV Bypass	FV Fill	SIV Fill	LFC-2 Open	TV-2 W Cell VAC		Apply Vacuum
C.2 Purge Measured Volume Chamber with Nitrogen		GFC-2 Open First						TV-2 W← Cell VAC		N_2 Flush
D.1 Evacuate Mixing Reservoirs	GFC-1 Close	GFC-2 Close	GFC-3 Close	SV Bypass	FV Fill	DV Any Cell	TV-1 Cell Waste VAC			Apply Vacuum
D.2 Purge Mixing Reservoirs with Nitrogen	GFC-1 Open First						TV-1 Cell → Waste VAC			N_2 Flush

Table F.2

Control Positions for Manipulating Trench Water in the Sample Preparation Manifold

FUNCTION	CONTROL POSITIONS										
	LFC-1	PCV	SV	GFC-1	GFC-2	FV	DV	GFC-3	SIV	LFC-2	RVV
Clear Stream	open	)(	↖ bypass	open	open		waste	open		open	≍
Measure pH, Eh, Temperature	open	≍	↗ bypass	open	open		waste	open		open	
Fill Mixing Reservoir	open	≍	↗ fill	open	open	↖ fill	cell	open		open	
Mix Sample in Reservoir	close		↖ bypass	open	open	↖ fill	cell	open	↖ fill	open	
Fill Measured Volume Vessel	close			open	open	↗ empty	cell	open	↗ deliver	open	
Transfer Measured Volume to Reaction Vessel	close							open		close	)(fill

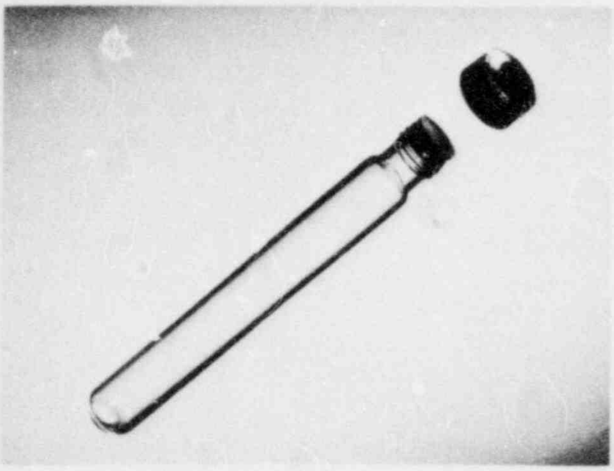

Figure F.7. Glass tube with screw cap and septum.

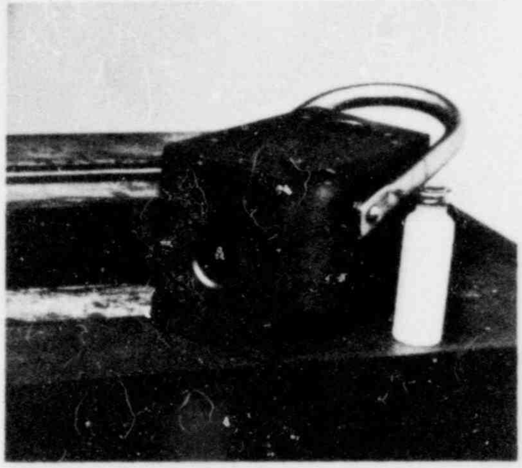

Figure F.8. Teflon bottle with aluminum capped septum along side of collimated counting shield.

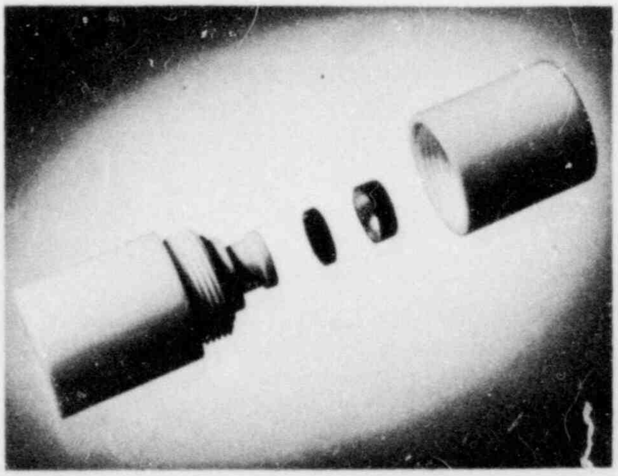

Figure F.9. Teflon bottle with septum aluminum cap and o-ring seals.

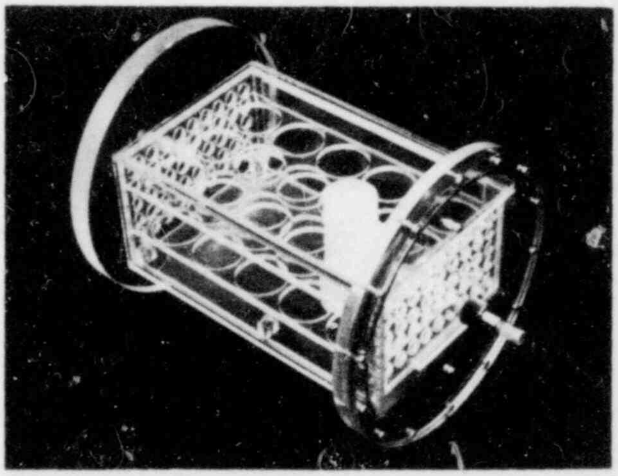

Figure F.10. Sample tumbling chamber with provision for maintaining nitrogen atmosphere.

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