

Docket No.: 50-341

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Mr. Harry Tauber
Vice President
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Dear Mr. Tauber:

Subject: Post Accident Chemical Analysis Procedures for Fermi 2

The staff is conducting a generic review of the accuracy and sensitivity of the chemical analysis procedures and on line instrumentation to be used for analysis of reactor water following an accident. (SER Supplement No. 2 Section 22.2, Item II.B.3).

The NRC staff and consultants have reviewed your letter dated December 18, 1981, pertaining to suitability of proposed post-accident chemical analysis procedures. We have determined that additional information identified in the enclosure is required to demonstrate suitability of analysis for boron, chloride, pH, oxygen and hydrogen.

Please amend your application to comply with the enclosed request for additional information. Our review schedule is based on the assumption that the additional information will be available for our review within 90 days of receipt of this letter. If you wish clarification of the request or if you cannot meet these dates, please telephone the Licensing Project Manager, L. Kintner, within 7 days after receipt of this letter.

Sincerely,

Original signed by:
B. J. Youngblood,
B. J. Youngblood, Chief
Licensing Branch No. 1
Division of Licensing

Enclosures:
Request for Additional
Information

cc w/encls.: See next page



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Request for Additional Information
and

Evaluation of Post-Accident Chemistry Procedures
by the Office of Nuclear Reactor Regulation
Enrico Fermi Atomic Power Plant, Unit No. 2
Detroit Edison
Docket No. 50-341

Consistent with our SER requirements, we have completed our generic review of the procedures which you proposed in your letter dated December 18, 1981, for post-accident analysis. We have determined that the procedure for measuring conductivity (conductivity cell) is suitable. The remaining procedures which were supplied by GE, require changes or modifications as listed below.

Boron (spectrophotometric) -

Testing is required, utilizing the enclosed standard chemical test matrix. Further testing with the induced gamma radiation is not required.

Chloride (turbidimetric) -

This procedure is inappropriate because the halide species released from a core degrading accident will interfere with the analysis. This procedure should be replaced with a more suitable method as indicated in Attachment 1.

Dissolved Oxygen (gas chromatography) -

This method is not sufficiently accurate to verify that dissolved oxygen is <0.1 ppm, but can be used during the initial stages of a core degrading accident to verify that oxygen is less than its minimum detectability. Within 30 days of a core degrading accident a direct measurement of oxygen to verify <0.1 ppm is required, consistent with ALARA. Testing with the induced gamma radiation field in the test matrix is required.

The additional procedure proposed by you to verify that oxygen is >0.1 ppm by measurement of a hydrogen residual of >10 cc/kg until ALARA considerations permit direct measurement of oxygen is acceptable.

pH (pH paper) -

This procedure is inappropriate due to radiation interferences and should be replaced if additional testing with "color fast" pH paper does not verify suitability (attachment 1).

Dissolved Hydrogen
(gas chromatography) -

Testing is required, utilizing the induced gamma radiation field in the test matrix.

Within ninety days of receipt of this evaluation provide a commitment to perform a program to change the procedures in accordance with the above listed guidance. Justification should be provided for use of any alternatives to the guidance identified herein. The commitment should include a statement that within 270 days from the date of the commitment, the results of the completed program will be provided to the staff, including a summary of suitably verified procedures. To aid in the verification of alternative procedures, guidance for acceptable range, accuracy and testing of post-accident procedures is included as Attachment 1. Additionally, a summary of the results of an independent review of the General Electric procedures which you provided are included as Attachment 2.

Post-Accident Ranges, Accuracy and
Text Matrix for Demonstrating
the Suitability of Analytical Chemistry Procedures

Introduction

The primary purposes of post-accident sampling are to estimate the degree of core degradation by monitoring for radionuclides and to monitor reactor coolant boron concentrations to confirm shutdown margin. Additionally, determinations of potentially corrosive conditions, e.g., chloride in the reactor coolant are required consistent with ALARA. Methods for the determination of radionuclides, boron (PWR's only), chloride and either total dissolved gases or hydrogen are required by NUREG-0737, II.B.3. Regulatory Guide 1.97, Rev. 2, establishes additional requirements for analyzing pH, dissolved oxygen and boron in all plants (BWR's inclusive). The required ranges and accuracy for the analyses are provided by this document, along with a standardized test matrix to demonstrate the suitability of selected procedures.

Ranges for Post-Accident Analytical Procedures

	<u>BWR</u>	<u>PWR</u>
Gross Act.	10 uCi/ml to 10 ci/ml	Same
Spectrum	Isotopic Analysis	Same
Boron	0-1000 ppm	0-6000 ppm
Chloride	0-20 ppm	Same
H ₂ or T.G.	0-2000 cc (STP)/KG	Same
Oxygen (dissolved)	0-20 ppm	Same
pH	1-13	Same

Accuracy for Post-Accident Analytical Procedures

- Gross activity, gamma spectrum: measured to estimate core damage. These analysis should be accurate within a factor of two across the entire range.
- Boron: measured to verify shutdown margin.

In general, this analysis should be accurate within + 5% of the measured value (i.e. at 6000 ppm B the tolerance is + 300 ppm while at 1,000 ppm B the tolerance is + 50 ppm). For concentrations below 1000 ppm the tolerance band should remain at + 50 ppm.

- Chloride: measured to determine coolant corrosion potential.

For concentrations between 0.5 and 20.0 ppm chloride the analysis should be accurate within + 10% of the measured value. At concentrations below 0.5 ppm the tolerance band remains at + 0.05 ppm.

- Hydrogen or Total Gas: monitored to estimate core degradation and corrosion potential of the coolant.

An accuracy of $\pm 10\%$ is desirable between 50 and 2000 cc/KG but $\pm 20\%$ can be acceptable. For concentrations below 50 cc/KG the tolerance remains at ± 5.0 cc/KG.

- Oxygen: monitored to assess coolant corrosion potential.

For concentrations between 0.5 and 20.0 ppm oxygen the analysis should be accurate within $\pm 10\%$ of the measured value. At concentrations below 0.5 ppm the tolerance band remains at ± 0.05 ppm.

- pH: measured to assess coolant corrosion potential.

Between a pH of 5 to 9 the reading should be accurate within ± 0.3 pH unit. For all other ranges ± 0.5 PH unit is acceptable.

The above-stated analytical accuracies are consistent with providing information that is pertinent to describe the radiological and chemical status of the reactor coolant system. Because the determination of corrosion potential is of secondary importance during the early phases of an accident, the initial accuracy for chloride, dissolved oxygen and pH can be less accurate, providing approximate results can be obtained for these analyses which demonstrate that a gross corrosion potential does not exist.

The requirements of NUREG-0737 - II.B.3, clarifications No. 2C and 5, to monitor chloride within 24 or 96 hours (site dependent) is intended to provide information to the operator on the potential for chloride stress corrosion cracking (CSCC) of the reactor coolant stainless steel pressure boundary during the post-accident outage period. The two primary staff concerns are:

- a. CSCC during a long outage may affect integrity of a critical system.
- b. During recovery, an assessment will be made of chloride/oxygen/pH history to determine the extent of examination required for CSCC, prior to approving a restart.

Due to the multiple potential sources of chloride (plant cooling water, makeup water, chemical additives, resin degradation, etc.) we consider it possible that chloride contamination will exist at some point during the accident, as is the case at TMI-2 where 2-6 ppm chloride exists in the reactor coolant system. Therefore, our only means of assessing its effect is to be able to monitor chloride.

The primary factors which influence CSCC are temperature, stress, time, pH, chloride and oxygen concentration. During an accident condition temperature, stress and time are dictated by the accident. Therefore, to minimize the potential for and assess the possibility of CSCC we must monitor and control chloride, oxygen and pH. The verified absence of either chloride (<0.15 ppm) or oxygen (<0.1 ppm) in the reactor coolant system will practically eliminate concern for CSCC. Additionally, if pH is ≥ 7.0 the propensity for CSCC is further reduced.

Following an accident, the staff is interested in obtaining information on the potential for CSCC at the earliest opportunity, consistent with ALARA. Ideally, the capability to monitor oxygen and chloride with on-line instrumentation would exist. The back-up capability to verify those analyses by grab sample when sufficient radioactive decay of the sample has occurred to meet ALARA should be provided.

Consistent with the above discussion, the following analytical accuracies/ techniques are considered acceptable for the measurement of chloride, dissolved oxygen and pH.

The initial chloride analysis can be performed on samples diluted up to a factor of 10^3 , provided the results are reported as \leq ppm Cl^- (the applicant should establish this value; the number in the blank should be no greater than 10.0 ppm Cl^-) in the reactor coolant. A backup, undiluted sample must be obtained and analyzed within 30 days, consistent with ALARA, to provide the final required accuracy of <0.15 ppm Cl^- .

Dissolved oxygen, the measured presence of a dissolved hydrogen residual of >10 cc/KG of reactor coolant is acceptable verification that dissolved oxygen is <0.1 ppm. Oxygen must be measured directly within 30 days of an accident, consistent with ALARA.

pH, initial pH measurements on diluted samples are acceptable, provided that they are reported with an error band and a backup undiluted sample is retained and analyzed within 30 days, consistent with ALARA.

Conductivity, initial conductivity measurements on diluted samples are acceptable, provided they are reported as estimated conductivity (based on diluted samples) and an undiluted sample is retained and analyzed, consistent with ALARA.

NOTE

The determination of conductivity is not a regulatory requirement. This discussion is included because a number of plants are electing to perform conductivity measurements.

The reactor water chemistry environment during an accident in which there is core degradation will vary significantly from normal reactor coolant chemistry. Core degradation products such as elemental iodine and cesium may be present in parts per million quantities and radioactivity can increase significantly. These core degradation products and radioactivity may interfere with the normal chemistry procedures and cause the results to be inaccurate. Therefore, to obtain accurate chemistry data the post-accident chemical analysis procedures must be shown to be applicable in the presence of interferences which can exist after a core degrading accident. The table below provides a standardized test matrix for determining the applicability of chemical analysis procedures in a post-accident water chemistry environment.

Standard Test Matrix for
Undiluted Reactor Coolant Samples in a Post-Accident Environment

<u>Constituent</u>	<u>Concentration (ppm)</u>	<u>Added as (chemical salt)</u>
I ⁻	40	Potassium Iodide
Cs ⁺	250	Cesium Nitrate
Ba ⁺²	10	Barium Nitrate
La ⁺³	5	Lanthanum Chloride
Ce ⁺⁴	5	Ammonium-Cerium Nitrate
Cl ⁻	10	
B	2000	Boric Acid
Li ⁺	2	Lithium Hydroxide
NO ₃ ⁺	150	
NH ₄ ⁺	5	
K ⁺	20	
Gamma Radiation (induced field)	10 ⁴ rad/gm of Reactor Coolant	Absorbed Dose

Notes:

1. Instrumentation and procedures which are applicable to diluted samples only should be tested with an equally diluted chemical test matrix. The induced radiation environment should be adjusted commensurate with the weight (GM's) of actual reactor coolant in the sample being tested.
2. Applicable to PWR's only - procedures which may be affected by spray additive chemicals must be tested in both the standard test matrix and the standard test matrix plus appropriate spray additives. Both procedures (with and without spray additives) are required to be available.
3. For BWR's, if procedures are verified with boron in the test matrix, they do not have to be tested without boron.
4. In lieu of conducting tests utilizing the standard test matrix procedures, provide evidence that the selected instrument or procedure has been used successfully in a similar environment.

EVALUATION OF GE AND SEC CHEMICAL PROCEDURES FOR POSTACCIDENT
ANALYSIS OF REACTOR COOLANT SAMPLES

November 1981

Prepared by

Exxon Nuclear Idaho Company, Inc.
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Idaho Falls, Idaho 83401

for

The Nuclear Regulatory Commission

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EVALUATION OF SEC AND GE ANALYTICAL CHEMICAL PROCEDURES
FOR POSTACCIDENT ANALYSIS OF REACTOR COOLANT SAMPLES

1.0 SUMMARY AND CONCLUSIONS

Summary

As a result of the Three Mile Island Unit 2 incident, the Nuclear Regulatory Commission (NRC) required licensees of nuclear power plants to implement, by January 1, 1982, the capability to collect and analyze reactor coolant samples following an accident. A number of licensees have proposed the use of postaccident sampling and analysis systems supplied by Sentry Equipment Corporation (SEC) or General Electric Company (GE).

Under a technical assistance contract to the NRC, Exxon Nuclear Idaho Company, Inc. (ENICO) evaluated the sample collection and chemical analysis procedures associated with the two systems. The objective of the evaluation was to determine applicable procedures and to identify the most appropriate method. The study involved a review of the NRC requirements, the establishment of review criteria, and the evaluation of the proposed analysis methods and test data against the requirements and evaluation criteria.

The most appropriate methods selected by ENICO for the required chemical analysis of postaccident reactor coolant samples are shown below. Detailed descriptions, advantages, disadvantages, and/or deficiencies of the selected procedures are summarized in section 4.2. Also in section 4.2 is the same information for other procedures proposed by SEC and GE. It is worthy of note that a number of the other procedures proposed are also appropriate, as indicated; included below are only those deemed most appropriate.

1. Boron - Fluoroborate Selective Ion Electrode
2. Chloride - Ion Chromatography
3. Dissolved Hydrogen - Gas Chromatography
4. Dissolved Oxygen - Oxygen Probe
5. Conductivity - Conductivity Cell
6. pH - pH Probe

Although ENICO did not conduct tests to evaluate the suitability of any of the procedures; in ENICO's judgement, the laboratory tests performed by SEC and GE are sufficient to provide a high degree of assurance of the suitability of the selected and the noted alternate procedures for analysis of accident reactor coolant samples.

For suitability testing of additional analytical procedures, ENICO recommends that standard test matrix samples be utilized to demonstrate their acceptability. Standard matrix solutions similar to test solutions employed by SEC are recommended as they contain the most significant core degradation products in concentrations equal to or greater than those projected from an accident with a Regulatory Guide 1.3 or 1.4 source term. Test solutions used by SEC consider the effects of chemicals which might be added to the reactor coolant following an accident.

For chemical procedures that are to be used for the analysis of undiluted reactor coolant samples, the following standard test matrix containing nonradioactive species is recommended.

<u>Constituent</u>	<u>Concentration (ppm)</u>
I ⁻	40
Cs ⁺	250
Ba ⁺²	10
La ⁺³	5
Ce ⁺⁴	5
Cl ⁻	10
B	2000
Li ⁺	2
NO ₃ ⁺	150
NH ₄ ⁺	5
K ⁺	20

For chemical procedures that are to be used for analysis of diluted reactor coolant samples, testing should be performed with a standard matrix diluted by a volume equal to the dilution to be used in the procedure to be tested. It is also recommended that the procedures and associated instrumentation be tested in an induced gamma radiation field which will yield a total absorbed dose of 10^4 rads per gram of reactor coolant.

2.0 BACKGROUND

From studies of the incident at Three Mile Island Unit 2 (TMI-2), the need for improvement of the capability of licensees of nuclear power plants to determine plant conditions in a more timely manner was identified. Subsequently, the NRC issued,¹⁻⁵ for implementation by the licensees, specific requirements in several areas for improvement of the capability. In addition to the development and implementation of the upgraded capabilities, the requirements specified that the licensees should prepare and have available documentation of the capabilities for a post-implementation evaluation of compliance.

Exxon Nuclear Idaho Company, Inc. (ENICO) was contracted by the NRC's Division of Licensing to provide technical assistance for the evaluation of the post-implementation documentation in a number of areas. One area was "Postaccident Sampling Capability", Item II.B.3 of NUREG-0737.⁶ It pertains to the ability of the licensees to obtain reactor coolant and containment atmosphere samples and to analyze the samples for selected radionuclides and chemical species under accident conditions.

In order to facilitate the evaluation of the post-implementation documentation, ENICO was requested⁷ to evaluate the applicability of the chemical and radiological analysis capabilities associated with two postaccident sampling systems proposed⁸ for use by several power plants (Table 1). The two system vendors are Sentry Equipment Corporation (SEC) and General Electric Company (GE).

The initial plan⁹ called for ENICO to evaluate the SEC system only and to perform the evaluation in two phases. As it was believed that current technology was suitable for radiological analysis, the two phases were to be a brief summary report on the chemical analysis procedures and a more detailed report on both the chemical and radiological analysis procedures. However, due to manpower shortage at ENICO and an NRC request to incorporate the GE system into the evaluation, an alternate approach was taken. The alternate approach is to: 1) evaluate and prepare a detailed report of the chemical procedures for both the SEC

TABLE 1
STATIONS WITH PROPOSED USAGE OF SEC
AND GE POSTACCIDENT SAMPLING SYSTEM

GENERAL ELECTRIC

Brunswick 1/2
Nine Mile Point 1
Fitzpatrick
Oyster Creek
Pilgrim 1
Duane Arnold
Monticello
Peach Bottom 2/3

SENTRY

Dresden 1/2
Quad Cities 1/2
Zion 1/2
Browns Ferry 1/2/3
Salem 1
Kewaunee
Indian Point 2
Surry 1/2
North Anna 1/2
Palisades

and GE system and 2) evaluate and document the radiochemical analysis procedures associated with both sampling systems later. The detailed evaluation of the chemical analysis procedures is the topic of this report, which is limited to the analysis of reactor coolant samples.

3.0 REQUIREMENTS AND EVALUATION CRITERIA FOR THE CHEMICAL ANALYSIS OF REACTOR COOLANT SAMPLES

3.1 Requirements

To provide information for the assessment of core integrity, shutdown neutron absorber concentration, and reactor coolant corrosion potential; licensees or applicants for licenses of nuclear power plants are required to establish a capability for the timely collection and chemical analysis of reactor coolant samples under accident conditions. Per NUREG-0737 the required chemical analyses for reactor coolant samples are boron (PWR only), chloride, and either total dissolved gases or hydrogen; the measurement of dissolved oxygen is recommended in NUREG-0737 but not required. Per Regulatory Guide 1.97¹⁰ the measurement of dissolved oxygen, pH, and boron in all plants is required. NUREG-0737 also specified that the analysis could be performed by employing a combination of pressurized/unpressurized, diluted/undiluted grab samples or inline monitoring methods. However, for analyses performed by inline methods, a capability to collect backup grab samples and to provide procedures for their analysis is required. In all cases, the collection of grab samples for analysis and the inline analysis must be able to be performed with or without the operation of an auxiliary reactor coolant system, e.g., letdown.

With the exception of the chloride analysis, the time allotted for sampling and on site analysis of the samples is three (3) hours or less. Time allotted for the chloride analysis, which can be performed offsite, depends on the type of reactor coolant water and the number of barriers between the reactor coolant water and the primary containment system. For plants with seawater or brackish reactor coolant water or with a single-barrier, primary coolant containment system, chloride analyses are required within twenty-four (24) hours. For other plants the chloride analysis is required within ninety-six (96) hours.

In addition, the licensees or applicants are required to consider the radiological hazards associated with the sample collection and analyses. The assumptions of a Regulatory Guide 1.3¹¹ or 1.4¹² source term and radiation exposure limits¹³ of five (5) rem to the whole body

or seventy-five (75) rem to the extremities of any individual are to be used in system design and selection of chemical analysis methods.

Last, the licensees or applicants are to provide provisions for restricting background radiation levels in the chemical analysis facility and for insuring the validity and accuracy of the sample analyses. These provisions include such things as sample shielding, adequate ventilation air and filtration, proper sample disposal, sample line purging, reduction of plate-out in sample lines, etc.

The requirements for post accident chemical analysis of reactor coolant samples are presented in Table 2.

3.2 Evaluation Criteria

The objective of the present evaluation of potential methods for the chemical analysis of reactor coolant samples under postulated accident conditions is to determine applicable procedures and to identify the most appropriate procedure for each of the required analyses.

Many factors were considered in the evaluation of the proposed methods. Obviously, compliance with the requirements of sensitivity, accuracy, range, analysis time, radiological dose limitations, and sample collection methods were evaluated. This included comparisons of the advantages (lower radiological exposures) and disadvantages (reduced sensitivity and accuracy) of utilizing diluted or very small reactor coolant samples versus larger undiluted reactor coolant samples. It also involved an estimation of the significance of chemical and radiologically-induced interferences. Other factors which were considered are the complexity of the procedures and the applicability of the technique to both accident and normal condition usage.

Due to the unavailability of information in a number of instances, factors not considered were specific design features of the two sampling systems. Examples are sampling locations, shielding, sample line purging, sample validity, ventilation, etc.

TABLE 2

SUMMARY OF REQUIREMENTS FOR POSTACCIDENT CHEMICAL ANALYSIS
OF REACTOR COOLANT SAMPLES

Analysis Capability Units	Boron (ppm)	Chloride (ppm)	Total scc/kg	Dissolved Gases ⁽¹⁾ Hydrogen scc/kg
<u>Requirement</u>				
Range	0-1000 ⁽³⁾ 0-6000 ⁽⁴⁾	0-20	0-2000	0-2000
Accuracy ⁽⁶⁾ Percent Units	+5 if >1000 <u>+50</u> if <1000	+10 if >0.5 <u>+0.05</u> if <0.5	+10 if >50 <u>+5</u> if <50	+10 if >50 <u>+5</u> if <50
Sampling Method ⁽⁷⁾ Inline Grab Sample	Optional Required	Optional Required	Optional Required	Optional Required
Analysis Location Onsite Offsite	Required Optional	Optional ⁽⁸⁾ Optional	Required Optional	Required Optional
Sample Collection and Analysis Time (hours)	3	24 ⁽⁸⁾ 96	3	3
Radiological Exposure Limits	(9)	(9)	(9)	(9)

Notes:

- 1) A pressurized reactor coolant sample is not required if the dissolved gases can be determined with an unpressurized sample.
- 2) The measurement of conductivity is not required in NUREG-0737 or Reg. Guide 1.97, Revision 2; however, methods to measure conductivity are proposed by SEC and GE. Accordingly, the measurement of conductivity has been included in this study.

TABLE 2 (Continued)

SUMMARY OF REQUIREMENTS FOR POSTACCIDENT CHEMICAL ANALYSIS
OF REACTOR COOLANT SAMPLES

Analysis Capability Units	Oxygen (ppm)	pH (pH units)	Conductivity ⁽²⁾ μS/cm
<u>Requirement</u>			
Range	0-20	1-13	1-1000 ⁽⁵⁾
Accuracy ⁽⁶⁾ Percent Units	+10 if >0.5 +0.05 if <0.5	Not applicable + 0.3 if 5 >pH<9 ± 0.5 if 5 <pH>9	+ 20 Not Applicable
Sampling Method ⁽⁷⁾ Inline Grab Sample	Optional Required	Optional Required	Optional Required
Analysis Location Onsite Offsite	Required Optional	Required Optional	Required Optional
Sample Collection and Analysis Time (hours)	3	3	3
Radiological Exposure Limits	(9)	(9)	(9)

Notes: (Continued)

3) Boiling Water Reactors

4) Pressurized Water Reactors

5) The required range for measurement of conductivity was taken
from reference 14.

- 6) The designation of percent accuracy as ± 5 if >1000 indicates the required accuracy is ± 5 percent if the required measurement is greater than 1000 units. The designation of units accuracy as ± 50 if <1000 indicates that the required accuracy is ± 50 measurement units if the required measurement is less than 1000 units. The required accuracies were taken from reference 7.
- 7) Analysis may be performed with either grab sampling or inline monitoring methods. However, for inline analysis methods the capability to collect and analyze backup grab samples is required. The capability to collect and analyze at least one sample per day for seven (7) days following the onset of the accident and at least one sample per week until the accident no longer exists is also required.
- 8) For nuclear power plants which utilize seawater or brackish water as a source of reactor coolant water or which have a single-barrier, reactor coolant containment system, the chloride analysis must be performed within 24 hours; for other nuclear power plants, the required chloride analysis time is 96 hours. The chloride analysis may be performed offsite.
- 9) The radiation exposures to any individual involved in the collection and analysis of reactor coolant samples under accident conditions may not exceed 5 rem to the whole body or 75 rem to the extremities.

The evaluation criteria used in the study were:

1. Analysis Time - As the time required for sample collection was not specified by SEC or GE, it was assumed sample collection could be performed within one hour. Accordingly, an upper limit of two hours was allotted for sample analysis; chemical analysis procedures which required two hours or less for analysis were satisfactory.
2. Sensitivity, Range, Accuracy - Chemical procedures which encompassed the entire measurement range with the required accuracy were considered adequate. To cover the full range of measurement as required, sample dilution methods were considered satisfactory.
3. Radiological Exposure Limits, Sample Size - Radiological exposure to any individual is limited to 5 rem to the whole body and 75 rem to the extremities during the collection and analysis of reactor coolant samples. Under the assumption of Regulatory Guides 1.3 or 1.4 releases of fission products to the reactor coolant, calculated¹⁴ dose rates from reactor coolant samples are nominally 140 R/h/g at 10 cm with a one hour decay. Maintenance of radiological exposures within acceptable limits requires the usage of safety factors such as: shielding, distance, exposure time, sample dilution, very small undiluted sample, and/or inline monitoring.

The chemical analysis procedures, including dissolved gases, proposed by GE and SEC make use of inline monitoring, very small undiluted samples, and remote dilutions of the initial reactor coolant sample. The diluted reactor coolant samples are used for subsequent "hands-on" analysis. With the exception of the subsequent hands-on analysis, this study did not evaluate the radiological hazards associated with the above methods. It was assumed that adequate shielding and/or remote operation would minimize radiological exposures to personnel. In regard to the subsequent analysis of diluted reactor coolant samples; only estimates of radiological exposures could be made as they are

not only a function of the amount of reactor coolant in the sample, but also depend on the techniques of the analyst and the design of the analytical facility.

The method which was established to lessen exposure is to limit the amount of reactor coolant in the sample taken for analysis to 0.1 ml. The basis for this criterion is the knowledge that doses to the extremities will be the limiting factor for hands on chemical procedures. For example, calculated exposures to the extremities, using the above value of 140 R/h/g of reactor coolant at 10 cm, will exceed the 75 rads limit by a factor of almost two for a two hour exposure to a 1. ml sample. It would require approximately five hours of continuous exposure to exceed the dose limits for a 0.1 ml sample. It is realized that the limitation to a 0.1 ml reactor coolant sample size is conservative as exposure time will, in reality, be less than two hours and techniques to reduce the exposures will probably be employed. However, to allow a sufficient margin of safety, a 0.1 ml reactor coolant sample was considered an acceptable size sample in this study. In a final evaluation of acceptable sample sizes, larger samples may be permissible, but all factors must be considered.

4. Complexity, Routine/Accident Usage - Two other criteria which were used are the complexity of performance of the procedures and the applicability of the procedures to both routine and accident condition usage. The procedures were assigned low, medium, or high levels of complexity based primarily on the number and nature of manipulations involved in the procedure. Procedures with applicability to both routine and accident conditions were considered more satisfactory than procedures applicable to accident conditions as the use of nonroutine procedures can create confusion and cause errors under accident conditions.
5. Chemical and Radiologically-Induced Interferences - The release of large quantities of both radioactive and nonradioactive fission products will result in high radiation fields and chemical-

ly significant levels of various ionic species in the reactor coolant. Both the radiation and ionic species can interfere with the accuracy of chemical procedures used to analyze reactor coolant samples. In the selection of an appropriate chemical analysis method, these matrix effects should be considered. In this study a chemical procedure was considered unsatisfactory if the interferences cause the accuracy of the procedure to exceed the required limits. The evaluation included a review of available test data and professional judgements based on past experiences of personnel involved in the review.

4.0 EVALUATION OF CHEMICAL PROCEDURES FOR ANALYSIS OF POSTACCIDENT REACTOR COOLANT SAMPLES

In the evaluation of the applicability of chemical procedures for analysis of postaccident reactor coolant samples, ENICO studied the chemistry of the procedures, compared their capabilities with NUREG-0737 requirements and the established evaluation criteria, and ranked the procedures in order of appropriateness. Some of the procedures are similar to ones used at the Idaho National Engineering Laboratory (INEL); this experience added to the data base.

Presented below in Section 4.1 is a summary of the sample collection and chemical analysis procedures proposed by SEC and GE and a general outline of the testing program conducted by SEC and GE. This is followed by a presentation of ENICO's evaluation of the procedures. Included are brief descriptions of the procedure methodology and the advantages and/or disadvantages of each procedure. Last, the overall evaluation of the individual procedures are summarized for a given type analysis.

4.1 SEC and GE Sample Collection, Recommended Analysis Methodology and Chemical Procedure Evaluation Program

Methods for analysis of postaccident reactor coolant samples proposed by SEC¹⁵ and GE¹⁶⁻¹⁹ include inline monitoring and laboratory analysis of grab samples. For inline monitoring, sample streams are diverted either continuously or intermittently through inline sensors. For laboratory analysis, the reactor coolant grab samples are diluted inline before transfer to the laboratory or directly to an analytical instrument. Either diluted liquid or dissolved gas grab samples can be obtained. To obtain liquid samples, 1:100 dilutions of 0.1 ml reactor coolant samples are typically performed; larger initial dilutions or secondary dilutions of the initial dilution can also be performed. To obtain a dissolved gas grab sample; thirty (30) to seventy (70) milliliters of pressurized reactor coolant are isolated, the sample is depressurized, and the dissolved gases are purged into a gas holding chamber with an inert gas. One milliliter or larger aliquots of the diluted sample are analyzed following dilution with the inert gas to a known pressure.

The chemical procedures associated with the proposed methods are either conventional or modifications of conventional chemical analysis procedures. A summary of the methodology, including chemical analysis procedures, recommended by SEC and suggested by GE is presented in Table 3. Not included in Table 3 are other methods detailed by SEC and GE; this information is included in section 4.2.

TABLE 3
SEC AND GE REACTOR COOLANT ANALYSIS METHODOLOGY

<u>ANALYSIS</u>	<u>SYSTEM</u> <u>VENDOR</u>	<u>SAMPLE</u> <u>TYPE</u>	<u>ANALYSIS</u> <u>METHOD</u>
Boron	SEC	Grab	Fluoroborate
	GE	Grab	Electrode Spectrophotometric (carminic acid)
Chloride	SEC	Inline, grab	Ion Chromatography
	GE		Turbidimetric
Dissolved Hydrogen	SEC	Inline, grab	Gas Chromatography
	GE	Grab	Gas Chromatography
Dissolved Oxygen	SEC	Inline	YSI Oxygen Analyzer
	GE	Grab	Gas Chromatography
pH	SEC	Inline	pH probe
	GE	Grab	pH paper
Conductivity	SEC	Inline	Conductivity Cell
	GE	Inline	Conductivity Cell

Chemical procedures recommended by SEC are the result of a development and testing program conducted by Nuclear Utility Services (NUS) for SEC. In the study the recommended methods and several other chemical analysis methods were evaluated in the laboratory to identify chemical interferences due to sample matrices, to determine operational characteristics of instrumentation, and to measure the sensitivities, ranges, and accuracies of methods. Employed in the study were simulated post-accident reactor coolant test samples. They contained, in addition to the chemical species of interest, high-yield, stable fission products and appropriate concentrations of chemical additives anticipated to be present in the reactor coolant following an accident. The study did not include actual measurements of possible effects of high radiation fields on the procedures; however, it did include the results of a survey of personnel with prior experience in the analysis of samples with high radiation fields and a literature review of effects of high irradiation on different materials.

Chemical procedures suggested by GE, except those coincidental to the SEC tested methods, are not the result of detailed laboratory testing. The only testing of the procedures is related to the effects of high irradiation of the samples. The suggested procedures were selected primarily on the basis of simplicity, stability and availability of reagents, minimum radiation exposure, and likelihood of causing contamination problems.¹⁸

4.2 Chemical Procedure Descriptions, Advantages/Disadvantages and Evaluation Summaries

In the selection, recommendation, and/or suggestion of chemical procedures for analysis of postaccident reactor coolant, SEC and GE considered a total of twenty-seven (27) procedures. The chemical procedures considered by the two vendors are shown in Table 4; also noted in the table are known procedures in use at the INEL. As many of the procedures are similar or identical, they have been grouped together, as appropriate, in ENICO's evaluation of the procedures. Presented in order below are the evaluations of the boron, chloride, hydrogen, oxygen pH and conductivity measurement procedures.

TABLE 4

CHEMICAL ANALYSIS PROCEDURES CONSIDERED BY SEC AND GE

CHEMICAL ANALYSIS	VENDOR	PROCEDURE
Boron	SEC	Fluoroborate selective ion electrode
	SEC	Curcumin Spectrophotometric
	SEC	Plasma Spectroscopy
	SEC	Boronmetry*
	SEC	Digi Chem Analyzer Mannitol Titration
	SEC, GE	Carminic acid Spectrophotometric
	SEC	Ion chromatography*
	SEC	Manual Mannitol Titration*
	GE	Conductivity of Boron Solutions
Chloride	SEC	Ion Chromatography*
	SEC	Selective Ion Electrode.
	SEC	Mercuric Nitrate Titration
	SEC, GE	Thiocyanate Spectrophotometric
	GE	Silver Chloride Colormetric
	GE	Conductivity of Chloride Solutions
Hydrogen	GE, SEC	Gas Chromatography
Oxygen	GE	Gas Chromatography
	SEC	YSI Oxygen Probe
pH	GE	pH Paper
	GE	Conductivity
	SEC	pH Probe*
Conductivity	SEC, GE	Conductivity Cell*

* Indicates a procedure that is in use at the Idaho Chemical Processing Plant (ICPP) or the Loss of Fluid Test Facility (LOFT) at the INEL.

4.2.1 Boron Analysis Procedures

4.2.1.1 Fluoroborate Selective Ion Electrode (FSIE). In the FSIE chemical analysis procedure, the boron content of a sample is determined by the measurement of the concentration of the tetrafluoroborate ion. In addition to the sensing electrode, which contains a membrane with a selective tetrafluoroborate ion exchanger, a single junction reference electrode (KCe/saturated AgCe) and a conventional millivolt meter with a relative millivolt mode are required.

The procedure requires precise laboratory techniques; care must be exercised to add the reagents to the standards or samples in sequence and to perform measurements at prescribed times. In the analysis procedure a standard and a sample are analyzed simultaneously. Initially, 1.0 ml of saturated sodium fluoride is added to 5.0 ml of the standard, and then 0.5 ml 10 N sulfuric acid is added (the sodium fluoride and sulfuric acid converts boric acid to the tetrafluoroborate ion). With the addition of the acid to the standard, a timer is started; five minutes later the same reagents are added to 5.0 ml of a previously diluted sample. At eight minutes the electrodes are inserted into the standard solution which is being stirred; at ten minutes the millivolt response is adjusted to correspond to a specific value on a pre-established calibration curve.

The millivolt response for the sample is recorded at fifteen minutes and related to the ppm boron from the calibration curve.

To minimize radiological hazards 1.0 ml samples and standards can be analyzed by the above procedure with the use of correspondingly less sodium fluoride and sulfuric acid. In addition, the analysis can be performed by using only 0.3 ml of the original 5.0 ml or 1.0 ml of sample taken for analysis. The analysis using 0.3 ml is performed statically in microdishes.

There are two types of calibration curves. One for the 5.0 ml and/or 1.0 ml samples analyzed by immersion of the electrodes into a stirring solution, and one for the 0.3 ml samples analyzed by immersion of the electrodes in the microdishes. The calibration curves are established using the same techniques employed for the samples; the calibration curves are valid only for the pair of electrodes used to establish them. Calibration curves are estimated to be valid for six months; however, frequent use of the electrodes shortens their life. Accordingly, routine checks of the calibration curves are recommended to maintain their currentness. Approximately a total of one hour is required, to generate new calibration curves for both large and small samples.

Numerous laboratory tests were carried out with simulated postaccident matrix samples to identify chemical interferences to the FSIE procedure. No sample matrix effects were observed when the procedure described above was followed.

The advantages of the procedure are its wide measurement range and accuracy, the small sample sizes required, the lack of chemical interferences, its adaptability to routine and accident condition usage, and the short analysis time required.

The main disadvantage of the procedure is its relative complexity, which will necessitate well-trained analysts and frequent usage of the procedure by the analysts in order to retain their familiarity with it. Another limitation of the procedure, under the assumption of a minimum initial sample dilution of 1:100, is the inability of the procedure to measure boron levels in highly radioactive reactor coolant below fifty ppm. However, in ENICO's opinion, this is not a serious limitation as under accident conditions the concentration of boron in the reactor coolant should be much higher than fifty ppm; and, if it isn't, confirmation that boron levels are fifty ppm or above is sufficient information to determine the need for subsequent corrective actions.

The FSIE analysis procedure has not been tested with high radiation field samples; however, ENICO does not believe irradiation associated with highly radioactive samples will significantly alter the applicability of the method.

4.2.1.2 Curcumin Spectrophotometric. The curcumin spectrophotometric boron analysis method is based on the measurement of a red-colored product, rosocyanine, formed by the reaction of boron and curcumin. To perform the measurement the 1.0 ml diluted sample and standards, which are analyzed concurrently with the samples, are mixed with 4.0 ml of curcumin; evaporated to dryness; dissolved in 95 percent isopropyl alcohol to a total volume of 25 ml; and transferred to a 1.0 cm spectrophotometer cell. In the spectrophotometer, a Bausch and Lomb Spectronic 20 or equivalent, the percent transmittance of the sample and

standard are measured at 540 nm. A calibration chart is prepared from the standards, and the concentration of the boron in the sample is determined from the calibration chart.

The curcumin spectrophotometric procedure was laboratory tested by SEC/NUS. In addition to sample matrix effect studies using samples containing selected nonradioactive fission products and chemicals anticipated to be present after an accident, experiments were performed to optimize the precision, accuracy, and required analysis time.

The advantages of the procedure are its wide measurement range, its accuracy, the small sample size required, the lack of chemical interferences, its utility under accident and routine conditions, and its relative simplicity. The disadvantages of the procedure are the long analysis times required and the necessity to generate calibration curves at the same time sample analyses are performed. The latter is considered a disadvantage as a significant amount of time could be wasted if a satisfactory calibration can not be obtained the first time. Another limitation of the procedure is the inability to measure levels of boron levels in reactor water below twenty ppm. However, as noted above, ENICO does not consider this a major limitation as required corrective action can be made based on the knowledge of boron concentrations of twenty ppm or more.

The effects of high radiation fields on the procedure have not been determined. In ENICO's judgement, the accuracy or sensitivity of the procedure would not be compromised; but this needs to be confirmed before the procedure is used.

4.2.1.3 Plasma Spectroscopy. The analysis of boron by plasma spectroscopy is achieved by vaporization of the sample in a plasma jet and analysis of the atomic emission spectra which is generated. The boron resonance wavelength of either 249.7 or 249.8 nm is used. Readout of the unknown is compared to standards. Five milliliters of a diluted reactor coolant sample is required. One milliliter of the sample and associated radioactivity is completely vaporized and released; the other

four milliliters are collected in a waste container as condensed spray droplets. The required analysis time is fifteen to thirty minutes.

No specific laboratory testing details were provided; however, it was indicated that limited tests were performed on simulated reactor matrix solutions with satisfactory reproducibility and accuracy. The measurement range associated with the procedure also was not provided; however, a lower detection limit of less than 1 ppm boron is reported. With this sensitivity and appropriate sample dilution, it appears the measurement range would be sufficient to cover the measurement range required.

The advantages of the procedure are its apparent simplicity, time required for analysis, and small sample sizes.

The disadvantages of the procedure are the lack of sufficient laboratory testing and the radioactivity releases associated with it. It is assumed that appropriate design modifications could be incorporated to circumvent this latter deficiency; but the design must include features to collect all the radioactive releases, not merely to contain them in a fumehood, as is done with the existing design. High radiation fields will not affect the applicability of the procedure.

4.2.1.4 Boronometry. The analysis of boron by boronometry is based on the attenuation of a collimated neutron beam by a solution of boron between the source of neutrons and the detector. The neutron count rate from the detector tube is converted directly to boron concentration on the readout electrometer or pulse counter. Californium-252 or plutonium-beryllium are typically used as sources of neutrons. Boron trifluoride (BF_3) tubes or fission chambers are two types of detectors. Although BF_3 tubes have been reported to operate satisfactorily in gamma-ray fields up to 100 R/hr, later boronmeters use fission chambers as they are virtually insensitive to gamma-ray fields.

Boronometers typically employ relatively large volume samples, 1-2 liters or more. Accordingly, massive shielding of the sample station and separation of the sample station and readout instrumentation is required for accident condition usage. As the detectors are sensitive to other sources of neutrons, location of the detectors within the plant should be considered, and the detectors should be located away from these sources.

The sensitivity of boronometers is on the order of 1 ppm boron with a useful range of 5000 ppm or more.

Calibration of boronometers can be performed statically or by flowing standards with a variety of boron concentrations past the detector.

Although no laboratory testing was performed on the effects of sample matrices, no chemical interferences are anticipated.

The advantages of boron analysis by boronometry are the continuous readout of the boron concentration, the wide measurement range with or without sample dilutions, the applicability of the method to routine and accident use, and existence of proven boronometers.

The disadvantage of the method is the use of large volume samples, which could create maintenance problems should a failure occur during an accident. However, the impact of such an occurrence could be minimized as a backup boron analysis capability using grab samples is required for inline monitoring methods.

As noted above, high radiation fields will not affect the performance of boron analysis performed by boronometry.

4.2.1.5 DigiChem Analyzer of Manual Mannitol Titrations.
The procedure for boron analysis using either the DigiChem Analyzer or manual titrimetry methods is, in principle, the same. Mannitol is added to the sample to form a boron mannitol complex; hydrochloric acid is added to initially adjust the pH of the solution to 4.4; and the sample

is titrated to the end point (pH 8.5) with sodium hydroxide. The boron content of the sample is derived from the volume of sodium hydroxide titrant used and comparison to standards data.

The difference in the two procedures is obvious; one employs hands-on techniques and the other employs remote analysis. The remote analysis is performed automatically with the DigiChem Analyzer. It makes use of a microprocessor for sample and reagent dispensing, solution mixing, and concentration measurements. The analyzer automatically calculates the boron content and outputs it on a computer-compatible tape. Analysis by the analyzer can be performed continuously, semicontinuously, or in the batch mode. Separation of the sensing element and the readout device is required to eliminate radiation effects on the system electronics; the sensor and electronics can be separated by at least twenty-five feet without degradation of the signal. The analysis times are seven minutes with the automatic analyzer and twenty minutes for the hands-on methods.

A total of two hundred micrograms of boron is required for analysis with either the automatic or manual procedure. Accordingly, the required sample sizes depend on the concentration in the sample. For example, under the assumption that 0.1 ml of reactor coolant is an upper limit for the reactor coolant sample size, the initial concentration of boron in the reactor coolant would have to be two thousand ppm or greater to provide sufficient boron for analysis. The two thousand ppm represents the lower limit of detection for 0.1 ml samples and, as a result, precludes the usage of the hands-on mannitol titration procedure usage on accident condition samples. However, it does not preclude the use of the DigiChem Analyzer for accident conditions as larger samples can be collected and analyzed remotely.

In fact, the DigiChem Analyzer has been laboratory tested on standards, with and without the presence of potential interferences; accurate, precise, interference free results obtained. The measurement range of the procedure for a 4.0 ml sample is 50-6000 ppm boron, which could be extended downward by the use of larger samples.

The advantage of the automatic mannitol titration procedure is its relative simplicity, remote operational characteristics, utility under routine and accident conditions, and wide measurement range.

The only apparent disadvantage of the procedure is the potential maintenance difficulty which might occur during replacement of sensing elements under accident conditions or rapid repair of the microprocessor. However, as backup capabilities to analyze boron samples are required for inline sample methods, the DigiChem analyzer should meet all measurement requirements.

The effects of high radiation fields have not been tested. ENICO feels that the effects probably will not be significant; however, this should be confirmed.

4.2.1.6 Ion Chromatography (IC). An ion chromatograph operates on the principle of selective retention and elution of ionic species on and from ion exchange media. It basically consists of a separator column and eluent, a suppressor column, a conductimetric detector, and a readout device. To perform an analysis for anions, such as borates or chlorides, the sample is first passed through the separator column - an anion exchange medium which retains the anions and replaces them with another anion from the exchange medium. The retained anions are then selectively removed from the separator column with the eluent, normally a dilute salt solution, and passed through the suppressor column. In the suppressor column - a cation exchange medium - the anions are converted to their acid forms which pass unretarded to the conductimetric detector. The conductivity of these dilute acid solutions is a function of the anion concentrations in the sample.

The time between sample injection and the appearance of conductivity peak for a particular anion depends on the sample size, the physical size of the columns, the types of exchange media, and the types, concentrations, and flow rate of the eluent. As a result different anions in a single sample can be separated and analyzed by proper selection of parameters.

In the development of an ion chromatographic procedure for the analysis of boron and/or chloride; SEC/NUS studied various combinations of eluents, separator columns, suppressor columns, and sample injection loop sizes. Initial testing resulted in a method which used a sodium tetraborate eluent and was applicable for chloride analysis of postaccident reactor coolant samples (cf Section 4.2.2.1). However, the analysis of boric acid solutions with the procedure showed inconsistent results.

Additional development and testing by Dionex, the manufacturer of the ion chromatograph used, resulted in a procedure for the simultaneous analysis of boron and chloride using a single sample.

In the test program a modified Dionex Model 10 Ion Chromatograph was used. The modifications included two 4 x 250 mm separator columns, a 3 x 250 mm suppressor column, a twenty cm (0.043 ml) sample injection loop, and a sodium carbonate/sodium hydroxide/mannitol eluent. An additional requirement identified was the need of a cation pre-column to remove excess base and convert borates to boric acid prior to loading highly basic samples into the injection loop. With a twenty-five percent pump stroke, the necessary times for the boron and chloride peaks to appear following injection to the sampling loop are respectively 5-6 and 9-10 minutes.

To consistently obtain satisfactory results, periodic washing and/or regeneration of the suppressor and pre-columns is necessary. The pre-column requires regeneration after the analysis of every two to three samples containing 0.4 M sodium hydroxide. The required frequency for washing and regeneration of the suppressor columns was not stated. However, based on the frequency noted in the initial chloride analysis development work, estimated frequency for regeneration is every four hours of continuous operation. The need for this is indicated by an erratic baseline on the readout device. The required frequency for washing the suppressor is once daily or prior to each regeneration.

If column washing and regeneration are not required, the analysis time is forty minutes. If column washing and regeneration are required prior to analysis, the sample analysis time is approximately two hours. Neither case includes system calibration time, which is fifteen minutes.

The IC procedure for simultaneous chloride and boron analysis has been laboratory tested using simulated postaccident reactor coolant samples, stable fission products, caustic, cooling water impurities, and normal reactor coolant chemical additives. No sample matrix effects were observed within the specified measurement range.

The advantages of the procedure are its adaptability to remote operation, the large chloride measurement range, the simplicity of operation, small sample sizes, potentially short sample analysis time, and the lack of chemical interferences.

The disadvantages of the procedure are the lack of a sufficient measurement range for boron, the need of a pre-column for basic samples, and the need for column washes and regeneration which might lead to long analysis times.

The effects of large irradiations associated with highly radioactive samples have not been evaluated. However, based on a literature study of radiation effects on the components of the IC and on limited laboratory tests used to determine the effects of 0-200 ppm hydrogen peroxide in samples, no radiological effects are anticipated. The literature showed that cation resins begin to degrade at approximately 10^8 rads and that the electronic components are resistant to exposure well above 10^5 rads. Both levels are well above those anticipated to be encountered by the IC during analysis of samples.

4.2.1.7 Carminic Acid Spectrophotometry. Two procedures were presented for boron analysis with carminic acid, one by SEC and one by GE. The one presented by GE was detailed; it was developed by HACH Chemical Company²⁰ and closely follows an ASTM procedure.²¹ The

procedure presented by SEC was only an outline. Since both methods were similar and the HACH procedure had a slightly larger measurement range, only the HACH procedure is discussed.

The HACH procedure is very simple. First the boric acid in preweighed tablet form is added to 75 ml of sulfuric acid and mixed; then, 35 ml of the prepared solution is added to 2.0 ml of the sample, blank, and/or standard. After the development of the color, 20-30 minutes, 25 ml of the solution(s) is transferred to spectrophotometric cells and the percent transmittance is measured at 605 nm with a Bausch and Lomb Spectronic 20 spectrophotometer, or equivalent. The measurement range is 0-15 ppm boron without sample dilution and 0 - several thousand ppm boron with sample dilution. The total analysis time is approximately 40 minutes.

The procedure has not been tested for postaccident reactor coolant sample chemical matrix effects; it has been tested for effects of high sample radiation fields. At the maximum anticipated source term, 8×10^3 rad/h for a 0.1 ml reactor coolant sample diluted to 25.0 ml the effects of irradiation should be equivalent to no more than 5 ppm boron. This would result in negligible error when compared to levels of boron in postaccident samples.

The advantages of the procedure are the small sample sizes required, the wide measurement range, the adaptability to routine and accident conditions, and the simplicity.

The disadvantage is lack of laboratory testing with postaccident chemical matrix samples.

4.2.1.8 Conductivity of Boron Solutions. A GE specification requires the Standby Liquid Control System (SLCS) at BWR's to be filled with a solution of borax and boric acid at a ratio of 1.028. GE proposed that, in the event the SLCS were actuated, the boron concentration in the reactor coolant could be estimated from conductivity. GE tested the

hypothesis with a 1.028 borax to boric acid solution by varying the boron concentration between 5.4 and 201 ppm boron. The calibration curve was linear between 10.8 and 201 ppm boron.

This suggests that, with sample dilution, the boron concentration of reactor coolant can be determined by conductimetric measurements. However, ENICO believes that under accident condition there are too many other variables which could affect the conductivity of the reactor coolant and cause erroneous measurement. Accordingly, the approach is not considered to be applicable for measurement of boron concentration in reactor coolant.

4.2.1.9 Summary and Conclusions for Boron Analysis

Procedures. The results of ENICO's evaluation of potential chemical analysis procedures and methods for postaccident reactor coolant sample boron analysis are summarized in Table 5. Included are the measurement ranges, sensitivities, accuracies, analysis times, sample sizes, and analysis methods. Also noted are the complexity of the procedures and the existence, based on actual testing and/or professional judgements, of known or anticipated chemical or radiological interferences. Finally, the applicability of the procedure to routine and accident condition use is indicated.

As all but one of the procedures met or exceeded the criteria for required sample size, radiological exposures, measurement range and accuracy, and analysis times; the selection and ranking of the procedures in order of applicability were based to a degree on the complexity of the procedure and the laboratory testing which had been performed. If two procedures had similar complexities or amounts of laboratory testing; other factors, like time of analysis, were considered. Inline analysis procedures were ranked lower than grab sampling procedures with similar qualifications as the capability to analyze backup grab samples is required for inline methods. Last, anticipated maintenance problems or potential contamination were considered.

TABLE 5

FEATURES OF PROPOSED ANALYTICAL PROCEDURES FOR BORON

Method Feature	Fluoroborate Electrode	Curcumin Spectrophotometric	Plasma Spectroscopy
RANGE (ppm)			
Direct Analysis	0.5 - 6.0	0.2 - 2.0	0-<1.0
With 1:100 Dilution	50-600	20-200	0-<100
With 1:1000 Dilution	500-6000	200-2000	0-<1000
With Other Dilutions >1:100 (2)	50-6000	20-6000	0-6000
Accuracy (%)	<u>+30</u> if B = 50	<u>+13</u>	<u>+20</u> (3)
(B in ppm)	<u>+10</u> if B > 300		
Sample and/or Analysis Method?			
Inline	No	No	No
Grab	Yes	Yes	Yes
Analytical Backup Required?	No	No	No
Sample Collection Method	--	--	--
Sample Analysis Method	--	--	--
Sample Size (ml)			
Diluted Analysis Sample	1.0-5.0	1.0	0.25
Actual RC ⁽⁴⁾	0.01-0.05	0.01	~0.006
Analysis Time (min)	20	120	30
Procedure Complexity	Medium	Medium	Low
Chemical Interferences? Tested	No	No	Unknown
Anticipated	Yes	Yes	Limited
	--	--	No
Radiological Effects? Tested	Unknown	Unknown	Unknown
Anticipated	No	No	No
	No	No	No
Application			
Routine	Yes	Yes	Yes
Accident	Yes	Yes	Yes

TABLE 5 (Continued)

FEATURES OF PROPOSED ANALYTICAL PROCEDURES FOR BORON

Method Feature	Carminic Acid Spectrophotometric	Mannitol Titrimetry (Manual or Digi-Chem. Analyzer)	Boronometer	Ion Chromatography
RANGE (ppm)				
Direct Analysis	0-10.0	50-6000	0-5000(1)	500-6000
With 1:100 Dilution	10-100	Not appropriate	0-500,000	Not appropriate
With 1:1000 Dilution	100-1000	due to lack	0-5,000,000	due to lack of
With Other Dilutions >1:100 (2)	0-6000	of sensitivity	0-6000	sensitivity
Accuracy (%) B in ppm (Sample and/or Analysis Method?)	<u>+15</u> (3)	<u>+5</u>	<u>+8</u>	<u>+8</u>
Inline	No	Yes	Yes	Yes
Grab	Yes	No	No	No
Analytical Backup Required?	No	Yes, For Inline	Yes, For Inline	No
Sample Collection Method	--	Available	Available	--
Sample Analysis Method	--	Not Specified	Not Specified	--
Sample Size (ml)	2.0	4.3(5)	1000-2000	0.04
Diluted Analysis Sample Actual RC(4)	0.02	1-2	10-20	0.04(5)
Analysis Time (min)	40(6)	5-30	continuous	40-120(7)
Procedure Complexity	Low	Low	--	Medium
Chemical Interferences? Tested	Unknown	No	Unknown	No
Anticipated	No	Yes	No	Yes
	No	--	No	--
Radiological Effects? Tested	No	Unknown	No	Unknown
Anticipated	Yes	No	yes	No
	--	No	--	No
Application Routine	Yes	Yes(8)	Yes	No(9)
Accident	Yes	Yes	Yes	No

Notes:

- 1) The range of measurements using neutron adsorption is based on boron densitometers used at the Idaho National Engineering Laboratory.

- 2) With dilutions greater than 1:100 the upper limit of the measurement range can be extended to ten-of-thousands of ppm. However an upper limit of 6000 ppm is noted as measurements above 6000 ppm are not required.
- 3) In the procedure presented the uncertainty of the method was not included; based on professional judgement the uncertainty has been estimated at +20 percent.
- 4) The actual volume of reactor coolant used in the analysis was determined from a 100-fold dilution of 0.1 ml of reactor coolant and the volume of diluted sample required for the analysis.
- 5) Due to a lack of sensitivity for boron, typical sample dilution of 1:100 of 0.1 ml reactor coolant samples is not appropriate. Consequently, boron analysis of grab samples can not be made with the procedure. However, the procedure has sufficient sensitivity to analyze chloride in diluted grab samples (see sections 4.2.2.1 and 4.2.2.5).
- 6) Two procedures were presented for boron analysis with carminic acid, one by SEC and one by GE. The analysis time specified by GE and SEC were 40 and 90 minutes, respectively. The difference in times is the number of minutes required for cooling following carminic acid addition and for color development. As GE had tested the procedure and SEC had not, 40 minutes is assumed to be correct.
- 7) The actual boron analysis time is forty (40) minutes. However, during continuous operation a column wash/regeneration/equilibration cycle is required every four hours. Accordingly, an analysis could require approximately two hours.
- 8) The manual mannitol titrimetry is appropriate for routine use only as the method lacks sensitivity to analyze small reactor coolant samples; the manual method is commonly used at PWR's under normal conditions. The DigiChem Analyzer method is applicable to routine or accident condition usage as the method uses remote analysis of larger reactor coolant samples.
- 9) The ion chromatographic procedure is not appropriate for routine or accident condition usage due to insufficient sensitivity. If the lower detection of 500 ppm boron were deemed to be sufficiently sensitive, the procedure would be appropriate for accident condition use only.

Listed in order of appropriateness is the result of ENICO's evaluation of the boron analysis procedures:

1. Fluoroborate Electrode
2. DigiChem Analyzer Mannitol Titrimetry
3. Curcumin Spectrophotometric
4. Boronometer
5. Carminic Acid Spectrophotometric
6. Plasma Spectroscopy
7. Ion Chromatography

It should be emphasized that the order of ranking is based on presently available information only. With additional testing the order could change. For example, with confirmation that there are no chemical interferences to the carminic acid spectrophotometric method, it would be ranked at or near the top due to ease of use. Likewise, modifications to the plasma spectroscopy instrument, which would insure containment of volatilized radioactivity, would improve its rating. Last, confirmation of the existence or nonexistence of radiological interferences could alter the order of ranking.

4.2.2 Chloride Analysis Methods

4.2.2.1 Ion Chromatography (IC). Described in Section 4.2.1.6 was an ion chromatographic procedure for the simultaneous analysis of boron and chloride. Included in the description were the columns, sample sizes, eluent, and operational characteristics required for satisfactory analysis of boron and chloride in a single sample.

The measurement range, accuracy, sample size, and analysis time for chloride analysis with the procedure are respectively 0.1-2000 ppm, ± 10 percent, 0.04 ml of undiluted reactor coolant, and 40-120 minutes. The procedure, which has been laboratory tested, is applicable for routine and accident condition use. It can also be used as an inline monitor or for analysis of grab samples.

The advantages of the procedure are the measurement range for chloride, normal and accident usage, small sample size, the lack of chemical interferences, remote operability, simplicity of operation, and potentially short analysis time.

The disadvantages of the procedure are the lack of a sufficient measurement range for boron, the required column washes/regenerations, which increase the analysis times, and the need of a pre-column for basic samples. Another unknown is the lack of data on the potential effects of highly radioactive samples.

Sentry Equipment Corporation also developed and tested another ion chromatographic procedure for chloride analysis. The procedure can not be used for boron analysis; however, it is very similar to the boron-chloride analysis described previously. The procedure uses a 3 x 250 mm separator column, a 6 x 250 mm suppressor column, a sodium tetraborate eluent, and a 0.04 ml sample. The procedure does not use a pre-column. To obtain satisfactory results the columns must be washed and regenerated. Washing frequency is once daily or prior to each regeneration.

Regeneration frequency is one every four hours of continuous operation. A high erratic baseline, a change in the time of the appearance of the chloride peak (normally six minutes), and/or a change in the peak height for the standard indicate a need for regeneration.

The tetraborate IC procedure has been tested in the laboratory with simulated samples of fission products and chemical additives. Special laboratory tests were performed to determine the effects of morpholine, hydrazine, ammonia, and natural and synthetic oils. The only effect observed was due to oils, which caused a progressive 10-30 percent increase in the chloride response and a memory effect. However, as the memory effect can be eliminated with column washing and regeneration and as the increase in chloride peak height is associated with longer elution times, the effect is not considered significant as it can be detected and corrected.

Laboratory tests were also performed with the tetraborate IC procedure to determine its ability to measure fluoride and iodide. The data indicated that the fluoride elution time was 1.5 minutes and that measurement of fluoride is possible down to 25 ppm (+10 percent) in the presence of fewer than 100 ppm boron. Attempts to measure fluoride in the presence of higher concentrations of boron were unsuccessful due to peak overlap. The iodide measurements indicate that iodide could not be detected at low concentrations (0.5 ppm), and at high concentrations (up to 100 ppm) small responses were observed. The iodide data indicates that iodide will not interfere with the tetraborate IC chloride analysis method.

The advantages and disadvantages of the tetraborate IC procedure are essentially the same as the ones presented above for the boron-chloride IC procedure.

4.2.2.2 Specific Ion Electrode (SIE). The procedure for chloride analysis by SIE is very simple and rapid. The pH of the solution is adjusted to 2-4 and the SIE and a reference electrode are immersed in the solution and the millivolt response is related to the chloride concentration.

The investigative studies performed by SEC/NUS employed a Graphic Controls Ultra-Sensitive Solid State Chloride Electrode (Model PHI 91100) and a Graphic Controls double-junction reference electrode (No. GC 54473). In the procedure 1.0 ml of nitric acid was added to 100 ml of sample to adjust the pH. The measurement range determined with standard chloride solutions was 0.01 to 35,000 ppm chloride.

With the above measurement range, the SIE is applicable to routine use only as approximately 10.0 ml of reactor coolant sample, diluted to the 100 ml sample analysis size, would be required to detect 0.1 ppm chloride. Furthermore, the method suffers from interference of other halogens. The interference problem possibly can be solved by a combination of selective oxidation and solvent extractions; however, at present the SIE is not applicable to postaccident chloride analysis due to the relatively large sample size required.

Conceivably, the SIE could be adapted to remote operation; but, as noted, the chemical interference problem must be solved. Overall, the method is not a good candidate.

4.2.2.3 Turbidimetric, Colorimetric, Titrimetric and Spectrophotmetric. General Electric and SEC/NUS evaluated or suggested a number of other candidate procedures for chloride analysis. All are basically hands-on methods; however, one (titrimetry) could be adapted to remote inline analysis. There has been limited or no laboratory testing of the procedures by SEC/NUS or GE in regard to their applicability to analysis of reactor coolant samples with potential fission product or chemical interferences. However, based on the judgement of personnel at ICPP who have prior experience with the same problems on similar procedures, it is anticipated that iodides and/or other halogens will interfere with all the procedures presented in this section. Furthermore, due to the relatively large size reactor coolant samples required for analysis, 2-50 ml, use of the procedures for hands-on analysis is prohibited under accident conditions. Accordingly, the procedures are not applicable to analysis of postaccident samples without further testing, modification, and development, or without remote use.

For informational purposes, each procedure is briefly outlined below.

Turbidimetric and Colorimetric

The turbidimetric and colorimetric procedures are very similar. Six drops of concentrated nitric acid are added to the sample, 12 ml for colorimetric and 25 ml for turbidimetric; the percent transmittance is recorded; seven drops of 1 N silver nitrate are added; and the percent transmittance is recorded again. The difference between the two recorded measurements is related to the concentration of chloride by the use of calibration standards. For turbidimetry a HACH Turbidimeter equivalent is recommended, and for colorimetry a Coleman Nephro-Colorimeter, or equivalent, is recommended.

Spectrophotometric

The spectrophotometric procedure presented is also simple and commonly used for chloride analysis. It involves the mixing of 10 ml of ferric ammonium sulfate solution, 5.0 ml of mercuric thiocyanate methanol solution, and 25 ml of sample. This is followed by the measurement of the percent transmittance at 463 nm in a 10 cm spectrophotometric cell.

Titrimetry

The titrimetry method is based on the formation of a mercury complex, diphenylcarbozone-bromphenol blue, and mercurous chloride. The end-point color development occurs when mercurous ions are in excess of the chloride. In the procedure 25 ml of sample, 1-2 ml of diphenyl-carbozone, and a few drops of the bromphenol blue indicator are mixed. This is followed by the addition of mercuric nitrate. The quantity of mercuric nitrate added is a function of the chloride concentration.

4.2.2.4 Conductivity of Chloride Solutions. For a dilute solution of an ionic species the specific conductance, K , in $\mu\text{S}/\text{cm}$ is given by:

$$K = 10^3 \Lambda C \quad (4-1)$$

where Λ is the equivalent conductivity and C is the concentration of the ionic species in solution in electrolytic equivalents. When the conductivity of a solution is due to several ionic species, the specific conductance of the solution can be expressed as the summation of the conductances of each of the separate ionic species:

$$K = 10^3 \sum (\lambda_i C_i) \quad (4-2)$$

where λ_i and C_i are respectively the limiting equivalent ionic conductance and concentration of the individual species in solution. Values, which are available in handbooks, of the equivalent conductance of different ionic species can be used to calculate the conductivity or, alternately, the concentration of the ionic species provided the ionic species concentrations are known or the conductivity of the solution is known.

The proposed procedure utilizes the above technique for estimation of upper limits of chloride concentration in postaccident reactor coolant samples. ENICO agrees such a technique is applicable for estimation of upper limits of chloride or other ionic species in solution, but does not believe the technique meets the intent of the NRC requirement for chloride analysis. For example, chloride concentrations calculated from the conductivity of postaccident solution will, in all probability, be in excess of the 0.1 ppm limitation due to the presence of fission products, high radiation fields, and/or other chemicals. As a result, corrective actions will be taken or, more likely, accurate analysis of chloride concentrations will be made. Initial accurate determinations will preclude undue concern and/or unnecessary actions.

4.2.2.5 Summary and Conclusion of Chloride Analysis

Procedures. At present there is only one applicable method for chloride analysis of postaccident chloride analysis: ion chromatography. The other procedures evaluated are not appropriate due to the large sample sizes required and known or anticipated chemical interferences to the procedures. The results and features of the procedures evaluated are shown in Table 6.

The chemical procedures have not been ranked in order of applicability. Of the methods not presently applicable, the specific ion electrode and the titrimetry methods appear to have the most potential due to adaptability to remote use, i.e., reduction of radiological exposures. Their use, however, will depend on elimination of chemical interferences, such as other halogens. Limited investigative work was performed by SEC/NUS to eliminate the chemical interferences. Their technique, which ENICO believes has good potential, was selective oxidation - solvent extraction. Consequently, with additional testing and development one or more of these procedures could be adapted for postaccident use. Specific procedures proposed in the future will require evaluation as they become available.

4.2.3 Dissolved Hydrogen and Oxygen

4.2.3.1 Gas Chromatography (GC) - Hydrogen Analysis. A gas chromatograph consists of a sample injection loop, a chromatographic

column containing a media such as charcoal or molecular sieves, a thermal conductivity cell, and a meter-readout device. The thermal conductivity cell, or detector, has two, matched hot wire filaments. Two streams of carrier gas, e.g., argon, are supplied to the GC from a common source. One stream flows directly past one of the filaments; the other stream flows through the GC column then to the second hot wire filament. In the absence of a sample, the two filaments reach thermal equilibrium (constant resistance) and no detector output is observed. Upon injection of a sample into the GC column, non-equilibrium between the two filaments is created due to the different thermal conductivities of the gases eluted from the GC column to the sample stream filament. The thermal conductivity imbalance generates a detector output.

As the different constituents of a sample are eluted from the GC column at different and specific times, the observed detector outputs can be attributed to the individual component of the gas sample. The magnitude of the outputs are proportional to the concentrations of the different gases in the sample. Quantification of the concentrations is achieved by comparison of the detector output of samples and standards.

The GC suggested by GE is a Baseline Model 1030, or equivalent. The Model 1030 is a microprocessor controlled instrument with thermal conductivity detectors. It is equipped with a gas conditioner, an automatic retention time indicator, and thermal conductivity peak integrator. The suggested GC column is ten feet of 1/8 to 3/16 inch tubing with 5A molecular sieves. The carrier gas (helium) flowrate and pressure are 30 cm³/minute and 15-30 psig; the suggested column temperature was 30-50°C.

Although a Fisher Model 1200 Gas Chromatograph was used in the SEC/NUS development and testing program, SEC/NUS also suggests Baseline GC, or equivalent, for plant applications due to its larger measurement range. Specific GC columns and operational parameters were not given by SEC/NUS. It is assumed the specifications will be similar to those noted by GE. Many combinations of columns, carrier gas flowrates, and temperatures have been used successfully in the past.

TABLE 6

FEATURES OF PROPOSED ANALYTICAL PROCEDURES FOR CHLORIDE

Method Feature	Ion Chromatography	Specific Ion Electrode	Turbidimetric
RANGE (ppm)			
Direct Analysis	0.1 - 100	0.010 - 35,000	0.02 - 10
With 1:100 Dilution	10 - 10,000	Not Applicable	Not Applicable
Overall Range	0.1 - 10,000	due to lack of sensitivity	due to lack of sensitivity
Accuracy (%) (Cl in ppm)	<u>+15</u> (1)	<u>+ 20</u>	<u>+ 30</u> (2)
Sample and/or Analysis Method			
Inline	Yes	Yes	No
Grab	Yes	Yes	Yes
Analytical Backup Required?	Yes, For	Yes, For	No
Sample Collection Method	Inline Available	Inline(4) Available	-- --
Sample Analysis Method	Not Specified	Not Specified	
Sample Size (ml)			
Diluted Analysis Sample	~0.04(6)	100	25
Actual RC	~0.04	10(7)	5(7)
Analysis Time (min)	40 - 120(8)	15	20
Procedure Complexity	Medium	Low	Low
Chemical Interferences? Tested	No	Unknown	Unknown
Anticipated	Yes	Limited	No
	--	Yes	Yes
Radiological Effects? Tested	Unknown	Unknown	Yes
Anticipated	No	No	Yes(9)
	No	No	--
Application			
Routine	Yes	Yes	Yes
Accident	Yes	No	No

TABLE 6 (Continued)

FEATURES OF PROPOSED ANALYTICAL PROCEDURES FOR CHLORIDE

	Colorimetric	Titrimetric	Spectrophotometric
RANGE (ppm)			
Direct Analysis	0.04 - 10	0.1 - 10	0.02 -10.0
With 1:100 Dilution	Not Applicable	Not Applicable	Not Applicable
Overall Range	due to lack of sensitivity	due to lack of sensitivity	due to lack of sensitivity
Accuracy (%) (Cl in ppm)	$\pm 25(2)$	$\pm 20(3)$	$\pm 20(3)$
Sample and/or Analysis Method	No Yes	Yes Yes	No Yes
Inline			
Grab			
Analytical Backup Required?	No --	Yes, For Inline(5)	No --
Sample Collection Method		Available Not Specified	--
Sample Analysis Method			
Sample Size (ml)	12	100(8)	25
Diluted Analysis Sample	2.4(7)	50	5(7)
Actual RC			
Analysis Time (min)	30	20	20
Procedure Complexity	Low	Low	Low
Chemical Interferences? Tested	Unknown No	Unknown No	Unknown No
Anticipated	Yes	Yes	No
Radiological Effects? Tested	Unknown No	Unknown No	Unknown No
Anticipated	Yes	No	Yes
Application	Yes	No	Yes
Routine	No	No	No
Accident			

Notes:

- 1) The accuracy of the IC measurements is $\pm 15\%$ in the 0.1 to 1.0 ppm chloride range and is $\pm 25\%$ for higher concentrations. By calibration at higher concentrations, the accuracy can be maintained at $\pm 15\%$.

- 2) The uncertainties were estimated from calibration curve data presented in the associated documentation.
- 3) The uncertainties are based on professional judgement.
- 4) The SIE method could be adapted for inline use.
- 5) The titrimetry procedure could be used as the inline method by employment of a technique similar to the DigiChem Analyzer method for boron analysis.
- 6) The ion chromatographic procedure uses small (≈ 0.4 ml) undiluted reactor coolant samples.
- 7) Due to insufficient sensitivity, smaller reactor coolant samples are inappropriate for these methods.
- 8) The titrimetry procedure has sufficient sensitivity to measure 0.1 ppm chloride; however, 50 ml of reactor coolant is required. The method is now in use at LOFT at INEL.
- 9) Limited radiological effect testing was performed by GE on the turbidimetric procedure. At the maximum anticipated dose rate, 8×10^3 rad/h in a diluted 25 ml sample (0.1 ml diluted to 25 ml), an equivalent response of 1.8 ppm of chloride was calculated from measurement data.

The sample collection procedures for dissolved gases proposed by SEC/NUS and GE are similar. The GE procedure involves the isolation of 70 ml of pressurized reactor water, the depressurization of the sample into a 20 ml gas holding container, and the transferral of aliquots from the gas holding container to 15 ml septum bottles. The 15 ml septum bottles are transferred to the laboratory for GC analysis and/ or further dilution. In the laboratory, gas tight syringes are used to take 1.0 ml aliquots from the septum bottles for injection into the GC. The procedure employs Henry's Law and a tracer gas, which is injected into the sample prior to depressurization, to determine sample yield.

The sample collection procedure of SEC/NUS involves the isolation of a 30 ml pressurized reactor water sample, depressurization of the sample, the quantitative transferral of the dissolved gases into a 300 ml gas holding cylinder via an argon gas purge, and the pressurization of the 300 ml cylinder to atmospheric pressure with the argon purge gas. From the 300 ml gas holding cylinder small samples, 0.25 or 1.0 ml are injected remotely into the GC for analysis.

Following collection of the dissolved gas samples the time required for GC analysis is less than ten minutes.

The measurement range reported by SEC/NUS is based on extensive laboratory studies and is applicable for 25-25,000 ppm hydrogen for a 1.0 ml dissolved gas sample. The dilutions associated with the sample collection procedure and the 30 ml sample used for depressurization create a range of 0.5 - 2000 cm^3 of dissolved hydrogen per kilogram of reactor coolant. The accuracy of the measurements is ± 10 percent.

General Electric did not report a measurement range; however, an estimate of the lower limit of detection was mentioned. Their estimate of the lower detection limit, based on limited laboratory studies, is 0.1 volume percent or 1000 ppm for a 1.0 ml dissolved gas sample. ENICO believes this detection limit is a factor of ten or more high and that the actual detection limit will be similar to the one measured by SEC/NUS, i.e., 100 ppm or lower. If such a detection limit is verified by GE, ENICO estimates the measurement range of the GE gas

chromatograph method for dissolved hydrogen in reactor water will be $\sqrt{0.1-2000}$ cm³ per kilogram of water. The estimate is based on the relative size of reactor water samples taken for analysis and the relative volumes of the gas holding cylinders of the SEC/NUS and GE sample collection systems.

The advantages of the GC methods proposed by the two vendors are sufficient measurement ranges, the application to routine and accident usage, the simplicity of operation, and the selective measurement of hydrogen, not total gases. The advantages of the SEC/NUS method over the GE method are the extensiveness of laboratory testing performed by SEC/NUS and the remote analysis capability of the SEC/NUS system. The latter advantage is quite significant as calculated¹⁴ dose rates due to noble gases associated with the dissolved gases in unit volumes of reactor water are in excess of 10^4 R/h at one centimeter. As a result the dose rates associated with the GC samples, even with dilution, are potentially a few R/h and will require more caution for hands-on analysis than remote analysis.

The disadvantage of the GC method in general is related to maintenance of the instrument; however, this is not considered significant as GC's are generally very dependable. Another limitation of the method is the lack of laboratory tests on the effects of high radiation field on the procedure; however, there are no anticipated effects.

4.2.3.2 Gas Chromatography, Yellow Springs Analyzer -

Dissolved Oxygen Analysis. As described in the previous section, different constituents in a gas sample are separated in a GC column due to their characteristic diffusion rates through a medium such as charcoal, molecular sieve, etc. As a result GC lends itself to the simultaneous determination of oxygen and hydrogen from the analysis of a single sample.

General electric proposed to use this technique for dissolved oxygen analysis, i.e., simultaneous measurement of hydrogen and oxygen in a single sample. The sample collection procedure, instrumentation, and associated equipment proposed are identical to the ones described above. Specific measurement ranges were not provided by GE.

ENICO's estimate of the measurement range is $\sqrt{1}$ to 400 ppm in the reactor coolant. The basis of the estimate are the relative thermal conductivities²² (detector responses) of oxygen and hydrogen and the hydrogen measurement range estimated for the GE system in the above section. This estimated oxygen is inadequate for postaccident analysis of reactor coolant samples as the sensitivity of the procedure is insufficient to measure below 1 ppm dissolved oxygen. However, before the GC procedure is precluded from postaccident application, it should be experimentally verified that the sensitivity of the GC method is inadequate.

Sentry Equipment Corporation proposed an inline monitor for postaccident determinations of dissolved oxygen in reactor coolant. The instrument selected and laboratory tested was a Yellow Springs Instrument (YSI) Model 54 Oxygen Analyzer. The sensing probe, which contains a semipermeable membrane, is remotely located from the meter and output device. The probe holder was redesigned to minimize fluid volume and associated radiation exposure. Calibration of the system is achieved with an oxygen saturated demineralized water source. The actual oxygen content of the standard solution is determined from the temperatures of the water and a solubility chart relating dissolved oxygen to water temperature.

Laboratory tests verified that there were no interferences due to hydrogen in solution or variations in sample flowrate. One problem observed during the tests was a pin hole in one of the probe membranes. This resulted in erratic results. Replacement of the membrane corrected the problem.

Laboratory testing also verified that the accuracy ($\pm 5\%$) was sufficient to measure 0.1 ppm dissolved oxygen. The measurement range was linear between 0.1-7.85 ppm oxygen. Concentrations above 7.85 ppm oxygen were not laboratory tested. It is anticipated the measurement range will be valid up to 20 ppm oxygen; however, this needs verification.

Provided the measurement range can be demonstrated to be 0.1-20 ppm, the YSI Analyzer is applicable to postaccident

applications. The Model 54 Analyzer lacks sufficient sensitivity for routine use. SEC/NUS proposed a Rexnord Analyzer for routine use (sensitivity-ppb) or alternately a Model 56 YSI Analyzer with reported higher sensitivity. The routine condition monitor will be installed in parallel with the accident condition monitor.

The advantages of the YSI oxygen monitors are the remote operability, simplicity, and potentially adequate measurement range.

The disadvantage of the systems is the time, 1-4 hours, required for the system to reach equilibrium after the internal portions of the sensing probe are exposed to air. Based on a review of the literature on the effects of irradiation on the components of the sensing probe, no radiological effects are anticipated. The maximum dose anticipated to the different materials of construction in the probe is 10^4 rads; the minimum doses causing damage to the materials was reported at 10^6 rads.

4.2.3.3 Evaluation Summary of Dissolved Oxygen and Hydrogen Analysis. The gas chromatographic methods proposed by SEC/NUS for dissolved hydrogen analysis is applicable to postaccident sample analysis. It has sufficient sensitivity, accuracy, and range of measurement (0.5-2000 cm^3 hydrogen per kilogram of reactor coolant, $\pm 10\%$). The measurement range associated with the GE method needs to be verified. After completing collection of the dissolved gas sample, the analysis time is ten minutes or less. The SEC/NUS sample handling has an advantage over the GE procedure due to its remote mode of sample handling. Precautions should be taken when manually handling the dissolved gas samples due to the potentially high radiological fields. The GC method is applicable to routine conditions also. Radiological interferences to the GC method are not anticipated.

The GC method proposed by GE for dissolved oxygen analysis appears to lack sufficient sensitivity for required measurement of low (<0.1 ppm) concentrations of oxygen. Without further testing to demonstrate the capability of the method to measure the low concentration, the GC method for oxygen analysis is not applicable to post accident sample analysis.

The inline oxygen monitor proposed by SEC is applicable to postaccident analysis provided information is available to verify its ability to measure dissolved oxygen over the entire range of 0.1-20 ppm. At present the measurement range has been demonstrated to be valid between 0.1 and 7.85 ppm only.

In ENICO's opinion, the proven measurement range is sufficient as the intent is to measure the absence of oxygen, not necessarily the presence. If NRC does not agree, additional laboratory studies need to be performed to extend the measurement range.

To meet all NUREG-0737 requirements, licensees which use inline method for analysis must have a backup capability to obtain grab samples and to perform analysis performed by the inline monitor. Dissolved oxygen analysis by hands-on techniques will require diluted, pressurized samples or techniques to collect the gases (oxygen) from a liquid sample. Conventional methods, eg., Winkler, of hands-on analysis can not be used due to the large sample sizes required and/or a lack of sensitivity. Alternative methods must be identified.

4.2.4 Conductivity and pH

4.2.4.1 Conductivity. Both SEC/NUS and GE propose the use of inline monitors for measurement of conductivity. Their proposed conductivity meters have measurement ranges of 0-500 $\mu\text{S}/\text{cm}$ and 0-100 $\mu\text{S}/\text{cm}$, respectively. The proposed probes have conductivity cells with 0.1 cm cell constants; they are located remote to the meters. The inline probe tested by GE was a standard, commercially available one, and the probe tested by NUS used a modified probe holder designed to minimize fluid volume. The actual cell volumes were not specified. The accuracy associated with the measurements was not specified either; however, high accuracy for 0-2 $\mu\text{S}/\text{cm}$ and decreasing accuracy for higher conductivities was noted.

Laboratory tests were performed by both GE and SEC/NUS. The GE tests involved measurements of the conductivity of water flowing first through a conductivity cell under irradiation and then through a second in-series conductivity cell not under irradiation. The irradiation fields were varied between 1.3×10^4 rads/h to 9.8×10^5

rads/h. GE also made static (no flow) measurements with the above arrangement. Finally, GE performed conductivity measurements on a 10 ppm chloride solution with (9.8×10^5 rads/h) and without irradiation and with and without flow through the cells. The SEC/NUS laboratory testing was limited to establishing the operability with a flowing sample stream, the effects air bubbles in the air stream, and the effects of hydrogen peroxide on conductivity measurements. SEC/NUS also conducted a literature review for potential radiation effects to the components of the sensing probe.

The results of GE tests on the two in-series cells indicated that the cell under irradiation and the one not under irradiation gave the same results and that the conductivity of the solution increased from 0.1 $\mu\text{S}/\text{cm}$ to 0.65 $\mu\text{S}/\text{cm}$ as the irradiation intensity was increased. The cause for the increase in conductivity is unknown; however, it obviously is due to the generation of an unknown conductive species. The hypothesis that the unknown species is hydrogen peroxide is not supported by the chloride solution tests performed by GE and the hydrogen peroxide tests performed by SEC/NUS; i.e., the conductivity did not change with the addition of chloride - added to decrease the generated species - or with the addition of hydrogen peroxide directly to the flowing stream.

Further results of the SEC/NUS tests show that the monitor is applicable to a flowing sample stream and that the presence of air bubbles at five percent of the water volume does not alter the accuracy of the measurements.

The literature review indicates that the resistance of the probe components to radiation exposure exceeds the anticipated radiation dose by a factor of one hundred or more.

The advantages of the method are its utility under accident and normal condition, its resistance to radiation damage, the remote operational mode, and its simplicity.

There are no apparent disadvantages even though the conductivity of water solutions increased with increasing radiation doses. This observation only implies that the monitor was operating

properly as its response increased with an increase in the conductivity of the solution.

A backup method for measurement of conductivity of grab samples was not noted. However, there are commercially available portable conductivity meters which are appropriate for this purpose.

4.2.4.2 pH. To investigate methods of determining pH under postaccident conditions, SEC/NUS evaluated an industrial grade inline pH probe and a sealed, permanently-filled reference electrode. The vertical probe holder, modified to minimize fluid volume, prevents entrapment of air bubbles. A double O-ring seal is used to prevent leakage. The probe can be calibrated in place by injection of buffer solutions (pH 7 and 10) into the sample loop. The probe output is recorded on an industrial grade meter mounted in a remotely located instrument panel.

Testing of the pH monitor was performed to determine its applicability to a flowing sample stream and to evaluate the effects of air bubbles in the liquid. Data indicated the pH monitor is not affected by variations in flow or by the presence of air bubbles.

The optimum operating temperature range of the pH probe is 75-90⁰F; the maximum temperature and pressure are 125⁰F and 100 psig. With constant control of the pH probe at a given temperature within the optimum operational range, the accuracy and measurement range will comply with NRC requirements, 1-13 ± 0.3 pH units.

As inline pH monitors have been used reliably for a number of years in the chemical and nuclear industries, there are no apparent disadvantages. The advantages are the application to accident and routine use, the remote operability, the simplicity, and the sufficient measurement range and accuracy.

To fulfill all NUREG-0737 requirements, however, a backup capability to measure the pH of grab sample must be provided. With the proposed grab sample collection systems, this will require pH measurements of diluted reactor coolant samples. ENICO anticipates that pH's measured in diluted samples cannot be used to accurately determine

the actual pH of the reactor water. For example, based on a 1:100 dilution of a 0.1 ml reactor coolant sample with deionized water (pH 7.0), the estimated pH of the reactor coolant water determined from the analysis of the diluted sample could be in error by 2-7 pH units. This takes into account the results of dilution only and not the presence of other constituents which can affect the pH. Accordingly, ENICO does not recommend the use of diluted grab samples for measurement of reactor coolant pH.

General Electric Company suggested the use of pH paper for measurement of pH in reactor water. In conjunction with this idea, a series of laboratory tests were performed to determine the effects of high irradiations on the accuracy of the method. The pH paper was immersed in solutions with pH 3.8 and 10.0 and irradiated for ten minutes (1.6×10^5 rads) in one study and one minute (1.6×10^4 rads) in another study. The colors of the solutions were completely destroyed in the ten minute test and significantly altered in the one minute test (0.5 pH unit shift).

To compensate for this effect, GE suggested that the procedure be modified to decrease the exposures to the pH paper. The suggestion was to moisten the paper with a drop or two of sample instead of total immersion of the pH paper in the sample solution. The proposed modified procedure was not demonstrated to be successful.

ENICO does not believe the pH paper method is satisfactory at present due to the irradiation effects observed. Its future applicability will depend on the additional testing and the development of a technique to collect a small, undiluted reactor coolant sample and to perform the measurement in a radiologically safe manner.

General Electric also suggested that the conductivity of a solution is a potential method to ensure that the pH of the reactor coolant is within certain acceptable ranges, i.e. 5.6 to 8.6. ENICO does not believe this technique meets the NRC intent as the conductivity of the reactor coolant can possibly vary over a large range under accident conditions and cannot be used as an indication of pH with the required accuracy.

4.2.4.3 Summary of Conductivity and pH Analysis Methods.

The method proposed by SEC/NUS and GE is applicable for measurement of the conductivity of reactor coolant water. It includes an inline conductivity cell with a remote readout meter. A backup capability to measure the conductivity of grab samples was not noted by SEC or GE. This backup capability can be provided with commercially available, portable conductivity meters for analysis of grab samples. Alternately, a backup capability, with NRC's concurrence, would be a second, independent inline monitor which could be put into service upon the failure of the first monitor. The monitors are applicable to accident and normal conditions.

Although there was an increase in conductivity of test solutions with an increase in radiation exposures, the effect was not due to monitor component failure. It was a result of an increase of the conductivity of the test solution. It is unknown if the increase in conductivity of the test solutions was inherent to the experimental conditions or whether one should anticipate the generation of a conductive species in postaccident reactor coolant water.

At present the only proven methods which has satisfactory accuracy and is applicable to measurement of pH under accident conditions are inline monitors. The use of pH paper is not applicable due to inaccuracies caused by high radiation fields. The pH paper method may be applicable with further testing; however, the method will require the development of techniques for the remote addition of small reactor coolant samples to the pH paper and for the remote comparison of the pH paper colors with standards.

The pH analysis of diluted reactor coolant samples is not recommended due to the potential inaccuracies of the measurements. The only alternative for a backup analysis capability is the use of two independent inline monitors; one in service and one in standby.

The pH inline monitors are applicable to both accident and routine use. There are no anticipated radiological effects.

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