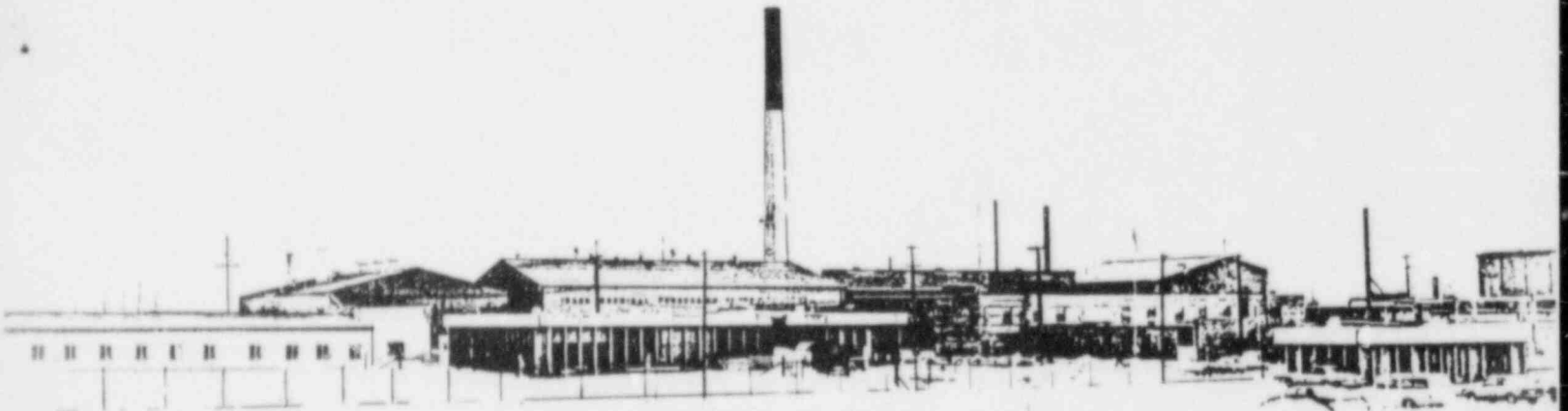# LABORATORY MEASUREMENTS OF PARAMETERS AFFECTING WET DEPOSITION OF METHYL IODIDE

SEPTEMBER 1984

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LABORATORY MEASUREMENTS OF PARAMETERS
AFFECTING WET DEPOSITION OF METHYL IODIDE

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ABSTRACT

The transfer of gaseous methyl iodide (CH_3I) to raindrops and the initial retention by vegetation of CH_3I in raindrops have been studied in a laboratory experimental program. The measured air-to-drop transfer parameters and initial retention factors both affect the wet deposition of methyl iodide onto vegetation. No large effects on the air-to-drop transfer due to methyl iodide concentration, temperature, acidity, or rain type were observed. Differences between laboratory measurements and theoretical values of the mass transfer coefficient were found. Pasture grass, lettuce, and alfalfa were used to study the initial retention of methyl iodide by vegetation. Only a small fraction of the incident CH_3I in raindrops was held by any of the three vegetation types.

SUMMARY

The ability to predict the behavior of radioiodine in the atmosphere
during periods of precipitation is important to evaluating the
consequences of both normal and accidental releases of radioiodine from
nuclear power plants. The processes controlling deposition of radioiodine
in the atmosphere to vegetation and the subsequent retention of the
radioiodine by vegetation are only qualitatively understood. To under-
stand these processes better, a program of laboratory measurements was
conducted to measure parameters used to describe the precipitation
scavenging and the retention of radioiodine in wet deposition. This
report contains results of laboratory experiments using methyl iodide
(CH_3I).

The effects on air-to-drop transport of methyl iodide of several environ-
mental variables were studied. The variables studied and the ranges
considered were: methyl iodide concentration (10^1--10^8 ng/m^3), temperature
(15--27°C), rain drop acidity ($3 \leqslant pH \leqslant 5$), and type of rain (coastal or
inland). Laboratory measurements show no large (factor of 10) differences
in the transfer of methyl iodide to drops for those variable ranges. Dif-
ferences between mass transfer rate constant derived from the measurements
and the theoretical value and between the laboratory results and recently
reported field measurements were identified. The mathematical model over-
estimates the transfer of CH_3I to raindrops under laboratory experimental
conditions. Field measurements reported in the literature showed CH_3I
concentrations in rain and snow that greatly exceed those observed in the
laboratory. They also exceed the values expected from equilibrium
partitioning calculations. However, the field measurements may reflect
mechanisms that would not be operative for raindrops scavenging CH_3I from
a plume.

Laboratory experiments to measure the initial retention by vegetation of
methyl iodide in wet deposition were also conducted. The results for
pasture grass, lettuce, and alfalfa indicate that the initial retention

is quite low, 1--3%. No correlation of the initial retention factor with vegetation density was found, which suggests that binding of the ^{131}I to plant surfaces is the principal determinant of the initial retention. On that basis, initial retention factors in the environment would be expected to be comparable to those observed in the laboratory, even though the laboratory raindrops were not falling at terminal velocity.

Losses of ^{131}I deposited as CH_3I in rainfall were significant during the first four hours after rainfall. Typically, 60% of the activity was lost from the vegetation as the plant surfaces dried. Further losses between 4 and 35 hours were minimal.

RECOMMENDATIONS

Laboratory measurements indicate that the model described in Section 2.1 provides conservative estimates of transfer of methyl iodide from air to raindrops. It is recommended that the model be used to estimate the scavenging of methyl iodide from effluent plumes during normal operations and following accidents. The laboratory measurements indicate that the normal range of environmental conditions would not greatly change the expected transfer rates, so site-specific modeling is unnecessary. However, caution is advised because some field measurements (Ref. 14) show that concentrations in rain and snow can greatly exceed those predicted by the model. Further investigation of the observed enrichment of methyl iodide in precipitation is recommended. Field measurements of scavenging of methyl iodide from plumes are highly desirable.

The initial retention of methyl iodide in wet deposition was estimated from laboratory experiments to be in the range of 1--3%. Until results of field measurements are available, it is recommended that an initial retention factor of 0.02 be used.

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1. INTRODUCTION

To estimate the wet deposition to vegetation of radioiodine released from nuclear facilities during normal operations or following accidents, it is necessary to quantify parameters that describe (a) atmospheric precipitation scavenging processes, and (b) subsequent retention of radioiodine species by vegetation. The radioiodine species of interest are radioiodine associated with particulates (such as CsI), elemental iodine (I_2), and organic iodides (such as CH_3I).

This study was undertaken to obtain data needed to compare the scavenging of various iodine species and the initial retention of the iodine species on vegetation. The first species studied was methyl iodide (CH_3I), a representative of the class of organic iodides. The two processes being examined are the transfer of airborne radioiodine to raindrops and the retention by vegetation of radioiodine carried to ground level by rain.

The drop scavenging experiments are discussed in Section 2. A theoretical approach to the problem of estimating the absorption and desorption of methyl iodide by raindrops is given in Subsection 2.1. The experimental apparatus, experimental techniques, and measurement methods are described in Section 2.2, and the results of the measurements made under various conditions are presented in Subsection 2.3. The significance of the experimental values is discussed and comparisons with theory are presented in Subsection 2.4.

The measurements of the initial retention by vegetation of CH_3I in precipitation are presented in Section 3. The experimental techniques are described in Section 3.1. Then the experimental results are presented (Section 3.2) and conclusions given (Section 3.3).

2. SCAVENGING OF CH$_3$I BY FALLING DROPS

2.1. Theoretical Considerations

Hales[1] developed a detailed theoretical analysis of the scavenging of gases by rain that considers both sorption and desorption from the drop. For a gas obeying Henry's Law, Hales gives the following expression for the change of concentration of gas in a drop as a function of fall distance:

$$\frac{dC}{dZ} = \frac{6K}{vd} \left[\chi - \frac{C}{H} \right] \tag{2-1}$$

where C = the average concentration (μCi/g) of gas in the drop,
    Z = the vertical fall distance (cm),
    K = the overall mass transfer coefficient (cm/s),
    v = the drop fall velocity (cm/s),
    d = the drop diameter (cm),
    χ = the concentration (μCi/g) of gas in the air, and
    H = the equilibrium partition coefficient.

Both C and χ vary with height in the atmosphere. The partition coefficient H is the dimensionless ratio of the concentration of the gas in the liquid phase to that in the gas phase. The partition coefficient is the inverse of the Henry's Law constant for the gas.

For drops falling through a constant concentration of methyl iodide in air, integration of Equation (1) yields

$$C(Z) = C_0 e^{-bZ} + H\chi (1-e^{-bZ}) \tag{2-2}$$

where C_0 is the concentration (μCi/g) in the drop, at the start of its fall through the airborne methyl iodide, and Z is the fall distance (cm), positive downwards.

The transfer rate constant b (cm^{-1}) is defined by

$$b = \frac{6K}{vdH} \qquad (2-3)$$

In the atmosphere, the concentration of methyl iodide in a drop encountering a plume would be close to zero, but in our experiments, drops are also exposed to approximately the same concentration of methyl iodide during formation as during fall.

The overall mass transfer coefficient (K) depends upon the gas and liquid phase mass transfer coefficients. For falling drops, the gas phase mass transfer coefficient, derived by analogy from heat transfer,[2] is taken to be:

$$k_g = (2 + 0.6\ Re^{1/2}\ Sc^{1/3})D/d \qquad (2-4)$$

where Re = the Reynolds number, $\rho dv/\mu$ (dimensionless),

Sc = the Schmidt number, $\mu/\rho D$ (dimensionless),

D = the diffusivity of the tracer in air (cm^2/s),

ρ = the density (g/cm^3) of air, and

μ = the viscosity (g/cm-s) of air.

For slightly soluble gases like methyl iodide the liquid phase resistance is the dominant factor in determining the overall mass transfer.[3,4] In analyzing the removal of methyl iodide by various types of reactive spray droplets in reactor containments, Coleman and Postma have employed a result of Danckwerts,[5] which is derived from a heat transfer result of Carlslaw and Jaeger.[6] Danckwerts gives the following expression for the amount of gas absorbed by a drop:

$$Q(t) = 2\pi\ HX\ D_L\ h^2\ d^2 \sum_{n=1}^{\infty} \frac{kt\ (k+D_L\gamma_n^2) + D_L\gamma_n^2\ (1-e^{-(k+D_L\gamma_n^2)t})}{(k+D_L\gamma_n^2)\ (d\gamma_n^2 + h(dh-1))\ (0.5)} \qquad (2-5)$$

where Q(t) = the amount of gas absorbed by a falling drop,

t = the time (s) the drop is exposed to the gas,

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D_L = the diffusivity (cm^2/s) of the gas in water, and

k = the first-order chemical reaction rate constant.

The parameter h is defined by Equation (2-6):

$$h = \frac{k_g}{HD_L} \tag{2-6}$$

and γ_n designates the successive roots of the equation:

$$(\gamma d/2) \cot (\gamma d/2) - (1-dh/2) = 0. \tag{2-7}$$

Reference 6 contains roots to Equation (2-7) for different values of the constant (1-dh/2).

For cases when h is large, Equation (2-5) can be simplified.[3] Data given below show that this simplification is appropriate for methyl iodide. The overall mass transfer rate can be obtained from the simplified expression for Q(t) and written as

$$K = \frac{4HD_L}{d} \sum_{n=1}^{\infty} \frac{\alpha + \frac{n^2\pi^2}{\alpha+n^2\pi^2} \quad 1-e^{-(\alpha+n^2\pi^2)}}{\alpha+n^2\pi^2\beta} \tag{2-8}$$

where $\alpha = kt$, and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (2-9)

$$\beta = \frac{4D_L t}{d^2}. \tag{2-10}$$

Much of the information needed for computations of mass transfer co-efficients for methyl iodide has been summarized by Knudsen.[7] Information on the first-order rate constant for the reaction of methyl iodide and water has been given by Schwendiman et al.[9] Measurements of the partitioning of methyl iodide were reported in Reference 8, and more recently by Hunter-Smith et al.[9] The two relationships for the partition coefficient for methyl iodide differ substantially at the temperatures of interest. Reference 8 gives the following relationship for the temperature range of 5--70°C.

$$\log H = -4.82 + 1597/T \tag{2-11}$$

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in which T is the absolute temperature (^OK). In Reference 9, the following best-fit equation

$$\ln H = -10.34 + 3541/T \qquad (2-12)$$

was derived from measurements made at temperatures of 10--25°C. Equation (2-12) reflects measurements made over the temperature range of interest and was chosen for calculations of H in this study. Table I contains the computed values of H and other parameters for two temperatures.

TABLE I.   PARAMETERS USED TO ESTIMATE MASS TRANSFER
OF METHYL IODIDE FROM AIR TO RAINDROPS

Parameter	Value at Specified Temperatures 25°C	15°C
μ (g/cm-s)	1.86×10^{-4}	1.81×10^{-4}
ρ (g/cm^3)[a]	9.92×10^{-4}	1.03×10^{-3}
D (cm^2/s)	0.134	0.013
D_L (cm^2/s)	1.41×10^{-5}	1.07×10^{-5}
H	4.64	7.00
k (s^{-1})	7.8×10^{-8}	3.9×10^{-8}
k_g (cm/s) (Equation 4)[b]	6.78	6.53
X (cm/s) (Equation 8)[b]	0.027	0.036
b (cm^{-1}) (Equation 3)[b]	5.7×10^{-4}	4.9×10^{-4}

a. For the average INEL pressure of 637 mm Hg.

b. For the laboratory experimental conditions: d=0.28 cm and v= 20 cm/s.

In results reported here, the average drop diameter was 0.28 cm and the mean fall velocity v was 220 cm/s. Values of k_g from Equation (2-4) are also shown in Table I. For 25°C, Equation (2-6) then yields a value of h

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of 1×10^5, and it is clear that the condition for simplification of Equation (2-5) is satisified. The same conclusion would be reached for the spectrum of raindrop sizes and fall velocities found in the environment.

The summation in Equation (2-8) approaches its true value asymptotically. Calculations were made using values of n as large as 1000. The 1000-term sums, 29.0 for $25^\circ C$ and 33.3 for $15^\circ C$, were used in calculations of K. The magnitude of the 1000th term was found to be about 10^{-5} of the total for those two temperatures. The fractional difference between the results for n=1000 and n=800 was 0.2%. Therefore, the use of 1000 terms in the summation was considered to be an adequate approximation of the true value. Computed values of the overall mass transfer coefficient and of the parameter b are also presented in Table I.

2.2. Experimental Apparatus and Techniques

The experimental apparatus, experimental techniques, and measurement methods are described in the subsections that follow. The chambers in which the experiments were performed are described first. That is followed by descriptions of the techniques used (a) to prepare methyl iodide labeled with ^{131}I tracer, (b) to prepare the four types of rain used in the experiments, and (c) to collect the raindrops and to determine their ^{131}I content. The final subsections describe the measurements of the concentration of CH_3I in chamber air, the air temperature, and the relative humidity.

2.2.1 Experimental Apparatus

Figure 1 is a diagram and Figure 2 is a photo of the experimental chamber currently being used for measurements of air-to-drop transport. Many of the initial experiments with CH_3I were conducted in a similar chamber which lacked the recirculation loop and associated equipment. Both chambers were constructed from 15-cm diameter Pyrex tube stock. The injection and sampling ports were made of smaller diameter glass tubing and fitted with appropriate stopcocks or connections to attached stainless steel inlet and exhaust lines.

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Rain Reservoir

Temperature/ Humidity Probe

Recirculation Arm

Sampling Port

Steam Bubbler

CH$_3$I Tank

Charcoal Filter

Off-Gas

Main Body of Chamber

Circulation Fan

Drop Collection Vial
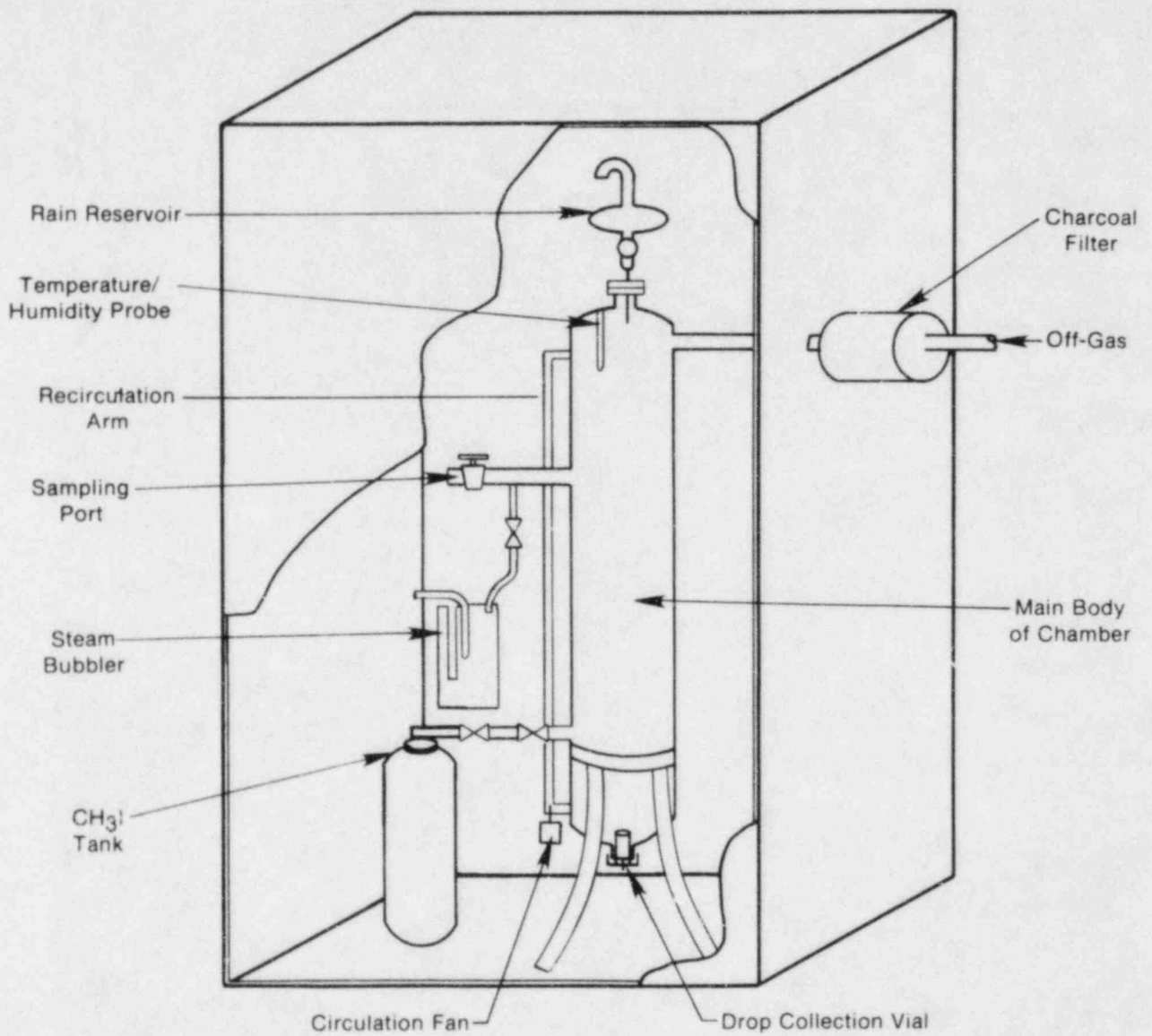
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Figure 1.   Chamber for Air-to-Drop Transfer Measurements
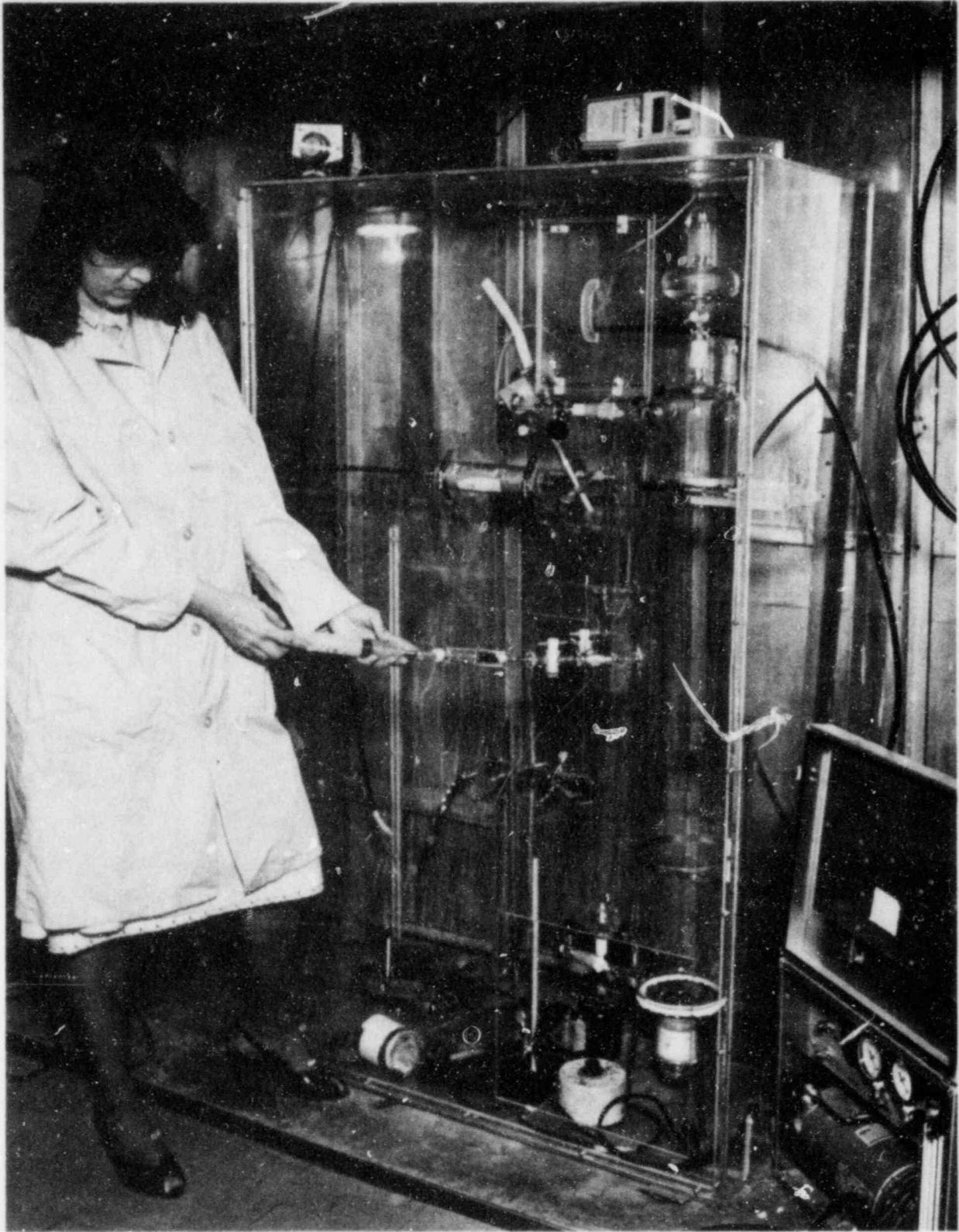
Figure 2. Experimental Chamber and Air Sampling Process

Centered at the top of the chamber is the glass reservoir (Figure 3) containing simulated rainwater (see Subsection 2.2.3). The reservoir liquid feeds through a Teflon stopcock to the stainless steel hypodermic needle used to produce drops of simulated rain. The rate of drop production was regulated manually using the stopcock. Centered in the removable bottom plug was the drop collection container (see Subsection 2.2.5). The drops fall from the tip of the needle to the collection medium, a distance of 100 cm in the chamber shown in Figures 1 and 2.

The injection point for CH_3I is located near the bottom of the chamber. Stainless steel tubing and valves were used to carry the CH_3I from the 8-liter steel cylinder to the experimental chamber. Kynar fittings were used for the glass-to-metal tubing connections at the chamber inlet and exhaust points. Air exhausted from the chamber was filtered through a 2.5-cm bed of Barnaby Cheney Type 151 (BC-151) KI_3-impregnated charcoal in the outlet line. A second 2.5-cm bed of the same charcoal was used as a protective backup filter. In several of the initial experiments the contents of the vessel were exhausted through an iodine species sampler to verify the methyl iodide content of the vessel. Water vapor from a steam bubbler (Figure 1) was injected through a port located near the center of the chamber. The T-shaped sidearm attached to the port was normally sealed using Teflon stopcocks. Sampling of the chamber air was accomplished through the same port (see Subsection 2.2.6).

A variable speed fan was operated at the bottom of the recirculation loop to assure good mixing of chamber air and to provide the air motion required for the measurement of relative humidity using a psychrometer. The wet and dry bulb temperature elements are located at the top of the loop (Figure 1). The relative humidity in the chamber was estimated using the wet and dry bulb temperature data. In the original chamber, measurement of the relative humidity was not possible. The air temperature in that chamber was measured using a thermocouple enclosed in a glass tube that protruded downward from the top of the chamber into the air space.
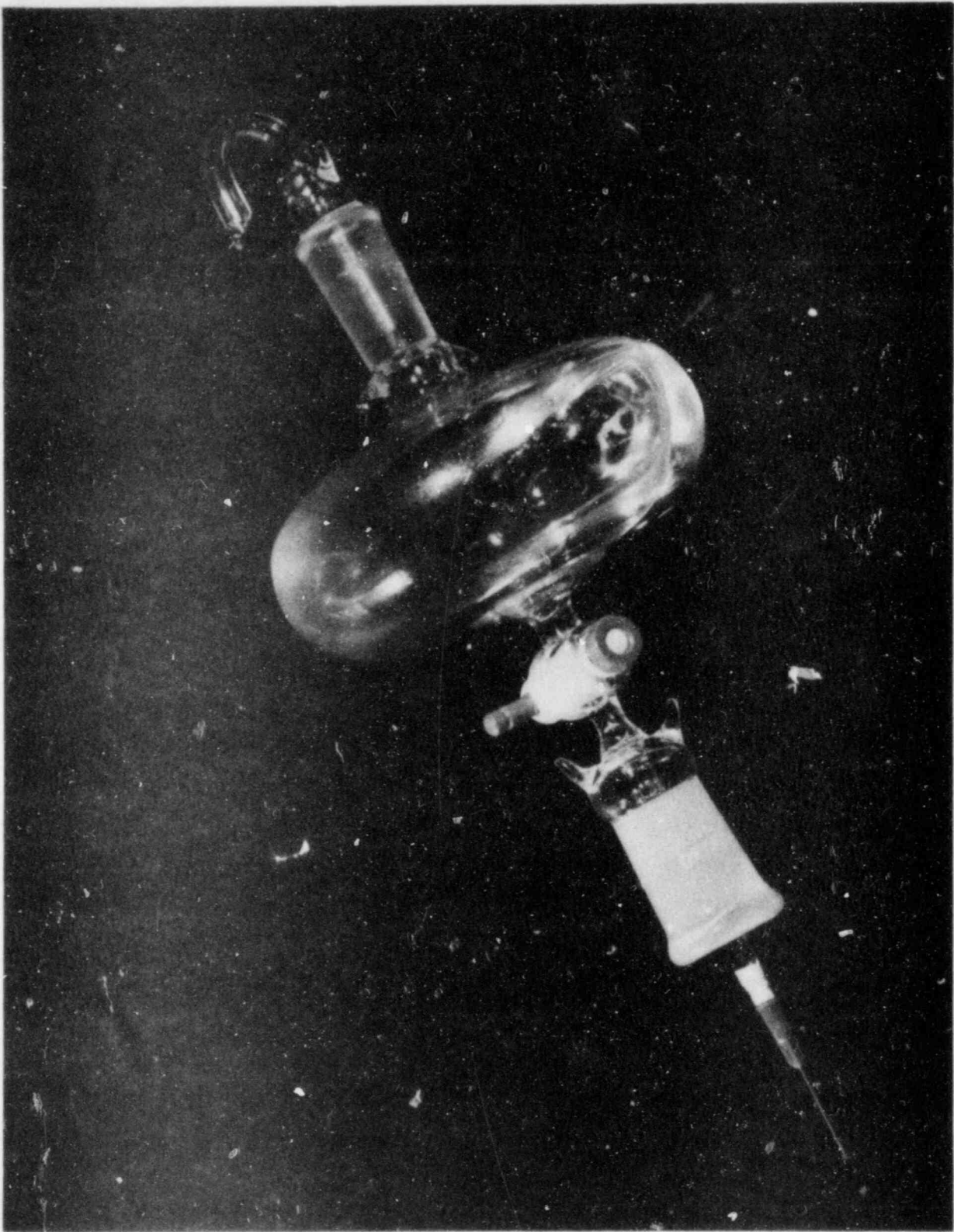
Figure 3. Rainwater Reservoir and Hypodermic Needle

A short chamber, having a volume of 3 liters and a drop fall distance of about 4 cm was used to measure the uptake of methyl iodide during drop formation. Injection of CH_3I, air sampling, and collection of drops were performed as described below for the taller chambers. The same drop generation apparatus was used in the short and tall chambers.

2.2.2 Preparation of CH_3I

Methyl iodide labeled with the radionuclide ^{131}I was prepared by reacting labeled sodium iodide with dimethyl sulfate in the presence of calcium carbonate.[10] The chemical reaction is shown below:

$$(CH_3)_2SO_4 + 2\ ^{131}INa \xrightarrow[CaCO_3]{heat} 2\ ^{131}ICH_3 + Na_2SO_4 \tag{2-13}$$
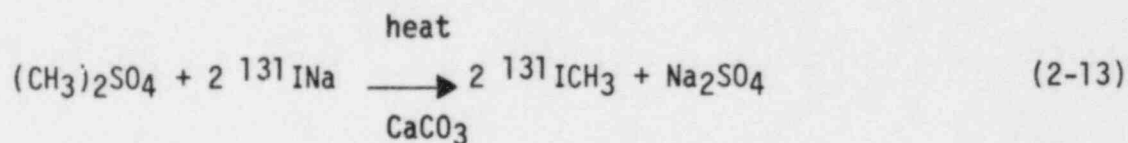
The reaction solution was purged with a flow of helium gas at 300 cm^3/minute to aid removal of the labeled methyl iodide. The gases then entered the receiving vessel, a previously evacuated 8-liter stainless steel tank. The methyl iodide generation and collection required about 20 minutes to complete. After the tank was disconnected from the generator, air was admitted to equilibrium with atmospheric pressure. The tank containing the radioactive methyl iodide was then taken to the laboratory containing the experimental chamber. A schematic diagram of the apparatus used to prepare CH_3I is shown in Figure 4.

2.2.3 Preparation of Simulated Rains

Four different types of simulated rain were used in the experiments. The two principal variants, termed inland rain and coastal rain, were prepared to match the reported constituents of natural rain at remote locations in the world. Data on the composition of rain from the Global Precipitation Chemistry Project[11] were used as the basis for preparing rain simulants. Average concentrations of ions in rain water are shown by category in
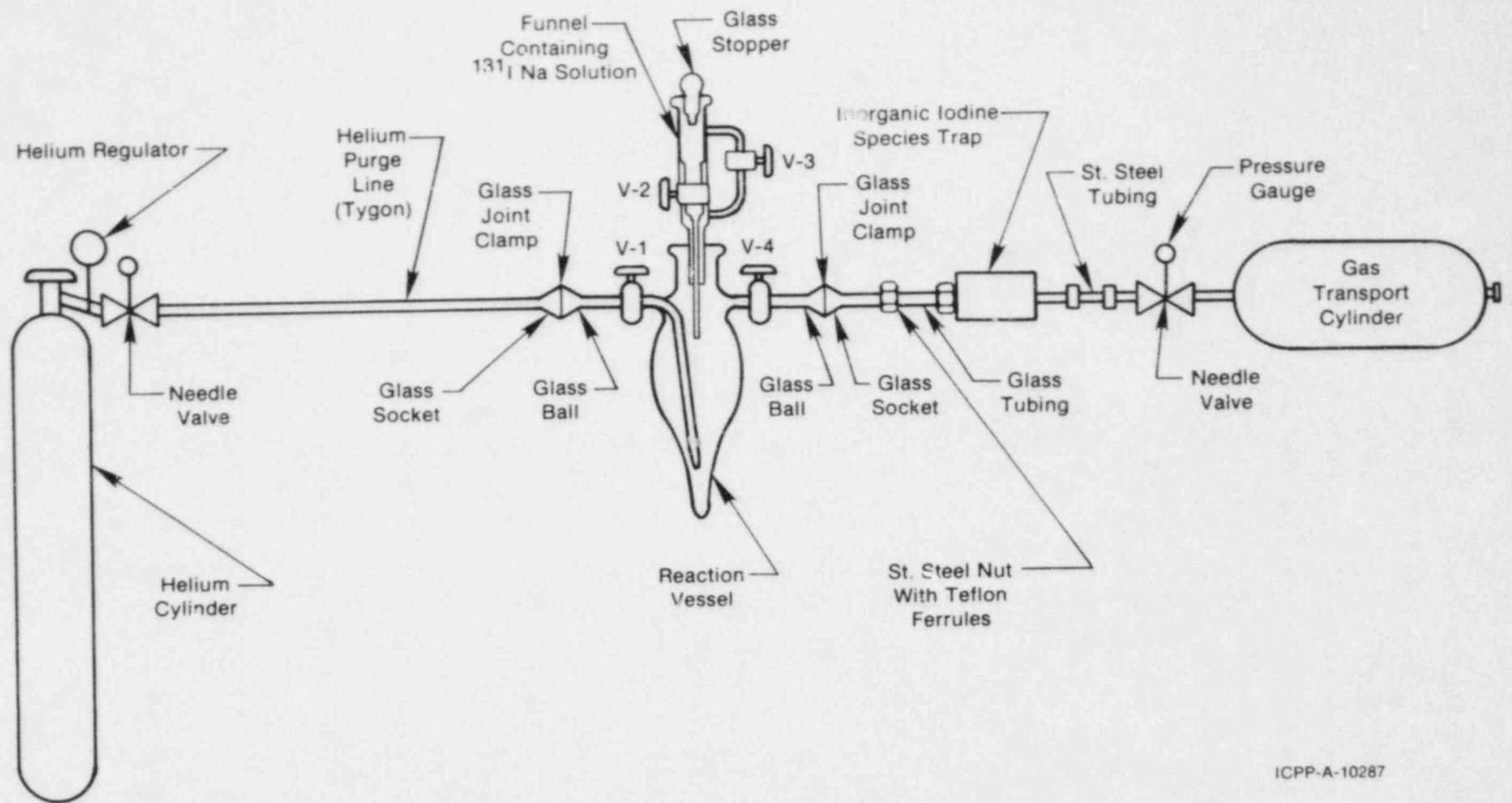
Figure 4.   Methyl iodide Generation Apparatus

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Table II. Concentrations of chloride and other ions in the rain from two coastal sites clearly differ from those in rain collected at the two inland locations. All locations exhibited some evidence of man-made pollution (excess SO_4^{--}), but the amount was not constant with time.[11]

The base material for simulated rain was distilled and deionized water. The compounds shown in Table III were added to one liter of water to prepare a concentrated solution for each type of rain. Stock solutions were prepared by diluting 10 ml of concentrated solution in 990 ml of distilled and deionized water. The rain simulants contained 10 ml of stock solution diluted in 240 ml of water. These mixtures yielded solutions with ionic concentrations similar to those in Table II.

TABLE II. COMPOSITION OF PRECIPITATION IN REMOTE AREAS OF THE WORLD

Location Category	Excess[b] SO_4^{--}	SO_4^{--}	NO_3^-	Cl^-	Mg^{++}	Na^+	K^+	Ca^{++}	NH_4^+	H^+
Inland	240	240	140	90	4.3	32	27	4.0	30	13
Coastal[d]	650	1600	220	6800	450	3730	160	170	50	14

Volume-Weighted Mean Concentrations (μg/l)[a]

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a. From Reference 11.

b. The concentration of SO_4^{--} in excess of that provided by sea salt.

c. Mean values for two inland sampling stations, Poker Flats, Alaska (16 samples) and San Carlos, Venezuela (14 samples). The volume weighted mean values of pH were 4.96 and 4.81, respectively, for rain water samples at those locations.

d. Mean values for two coastal sampling stations, Amsterdam Island in the southern Indian Ocean (26 samples) and St. Georges, Bermuda (67 samples). The volume-weighted mean values of pH were 4.92 and 4.78, respectively, for rain water samples at those locations.

Two types of acid rain were made by adding small amounts of nitric or sulfuric acid to the inland rain simulant. One drop of either 2.5 $\underline{M}$ H_2SO_4 or 6 $\underline{M}$ HNO_3 was added to 250 ml of inland rain. The pH of the sulfuric acid rain was 3.1, and that of the nitric acid rain was 3.0.

TABLE III. COMPONENTS OF CONCENTRATED SOLUTIONS USE TO PREPARE SIMULATED RAINS

	Quantities Used (mg)[a]	
Compound	Inland Rain Concentrate	Coastal Rain Concentrate
HNO_3	0.0372	0.224
H_2SO_4	0.233	0.523
NaCl	201	24,400
KCl	131	759
$MgCl_2$	56.7	891
$MgSO_4$	21.3	4,500
NH_4NO_3	338	556
$CaCl_2$	27.4	1,170

---

a. Amounts mixed with distilled and deionized water to prepare 1 liter of concentrate for preparation of rain simulants.

2.2.4 Drop Production

Approximately 250 ml of a prepared rain was placed in the reservoir prior to the start of an experiment. The rate of drop formation was adjusted by regulating the flow of rain simulant to the hypodermic needle using the Teflon stopcock at the base of the reservoir (Figure 3).

The simulated raindrops for the experiments reported here were all produced using a #21 hypodermic needle with a beveled tip. Drop size was determined by collecting 400 drops and weighing the liquid. The average drop mass was 12 mg. For a spherical water drop, the corresponding radius is 0.14 cm.

The average drop rate was determined by measuring the time required to produce a fixed number of drops (usually 40). The times were rounded to the nearest tenth of a second and recorded. The drop rate was normally measured three times during an 8-minute test run. The total mass of drops was measured by weighing the collection vial before and after the run.

2.2.5 Drop Collection and Analysis Techniques

The drops of simulated rain were collected in cylindrical plastic vials (2.5 cm x 10 cm) containing about 15 cm^3 of activated charcoal (BC-151). The collection vial was held in place in a small well in the center of the experimental chamber's removable bottom plug. The collection vial was capped promptly upon removal from the chamber.

Selection of activated charcoal as the collection medium was made after evaluating the retention of CH_3I in raindrops by a variety of media. Other activated charcoals, silver-loaded zeolite (AgX), a silver-loaded charcoal, silver-loaded alumina, and a solution of 1.1 $\underline{M}$ mercaptoacetic acid (MAA) were evaluated as possible collection media. None of the alternatives retained CH_3I better than the BC-151 charcoal; most were significantly worse. In addition, several different physical arrangements were tried and discarded when they proved less effective.

It is notable that the MAA solution proved less effective than activated charcoal for retaining the CH_3I in raindrops. Solutions of MAA have been used in field studies (References 12 and 13) to retain CH_3I in samples of wet deposition. The results of the collection media evaluation tests showed that the solution of MAA retained only 13% as much CH_3I in raindrops as a comparable amount of BC-151 activated charcoal.

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Vials containing collected drops were placed in the well of a NaI(Tl) scintillation counter equipped with a single-channel analyzer (SCA). The energy window of the SCA was set to count the 364-keV photons emitted following decay of ^{131}I. The sample counting efficiency was determined by placing a known quantity of ^{131}I in the same matrix and counting geoetry. The ^{131}I activity of the calibration samples was determined using a Ge(Li) detector with multichannel analyzer. The calibration of the Ge(Li) spectrometer is traceable to the National Bureau of Standards.

2.2.6 Air Sampling and Analysis

The air sampling apparatus consisted of a stainless steel hypodermic needle ~75 cm long, glass sample collection tube containing about 10 cm^3 of activated charcoal (BC-151) or silver zeolite, and a 60-cm^3 graduated plastic syringe. Air samples were collected by inserting the hypodermic needle through the septum and opened stopcock into the center of the chamber. One end of a glass chamber, which held the sampling medium, was attached to the needle; the other end was attached to the graduated syringe. The syringe was used to draw 30- or 60-cm^3 air samples through the needle for collection by the sampling medium (Figure 2).

The glass collection chamber was opened and the sampling medium was transferred to a plastic vial. The vials were the same as those used for drop collection and the contents were analyzed for ^{131}I using the equipment described in the previous subsection.

2.3 Results

The results of experiments comparing the methyl iodide uptake by falling drops under various conditions are presented in this section. Subsection 2.3.1 describes a typical experimental measurement sequence, which is important to understanding of the data analysis and presentation of results. The results obtained for simulated inland rain are presented in Subsection 2.3.2; most of the experiments were performed using this rain simulant. Experimental data for comparisons between inland rain and the

two types of acid inland rain are presented in Subsection 2.3.3, followed
by limited experimental data for coastal rain (Subsection 2.3.4). Uptake
of CH_3I during drop formation is discussed in Subsection 2.3.5.

2.3.1 Experimental Measurement Sequence

A typical experiment in the study of air-to-drop transfer of methyl iodide
lasted 4-6 hours. The first step was transfer of CH_3I from the stainless
steel tank into the evacuated experimental chamber and the addition of
humid air to increase the relative humidity and raise the chamber pressure
to that of the atmosphere. The concentration of CH_3I in the chamber was
measured at the beginning of each experiment and at several other times
during the test. The air-to-drop transfer was measured by collecting drops
that had fallen through the mixture of methyl iodide in air. Because
direct air-to-charcoal transfer also occurred during the measurements, it
was necessary to determine the amount of activity in the collection vial
due to that process. The "blanks" were measured by exposing charcoal in
collection vials in the chamber when no raindrops were falling. The fol-
lowing is a typical experimental sequence: air sample, blank, 2 separate
air-to-drop transfer measurements, air sample, blank, 2 separate air-
to-drop transfer measurements, air sample, blank.... The sequence was
repeated as required to obtain the desired number of measurements.

The air-to-drop transfer parameter was computed using

$$T_w = \frac{C}{X} \qquad (2\text{-}14)$$

where T_w = the dimensionless transfer parameter,

C = the concentration ($\mu Ci/g$) of radioiodine in collected drops, and

X = the concentration ($\mu Ci/g$) of radioiodine in chamber air through
which the drops fell.

The concentration of radioiodine in simulated raindrops was calculated
using

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$$C = \frac{Q_d - Q_b^\star}{M_d} \qquad\qquad (2\text{-}15)$$

where Q_d = the total radioiodine activity (μCi) in the drop collection vial,

$Q_b^\star$ = the estimated radioiodine activity (μCi) due to air-to-charcoal transfer during drop collection (the activity in the blank), and

M_d = the mass (g) of the water drops collected.

Because measurements of the activity in blank samples (Q_b) were not simultaneous with measurement of Q_d, it was necessary to interpolate between successive measurements of $Q_b^\star$ to estimate the value (Q_b) appropriate for use in Equation (14). A similar interpolation procedure was used to estimate the air concentration used in Equation (13) to calculate T_w.

Figure 5 illustrates the experimental measurement sequence and behavior of χ and Q_b during the course of an experiment. The measured values of χ normally decreased slowly with time during a sequence of experiments. This was expected because air samples were withdrawn periodically and also because the chamber was opened to insert and remove the collection vials. The measured values of Q_b also decreased with time during a run. The decrease in Q_b generally, but not always, paralleled the decrease in . If the activity Q_b resulted from air-to-surface deposition of CH_3I, the decrease in Q_b would be expected to follow that in χ. The reasons for variations from that behavior are not known.

Experimental uncertainties in the determination of T_w are similar for all the results. Table IV contains normal measurement uncertainties for the basic variables and propagated uncertainties for the derived quantities χ, C, and T_w. The uncertainties associated with radionuclide counting are seen to be small when compared with the variation in the air-charcoal transfer estimates ($Q_b^\star$).
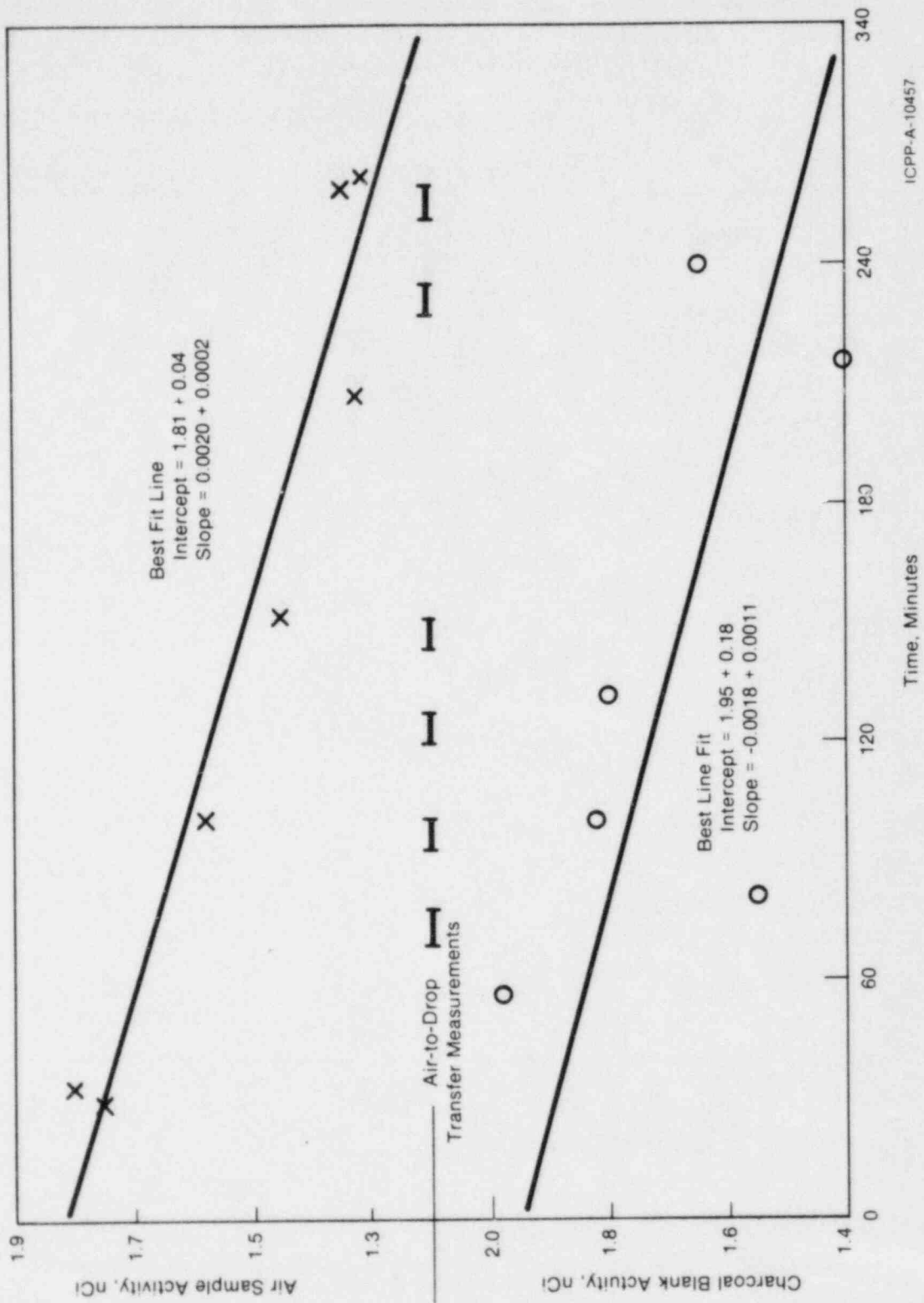
Figure 5. Experimental Measurement Sequence and Behavior of Air and Blank Activities

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TABLE IV. MEASUREMENT UNCERTAINTIES AND PROPAGATED
UNCERTAINTIES FOR x, C, AND T_w

Variable	Symbol	Nominal Fractional Uncertainty
Gross ^{131}I Activity in Air Sample	Q_a	0.5%
Apparent ^{131}I Activity Due to Background in ^{131}I Channel	Q_B	1%
Net ^{131}I Activity in Air Sample	Q_N	1.4%
Air Sample Mass	M_a	3%
Air Concentration	$x \ (=Q_N/M_a)$	3%
Apparent ^{131}I Activity in Collected Drops	Q_d	0.5%
^{131}I Activity Due to Air-Charcoal Transfer and Background	Q_b	20%
Mass of Water Drops Collected	M_d	0.03%
Net ^{131}I Concentration in Drops	C, Eq.(2-15)	20%
Transfer Parameter	T_w, Eq.(2-14))	20%

2.3.2 Results for Simulated Inland Rain

Most of the air-to-drop transfer experiments employed simulated inland
rain. Table V contains the results of all the experiments using drops of
that type. The measured transfer parameters are grouped by drop formation
time (t_f, s). The results in Table V include uptake during fall time and
drop formation. The latter is discussed in Subsection 2.3.5. The average

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TABLE V.   TRANSFER OF AIRBORNE CH_3I TO DROPS OF INLAND RAIN

Test	Range of Concentration of CH_3I (ng/m³)	Air & Drop Temperature Range (°C)	Experimental Determinations of T_W, Grouped by Drop Formation Time (t_f)									
			$0.5 \leq t_f < 1.0$		$1.0 \leq t_f < 1.5$		$1.5 \leq t_f < 2.0$		$2.0 \leq t_f < 3.0$		$3.0 \leq t_f < 4.5$	
			$t_f(s)$	T_W	$t_f(s)$	T_W	$t_f(s)$	T_W	$t_f(s)$	T_W	$t_f(s)$	T_W
1	$(1.2$--$1.4) \times 10^1$	25--26	0.81	0.019	1.28	0.032	1.96	0.029	2.02	0.030	3.18 3.50	0.034 0.011
2	$(1.0$--$1.4) \times 10^1$	25--27	0.98 0.65	0.027 0.020	1.39 1.22	0.039 0.034	1.75	0.037			3.70	0.019
3	$(3.7$--$5.2) \times 10^3$	21--22	0.82 0.88	0.023 0.027	1.34 1.00 1.09	0.040 0.046 0.041			2.51	0.046		
7A	$(1.5$--$1.8) \times 10^3$	26--27	0.82 0.58	0.047 0.030	1.30	0.039	1.80	0.038	2.82 2.61	0.035 0.023		
8A	$(1.9$--$2.4) \times 10^4$	24--26	0.98	0.038	1.17 1.43	0.050 0.037	1.88	0.047	2.16	0.039	3.30 4.35	0.015 0.012
9B	$(1.1$--$1.3) \times 10^4$	25--26	0.80 0.96	0.028 0.028			1.62	0.036			3.47	0.025
10A	$(4.8$--$5.2) \times 10^3$	24--25			1.11	0.031			2.50	0.042		
10B	$(3.4$--$3.7) \times 10^3$	Air: 25 Drop: 15-19	0.73	0.021	1.12 1.20 1.32	0.022 0.023 0.053						
10C	$(1.8$--$2.3) \times 10^3$	14--17	0.88 0.98	0.011 0.040			1.72	0.051				
11	$(2$--$3) \times 10^8$	25--26	0.83 0.61 0.68 0.63	0.026 0.020 0.019 0.019	1.01 1.05	0.028 0.035						
GROUP SUMMARIES	Number of Values: Mean: Std. Deviation of Mean:		17 0.026 0.002		15 0.037 0.002		6 0.040 0.004		6 0.036 0.004		6 0.019 0.004	

concentration of CH_3I in the air during the test is given in the second
column and the temperature range during the experiment is given in the
third column.

Perhaps the most notable feature of the fifty determinations of T_W shown
in Table V is that the overall range in values is less than a factor of
five. This shows that relatively large variations in: (a) drop formation
time (0.61--4.35 s), (b) methyl iodide concentration (10^1--10^8 ng/m^3),
and (c) ambient temperature (15--27°C) did not greatly affect the overall
air- to-drop transfer. The entire set of results was found to be
approximately normally distributed, with a mean ($\bar{x} \pm s_x$) of 0.0312 $\pm$
0.0016. However, small differences between subsets of the data can be
seen in Table V and some of the differences, while not large, were found
to be statistically significant. The standard statistical "t" test was
used to determine whether such differences were statisically significant
at the 95% level ($\alpha = 0.05$).

The drop formation time (t_f) appeared to have the greatest influence on
the observed transfer parameter. The mean transfer parameters for drop
formation times between 1.0 and 3.0 s are statistically the same and are
statistically greater than those observed for $0.5 \leqslant t_f < 1.0$ s and
$3.0 \leqslant t_f < 4.5$ s. The means for each category are shown in the summary data
at the bottom of the table. The summaries are for all determinations of
T_W for the specified drop formation times. Measurements of the effect of
drop formation time are presented in Subsection 2.3.5.

Because it was not possible to measure the relative humidity in the
chamber at the time of each determination, the effects of variations in
relative humidity are not known. The relative humidities measured during
the later tests showed that average values were 74% during the course of
these experiments. Variations in the relative humidity during a test and
from test to test may be the source of some of the variability of T_W that
can be seen in Table V.

Table VI summarizes data that can be used to examine the effects of airborne CH_3I concentration on the transfer parameter. The tests selected were all conducted at comparable temperatures and the results used are from the same range of drop formation times. There was no statistical difference ($\alpha = 0.05$) between the mean transfer parameter parameter determined for the lowest concentration range (~10 ng/m^3) and the mean

TABLE VI.   COMPARISONS OF MEAN TRANSFER PARAMETERS FOR INLAND RAIN EXPOSED TO DIFFERENT CONCENTRATION OF CH_3I IN AIR

Test(s)	CH_3I Concentration ng/m^3	Transfer Parameters ($1.0 \leqslant t_f < 3.0$ s)		
		Number of Values	Mean	Std. Dev. of Mean
1, 2	$(1.0\text{--}1.4) \times 10^1$	6	0.035[a]	0.002
7A, 10A	$(1.5\text{--}5.2) \times 10^3$	6	0.035[a]	0.003
8A, 9B	$(1.1\text{--}2.4) \times 10^4$	5	0.042[a]	0.003
11	$(2\text{--}3) \times 10^8$	2	0.032[a]	0.005

a. Differences between pairs of means are not statistically significant ($\alpha = 0.05$).

determined for concentrations that are 10^7 times greater. There was also no difference ($\alpha=0.05$) between the mean transfer parameters determined at intermediate concentration values (~10^3 and ~10^4 ng/m^3). On the basis of these results, air-to-drop transfer of CH_3I would be expected to be similar for routine CH_3I releases at low mass concentrations and accidental releases of CH_3I at much higher mass concentrations.

Table VII contains data that can be used to examine the influence of air and drop temperature on the transfer parameter. The results shown are for the same range of drop formation times from tests when the air and drop temperatures were approximately equal. Because variations in CH_3I

concentration were found not to produce significant changes in T_W, Table VII contains results for a variety of concentration values. The three mean values of T_W suggest a trend of increasing T_W with decreasing temperature and, in fact, the mean transfer parameter for Test 3 is significantly greater ($\alpha=0.05$) than that for the large number of results at higher temperatures. The same conclusion is reached if only data from Tests 7A and 10A, with CH_3I concentrations comparable to Test 3, are used in the higher temperature category. The data suggest that wet deposition could be approximately 50 percent higher at 15°C than at 25°C. This result is consistent with the measurements of the CH_3I partition coefficient, expressed in Equation (2-12) and the expected proportionality of T_W to H, which can be seen from Equation (2-2).

TABLE VII.   COMPARISONS OF MEAN TRANSFER PARAMETERS FOR INLAND RAIN AT DIFFERENT TEMPERATURES

Test(s)	Temperature Range (°C)	Transfer Parameters ($1.0 \leqslant t_f < 3.0$ s)		
		Number of Values	Mean	Std. Dev. of Mean
1, 2, 7A 8A, 9B, 10A, 11	24-27	19	0.036[a]	0.002
3	21-22	4	0.043[a]	0.002
10C	14-17	1	0.051[a]	NA

a. Means are significantly different ($\alpha=0.05$).

2.3.3 Results for Simulated Acid Rain

Two types of acidified rain simulant (HNO_3 and H_2SO_4) were used in the experiments. The results for both simulants are shown in Table VIII. A total of 22 determinations of T_W were made for inland rain acidified with HNO_3. Twelve determinations of T_W were made for rain acidified with

TABLE VIII. TRANSFER OF AIRBORNE CH_3I TO DROPS OF ACID RAIN

| Test | Range of Concentration of CH_3I (ng/m³) | Air & Drop Temperature Range (°C) | Experimental Determination of T_w, Grouped by Drop Formation Time (t_f) | | | | | | | | | |
| | | | $0.5 \leq t_f < 1.0$ | | $1.0 \leq t_f < 1.5$ | | $1.5 \leq t_f < 2.0$ | | $2.0 \leq t_f < 3.0$ | | $3.0 \leq t_f < 4.5$ | |
			$t_f(s)$	T_w	$t_f(s)$	T_w	$t_f(s)$	T_w	$t_f(s)$	T_w	$t_f(s)$	T_w
4 (HNO₃; pH=3.0)	$(5.9\text{--}7.0)\times10^2$	27	0.96 0.89	0.021 0.023	1.35	0.030						
5 (HNO₃; pH=3.0)	$(6.4\text{--}9.0)\times10^3$	25	0.74	0.010	1.13 1.44	0.031 0.032			2.88 2.13 2.73 1.32	0.013 0.015 0.021 0.018		
6 (H₂SO₄; pH=3.1)	$(2.8\text{--}3.5)\times10^2$	23			1.15 1.45 1.06	0.059 0.047 0.038					3.68	0.020
7 (H₂SO₄; pH=3.1)	$(0.75\text{--}1.3)\times10^3$	26--27	0.51 0.96	0.026 0.038	1.10 1.37 1.09 1.03 1.23	0.044 0.022 0.032 0.037 0.031			2.10	0.066		
8B (HNO₃; pH=3.0)	$(1.3\text{--}1.7)\times10^4$	22-23	0.68	0.024	1.27 1.44	0.034 0.042	1.68 1.60	0.041 0.048	2.10	0.050	3.85 3.62	0.041 0.066
8C (HNO₃; pH=3.0)	$(1.0\text{--}1.2)\times10^4$	21--22			1.10 1.13 1.⸏ 1.⸏	0.023 0.033 0.044 0.030						
GROUP SUMMARIES	n: x̄: $S_{\bar{x}}$:			6 0.025 0.003		17 0.036 0.002		2 0.044 0.005		6 0.031 0.010		3 0.046 0.016

H_2SO_4. The pH values for the rain simulants were comparable in each of the six tests conducted.

The range of values of T_W for acidified rain was comparable to that found for inland rain, 0.013--0.066. The 34 estimates of T_W were approximately normally distributed, with a mean $(\bar{x} + s_x)$ of 0.0341 ± 0.0024. The overall mean T_W for acid rain was not significantly different $(\alpha = 0.05)$ from that for inland rain. Comparisons for specific tests are discussed below. Statistical analysis also shows that the results for the three drop formation time groups between 1.0 and 3.0 s do not differ significantly from one another. The same result was found for inland rain. Other aspects of the data in Table VIII are discussed below.

The effect of temperature was examined for each type of simulated acid rain. Table IX summarizes the comparisons that can be made. For rain acidified with HNO_3, there was a significant difference between the two temperature ranges. However, for rain acidified with H_2SO_4 the difference between the two means is smaller and is not statistically significant $(\alpha = 0.05)$. Table VIII also contains the data used for comparisons by type of acid rain. For the 25-27°C temperature range, the mean T_W for HNO_3 acid rain is significantly different from that for H_2SO_4 acid rain. However, at the lower temperatures, there is no statistical difference between the mean transfer parameters. Independent measurements of the partition coefficient for CH_3I in these acidified solutions are not available to compare with these experimental results.

Tests 7 and 8 were designed to compare acidified inland rain with normal inland rain under nearly identical conditions. In these tests, the same charge of airborne methyl iodide was used to measure the transfer to drops of normal inland rain and then to drops of acidified rain. The concentration of CH_3I was slightly lower for the later tests in the sequence. Table X summarizes the results for these tests. In neither case was there a statistically significant difference between the mean transfer parameters for normal and acidified inland rain. The temperature was about 4°C lower for Tests 8B and 8C than for Test 8A, but this difference is not believed large enough to affect the conclusion drawn.

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TABLE IX. COMPARISONS OF MEAN TRANSFER PARAMETERS FOR TWO
ACID RAIN TYPES AT DIFFERENT TEMPERATURES

Test(s)	Temperature Range (^{o}C)	Transfer Parameter ($1.0 \leqslant t_f < 3.0$ s)		Std. Dev. of Mean
		Number of Values	Mean	
RAIN ACIDIFIED WITH HNO_3				
4, 5	25--27	7	0.023[a,c]	0.003
8B, 8C	21--23	9	0.038[a,d]	0.003
RAIN ACIDIFIED WITH H_2SO_4				
7B	26--27	6	0.039[b,c]	0.003
6	23	3	0 048[b,d]	0.008

a. Means at different temperatures are significantly different ($\alpha=0.05$).

b. Means at different temperatures are not significantly different ($\alpha=0.05$).

c. Means for different types of acid rain at same temperatures are significantly different ($\alpha=0.05$).

d. Means for different types of acid rain at same temperatures are not significantly different ($\alpha=0.05$).

TABLE X. COMPARISONS OF MEAN TRANSFER PARAMETERS FROM SEQUENTIAL
EXPERIMENTS USING INLAND RAIN AND ACIDIFIED INLAND RAIN

| | | Transfer Parameter $(1.0 \leqslant t_f < 3.0 \text{ s})$ | | |
Test(s)	Nature of Drops	Number of Values	Mean	Std. Dev. of Mean
7A	Inland Rain	4	0.034[a]	0.004
7B	H_2SO_4 Rain	6	0.039[a]	0.007
8A	Inland Rain	4	0.043[a]	0.004
8B, 8C	HNO_3 Rain	9	0.038[a]	0.003

a. Mean for acidified inland rain is not statistically different ($\alpha=0.05$) from inland rain.

2.3.4 Results for Coastal Rain

Seven determinations of T_W for coastal rain were made in Test 9A.
The results, again grouped by drop formation time, are shown in Table
XI. The mean value ($\bar{x}+s_x$) was 0.0259+.0020. For the five runs with
$1.0 \leqslant t_f < 3.0$ s, the mean of 0.0246+.0051 was about 50% less than the
mean (0.0359+.0015) of 19 values for drops of inland rain with the same
range of T_f and ambient temperature. The difference between the two means
was statistically significant ($\alpha=0.05$).

2.3.5 Measurements of Uptake During Drop Formation

Two series of measurements were made to determine the uptake of CH_3I
during drop formation. These experiments were performed, in the manner
described in Section 2.2, using a very short chamber to minimize the drop
fall time. Both tests were conducted using the inland rain simulant.

TABLE XI. TRANSFER OF AIRBORNE CH_3I TO DROPS OF COASTAL RAIN

Test	Range of Concentration of CH_3I (ng/m^3)	Air & Drop Temperature Range (^oC)	Experimental Determination of T_w, Grouped by Drop Formation Time (t_f)									
			$0.5 \leqslant t_f < 1.0$		$1.0 \leqslant t_f < 1.5$		$1.5 \leqslant t_f < 2.0$		$2.0 \leqslant t_f < 3.0$		$3.0 \leqslant t_f < 4.5$	
			$t_f(s)$	T_w	$t_f(s)$	T_w	$t_f(s)$	T_w	$t_f(s)$	T_w	$t_f(s)$	T_w
9A	$(1.4{-}2.1) \times 10^4$	25--26	0.87	0.030	1.14	0.017	1.76	0.022			3.82	0.030
					1.19	0.026	1.79	0.029				
							1.70	0.029				

GROUP SUMMARIES												
n:			1		2		3				1	
$\bar{x}$:			0.030		0.0214		0.0264				0.030	
$S_{\bar{x}}$:			NA		0.0061		0.0028				NA	

The results of the experimental measurements are presented in Table XII, in terms of the ratio C_0/χ. The quantity $C_0(\mu Ci/g)$ is the concentration of CH_3I in the drop at the start of its fall and χ is the average air concentration during drop formation. The values of the ratio have all been normalized to a temperature of 25°C to permit comparison with other measurements. The normalization was accomplished using the temperature dependence of the partition coefficient given by Equation (2-12).

TABLE XII. UPTAKE OF CH_3I DURING FORMATION OF DROPS OF INLAND RAIN

Test	CH_3I Concentration (ng/m^3)	Ratio (C_0/χ) Normalized to 25°C					
		$t_f < 1.0$		$1.0 \leqslant t_f < 3.0$		$t_f \geqslant 3.0$	
		$t_f(s)$	Ratio	$t_f(s)$	Ratio	$t_f(s)$	Ratio
DF-1	$(1.4-2.3) \times 10^4$	0.98	0.0059	1.14	0.0061	3.7	0.013
		0.43	0.0055	1.62	0.0042		
		0.61	0.0052	1.19	0.0052		
		0.93	0.0041	1.14	0.0042		
		0.71	0.0036	2.32	0.0056		
				2.14	0.0051		
DF-2	$(2.7-4.9) \times 10^4$	0.74	0.0032	2.02	0.0020	5.70	0.010
		0.82	0.0032	2.44	0.0053	3.70	0.0074
		0.86	0.0038	1.21	0.0047	3.52	0.0090
		0.83	0.0050	1.19	0.0044	11[a]	0.024
		0.83	0.0039	1.33	0.0068		

a. Due to a stopwatch failure, t_f for this run is uncertain. The value given is an estimate based on the mass of water collected and the total run time.

Analysis of the data in Table XII yielded a linear relationship between the ratio C_0/x and the drop formation time t_f ($r^2=0.90$). A linear least squares fitting routine was used to find the best-fit parameters, given in Equation (2-16) together with the associated uncertainties:

$$(C_0/x)_{25^\circ C} = 0.00277 \pm .00036 + (0.00174 \pm .00012) \, t_f \qquad (2\text{-}16)$$

The equation only applies for values of $t_f > 0.4$ s, the shortest drop formation time studied. At shorter drop formation times, a different relationship between C_0/x and t_f must apply, because (C_0/x) should be zero at $t_f = 0$.

For drop formation times in the range $1.0 \leqslant t_f < 3.0$ x, Equation (2-16) predicts the ratio C_0/x would vary from 0.0045 to 0.0080. The average value of T_W determined for such drops was 0.038 (see Table V). Thus, uptake during formation by drops is estimated to account for about 14% of the total transfer. Some measured values of T_W (Table V) are lower than would be expected on the basis of uptake during drop formation. The cause of the lower values that were observed is not known.

2.4 Discussion

The data obtained in this experimental program lead to several conclusions. The first is that there were not large (factor of 10) differences in the transfer of CH_3I to raindrops for the range of conditions studied. The following variables (ranges indicated) had relatively minor effects on the measured air-to-drop transfer:

> CH_3I concentration (10^1--10^8 ng/m^3)
> temperature (15--27°C)
> acidity of raindrops ($3 < pH < 5$)
> raindrop type (inland/coastal)

The effect of temperature on the partition coefficient was reflected in the measured transfer and produced ~50% greater transfer at 15°C than at 25°C. The observed lower (by ~50%) air-to-drop transfer for coastal rain compared with inland rain is also presumably related to differences in the partition coefficient.

Comparison of the measurements with predictions of theoretical models suggests that the mass transfer parameter that was computed in Section 2.1 may be incorrect. The measured net transfer to drops of inland rain falling 100 cm through methyl iodide at 25°C implies that the transfer rate constant b in Equation (2-2) should be ~7×10^{-5} cm^{-1}. The computed value of b (Table I) is larger, ~6×10^{-4} cm^{-1}. Thus the model overestimates the transfer observed in these laboratory experiments.

Some environmental data indicate that the model underestimates the actual transfer to drops. The measurements of trace gases in rain and snow reported in Reference 14 include data for CH_3I. The data show that the amount of CH_3I in rain and snow greatly exceeds that which would be predicted using the equilibrium partition coefficient in Table I. The observed concentrations of CH_3I in precipitation were 0-100 times greater than expected equilibrium values computed from air concentrations measured at the sampling location. It was hypothesized[14] that the CH_3I may have been attached to particulates and that the results therefore did not reflect gas scavenging. However, experience with radioactive methyl iodide gas is that it is not likely to deposit on surfaces. Another possibility is that the CH_3I was incorporated in the raindrops and snowflakes during their formation. A similar enrichment phenomenon was observed with ^{131}I in a condensing effluent plume.[15]

The reason for the observed enrichment of CH_3I in precipitation (Ref. 14) is not known. Until mechanisms are understood, they cannot be included in the model described in Section 2.1. The mechanisms were not operative in the laboratory experiments described in Subsection 2.3.

## 3. RETENTION BY VEGETATION OF CH₃I IN WET DEPOSITION

The retention by vegetation of CH_3I in wet deposition depends upon two factors. The first is the fraction of the incident rainfall that is intercepted by the vegetation. The second is the binding of the CH_3I to the vegetation during the time the raindrops are present on plant surfaces. Laboratory experiments to measure the initial retention of CH_3I in wet deposition are described in this section. Both of the factors cited above were evaluated using simulated rain and CH_3I labeled with ^{131}I. Subsection 3.1 describes the experimental apparatus and measurement techniques. The experimental results are presented in Subsection 3.2. Conclusions drawn from the measurements are presented in the last subsection.

3.1 Experimental Apparatus and Techniques

The experimental apparatus and techniques used in the retention experiments are described below. Some techniques are the same as those used in the drop uptake experiments. Descriptions of those methods were given in Section 2.2.

3.1.1 Experimental Apparatus

A plexiglass experimental chamber provided containment for the experimental work. The chamber was constructed in modules for assembly inside an experimental vault that provided secondary containment and ventilation around the experimental chamber. Figure 6 is a diagram of the experimental chamber used for retention measurements. Four vegetation plots were supported on a platform in the center of the chamber. Above the vegetation was a motor-driven drop generator that moved back and forth across the chamber to provide complete coverage of the vegetation by the simulated rain. The air conditioning section provided clean inlet air and humidity control. The chamber air was exchausted through activated charcoal filters to collect airborne CH_3I.

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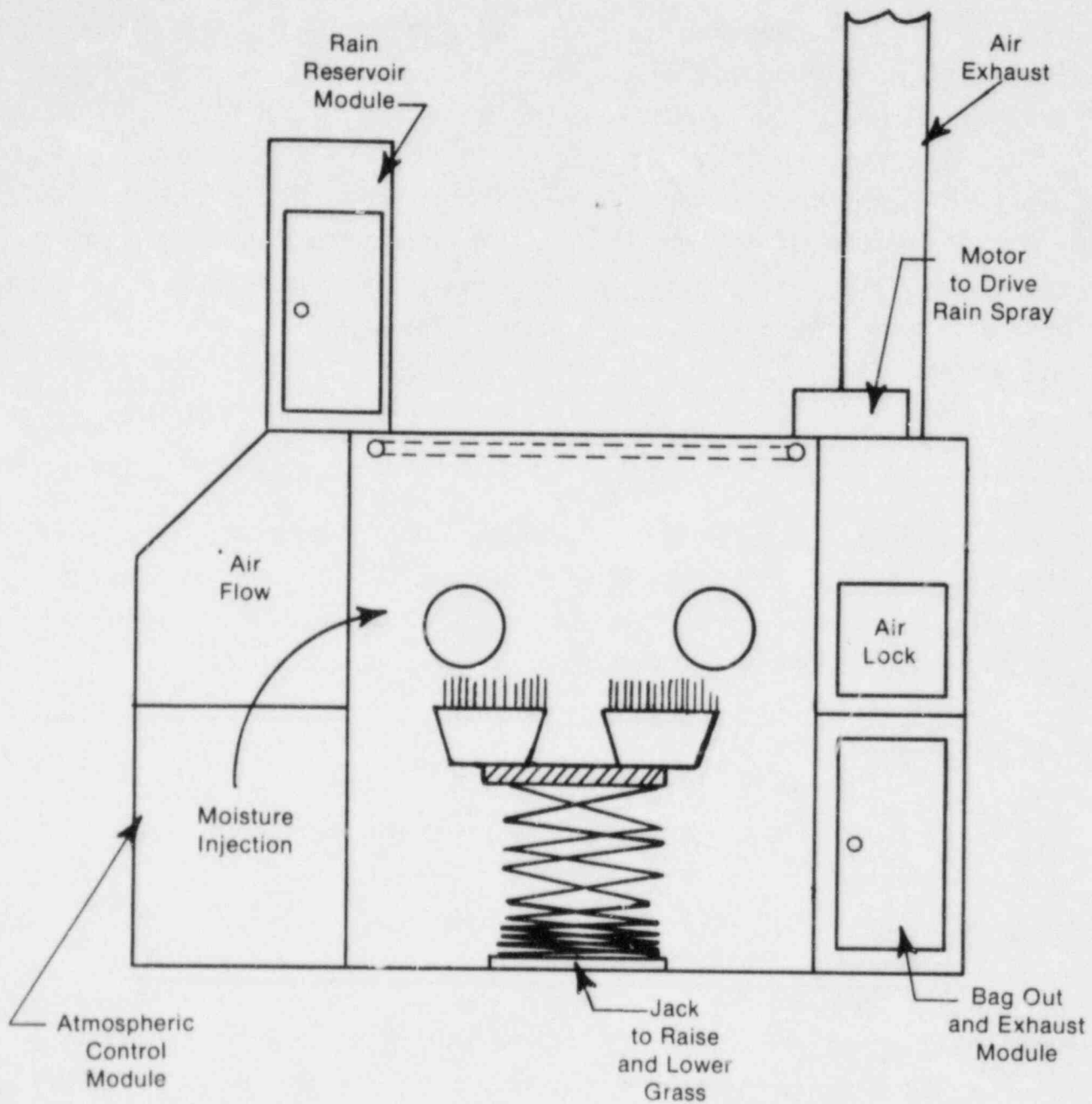
Figure 6. Chamber for Retention Measurements

Glove ports provided access to the upper part of the chamber. An isolated bag-out module was used to remove samples from the chamber. The vegetation could be raised and lowered using the jack shown supporting the platform and rain collection troughs.

Simulated rainwater was added to the reservoir at the top of the chamber. The glass reservoir was connected to the raindrop mechanism using flexible Teflon tubing. The body of the drop generator was specially fabricated of glass to distribute the rain simulant to each of the hypodermic needles used to form the drops. The needles used to form the drops were the same as those used in the experiments described in Section 2.

3.1.2 Preparation of Simulated Rain Containing CH_3I

Inland rain and CH_3I labeled with ^{131}I were prepared as described in Subsections 2.2.3 and 2.2.2, respectively. The rain simulant was equilibrated with labeled CH_3I by vigorous shaking prior to transfer of the liquid to the reservoir.

3.1.3 Preparation of Vegetation

Marion Bluegrass sod was grown in 25- by 25-cm pots containing about 1.4 kg of sandy loam soil. The grass was kept in a growth room with a 16-hr photo period and light intensity of approximately 19,000 lm/m^2. The temperature was held approximately constant at 24°C during the lighted period and 13°C during the dark period. Relative humidity was maintained between 45 and 50 percent.

Alfalfa was also grown in 25- by 25-cm pots in the same growth room described above and under the same conditions. Because of the extensive time required to prepare an adequate stand of alfalfa, some alfalfa was obtained from field locations for experimental use.

Oak Leaf lettuce was grown in 2.5- by 2.5-cm pots in a local greenhouse. The lettuce was grown to a height of 15 cm. Groups of six pots of lettuce were used in the chamber during the retention experiments.

3.1.4 Sample Collection and Analysis Techniques

Samples of the raindrops falling upon the vegetation were collected in vials as described in Subsection 2.2.5. The radioiodine counting techniques described there were used for the raindrop samples. Corrections for air-to-charcoal transfer were made using blanks, as described in Subsection 2.3.1.

Vegetation samples were obtained from measured areas. The samples were cut and bagged inside the chamber and double bagged prior to removal from the chamber via the bag-out module. The samples were placed in cylindrical containers to maintain a consistent counting geometry. The samples were counted using a calibrated NaI(Tl) scintillation detector. Following analysis for radioactivity, the samples were dried to constant weight.

Air samples were obtained by drawing air through a 2.5-cm bed of KI_3-impregnated charcoal (BC-151). The samples were counted using the equipment described in Subsection 2.2.5. These samples were collected during the simulated rainfall to measure the overall volatilization of labeled CH_3I from drops, wet vegetation, and o.. er wet surfaces inside the chamber.

3.2 Results of Retention Measurements

The initial retention factors determined under laboratory conditions are presented in Table 13 for the three vegetation types. The most notable feature of the results is the magnitude of the initial retention factors: in no case did the measured concentration of ^{131}I on vegetation per unit area exceed 3% of the incident ^{131}I activity in rainwater per unit area. Vegetation densities for the experimental plots ranged from 0.017 to 0.061 g/cm^2. No correlation between the vegetation density and the initial retention fraction was found.

Samples were also collected after the vegetation surfaces dried to observe whether the ^{133}I initially retained by the vegetation was tightly bound to

TABLE XIII. RESULTS OF MEASUREMENTS OF RETENTION BY VEGETATION OF CH_3I IN WET DEPOSITION

Test	Vegetation Type	Rain Sequence	Rainfall Duration (min)	Rainfall Rate (mm/hr)	Initial Retention Fraction[2]
R1	Grass	Contaminated Rain	15	2.3	7.2×10^{-3}
R2	Grass	Contaminated Rain	90	1.9	7.2×10^{-3}
R3	Grass	a. Uncontaminated Rain b. Contaminated Rain	15 100	3.7 1.4	8.0×10^{-3}
R4	Lettuce	Contaminated Rain	60	1.4	2.1×10^{-2}
R5	Lettuce	Contaminated Rain	84	1.9	1.0×10^{-2}
R6	Lettuce	a. Uncontaminated Rain b. Contaminated Rain	18 36	2.3 2.4	1.1×10^{-2}
R7	Alfalfa	Contaminated Rain	60	2.2	2.3×10^{-2}
R8	Alfalfa	Contaminated Rain	60	1.2	$0.7 - 3 \times 10^{-2}$

a. Measured immediately after cessation of contaminated rain.

plant surfaces. The concentrations of ^{131}I measured 4 hours after the rain were typically about 40% of those observed at the end of the rain. Volatilization of the CH_3I as the vegetation surfaces dried appears to be the most logical explanation for the observed loss of activity; however, this could not be conclusively demonstrated. In only one test (R8) was the ^{131}I concentration relatively unchanged after the vegetation dried. Samples collected at 1 and 2 hours after the rain contained the same concentrations as the sample collected at the end of the rain. In the other experiment which employed alfalfa (R7), 60% of the activity was lost during the first two hours. No measurements were made at 4 hours after the rain in either test.

In two tests (R2 and R5) samples were collected at times of up to 30 hours after the wet deposition occurred. They showed that, after the initial (4-hour) loss noted above, the ^{131}I concentrations remained relatively constant. These results also support the belief that the observed post-rainfall loss was associated with the drying of the plant surfaces.

3.3 Discussion

The initial retention fractions for CH_3I in wet deposition determined in the laboratory are small. It was believed that the laboratory tests would overestimate the true value because the raindrops were not falling at terminal velocity. An increased fall velocity would be expected to produce more drop splatter and a lesser interception fraction. However, the lack of correlation between the measured initial retention fractions and vegetation density suggests that binding of the ^{131}I to the plant surface, rather than interception of rainfall is the principal determinant of the initial retention. If that interpretation is valid, then initial retentions of ~1--3% could be expected in the environment. No environmental data are available for comparison with the laboratory results.

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12 SUPPLEMENTARY NOTES

13 ABSTRACT (200 words or less)

The transfer of gaseous methyl iodide (CH_3I) to raindrops and the initial retention by vegetation of CH_3I in raindrops have been studied in a laboratory experimental program. The measured air-to-drop transfer parameters and initial retention factors both affect the wet deposition of methyl iodide onto vegetation. No large effects on the air-to-drop transfer due to methyl iodide concentration, temperature, acidity, or rain type were observed. Differences between laboratory measurements and theoretical values of the mass transfer coefficient were found. Grass, lettuce, and alfalfa were used to study initial retention of methyl iodide by vegetation. Only a small fraction of the incident CH_3I in raindrops was held by any of the three vegetation types.

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