A SELECTIVE ADSORBENT SAMPLING SYSTEM FOR DIFFERENTIATING AIRBORNE IODINE SPECIES

J. H. Keller, F. A. Duce, and W. J. Maeck

Idaho Nuclear Corporation
Idaho Falls, Idaho

ABSTRACT

Atmospheric sampling devices capable of differentiating and measuring the various species of airborne iodine are required to interpret the behavior of airborne iodine under water-reactor accident-release conditions. To date, most sampling devices have consisted of a series of adsorbents which invariably include a silver metal surface for the retention of inorganic iodine and a charcoal bed for the retention of organic iodides. Operating experience with these types of samplers has shown the iodine adsorption efficiency of silver metal surfaces to be incomplete for submicrogram levels of incident elemental iodine and for hypoiodous acid in humid atmospheres. The sampler being developed in our laboratory is based on a high-efficiency particulate filter and a series of three inorganic material adsorbents that separate the containment atmosphere sample into the following four fractions in the order of sample flow through the sampler: noniodine particulate, elemental iodine, nonelemental inorganic iodine (hypoiodous acid) and organic iodine. The requirement for an adsorbent for hypoiodous acid is based on our finding that hypoiodous acid, which has a long airborne half-time, is the major inorganic iodine species after the initial washout of elemental iodine from a steam-air atmosphere. Because hypoiodous acid is only partially retained by silver metal surfaces in conventional samplers, it would collect on the charcoal bed resulting in erroneously high values for methyl iodide.

Introduction

One of the principal atmospheric sampling devices being developed for the LOFT Integral Test Program is the Particulate and Iodine (P-I) Sampler. Its purpose is to measure the concentration of airborne fission products other than noble gases, and to differentiate between the following: noniodine particulate activity, elemental iodine, nonelemental inorganic iodine, and organic iodine.

Atmospheric sampling devices capable of differentiating and measuring the concentration of various airborne iodine species under water reactor accident conditions are required for the interpretation of the iodine behavior. The first adsorbent sampling system, the so-called Maypack, developed by Megaw and May(1), suffered from several drawbacks and was not designed to meet the requirements of the current sampling problems. McCormack has had extensive experience, at the Containment Systems Experiment, with a modified Maypack which consisted of: a series of glass fiber filters, a section of six silver plated copper screens and one silver membrane, a charcoal loaded filter paper, and a bed of charcoal. He reports(2) that this form of the Maypack efficiently retains all forms of iodine and particulate material; however, the discrimination between iodine forms is not unequivocable. Parsly(3), who uses a similar type of Maypack at the Nuclear Safety Pilot Plant, questions the function of the charcoal paper.

In a somewhat different approach, Browning and Ackley(4) have used composite diffusion tubes to characterize volatile iodine forms. The results of Adams et al(5) indicate that the performance of the diffusion tubes can be adversly affected by the presence of water vapor, and that some iodine species are deposited by a mechanism which is not solely diffusion controlled. Bennett et al(6) developed a sampler designed to characterize iodine species in atmospheres of high relative humidity. The basic difference between this and previous Maypack samplers was the use of a silver plated honeycomb instead of the silver plated copper screens. The results of later data(7) indicate that at low iodine concentrations the adsorption efficiency of the silver honeycomb is low, even at zero percent relative humidity.

Experience in this laboratory(8) has shown that silver surfaces become less efficient for the removal of iodine from water-saturated air streams as the concentration of iodine incident on the silver surfaces is reduced. Because of the low fission product releases expected in the LOFT program and because of the difficulties with existing samplers, a sampler which is based on the use of selective inorganic adsorbents has been developed.

Experimental

Adsorbent Material Development: One of the necessary requirements for a sampler based on the use of selective adsorbents is that each material adsorb only the species of interest and pass the other species. Assuming a three-component system consisting of elemental iodine, hypoiodous acid, and methyl iodide, the elemental iodine adsorbent should exhibit low or zero adsorption efficiency for methyl iodide and hypoiodous acid; and the hypoiodous acid adsorbent should exhibit low methyl iodide adsorption efficiency. Based on laboratory studies, several materials were found which exhibited high elemental iodine adsorption efficiencies. Of these, cadmium iodide dispersed on an inert support of Chromosorb-P(a) most closely met the requirements for an elemental iodine adsorbent.

This material is prepared by dissolving cadmium metal in a medium containing an excess of HI to give a solution 0.1 M in cadmium. The

---

(a) Product of John Mansville, Inc.

solution is then poured onto the Chromosorb-P support until it is wetted with the solution. The mixture is stirred and air dried, after which it is placed in a tube furnace and purged with dry air at 200°C. The purge is continued until no further iodine evolves. After purging, the material is equilibriated with air in the laboratory for 48 hours.

Analysis of two different batches of this material gave an iodine to cadmium weight ratio of 2.7, which is higher than the theoretical ratio of 2.26 for pure CdI_2. The excess iodine is believed to be present as iodide but tightly bound such that it is not purged from the support at temperatures below 200°C. Only by air purging at temperatures greater than 200°C can the excess iodide be removed.

The elemental iodine adsorption efficiency of this material has been established for a variety of conditions ranging form ambient to 95°C and from 0.4×10^{-3} μg to 8000 μg of iodine on a bed 0.5 inch in diameter by 1.0 inch in length (1.3-gram bed). In all cases, the atmosphere was water-saturated air at the test temperature and the face velocity of the sample stream onto the bed was 50 ft/min. The elemental iodine was prepared by oxidation of iodide to iodine with iodate in an acid solution. The concentration of iodine in the test atmospheres was controlled by the amount of inactive iodide added to the high specific activity I-131 solution. Greater than 99 percent adsorption of elemental iodine by CdI_2 was measured up to a mass loading on the bed of 1000 μg. At 2000 μg the efficiency was 90 percent.

The methyl iodide adsorption efficiency for cadmium iodide dispersed on Chromosorb-P was also measured over a wide range of methyl iodide concentrations at temperatures from ambient to 90°C. In all cases, the methyl iodide adsorption was less than 0.1 percent.

The amount of hypoiodous acid that will be adsorbed by an elemental iodine adsorbent is more difficult to determine because of the difficulties in producing a pure hypoiodous acid atmosphere. Atmospheres which contain predominantly hypoiodous acid are best prepared in the laboratory by sparging the hypoiodous acid from a dilute alkaline iodine solution. In tests with atmospheres of low total iodine concentration (20 $\mu g/m^3$) prepared in the preceding manner, adsorption of what appears to be hypoiodous acid by cadmium iodide is 3 to 4 percent. The methyl iodide concentrations of these streams were found to be less than 1 percent. Whether the 3 to 4 percent adsorbed by the cadmium iodide beds is elemental iodine or partial hypoiodous acid adsorption has not been resolved; however, if the 3 to 4 percent adsorbed is due to hypoiodous acid, cadmium iodide would not necessarily be eliminated as a useful material for the particulate-iodine sampler.

Two materials have been studied for the adsorption of hypoiodous acid for use in the particulate-iodine sampler. The first was Linde Molecular Sieve Type 13X in the copper form (originally prepared by the Linde Division of Union Carbide) that was converted to the sulfide form by passing hydrogen sulfide through a bed of the material at

150°C. This material was then purged with air at 200°C to remove unreacted H_2S and then equilibrated in air in the laboratory for 48 hours prior to use.

The second material was a 10 weight percent mixture of 4-iodophenol dispersed on activated alumina. A 100-gram batch of this material was prepared by dissolving 10 grams of 4-iodophenol in 100 cm^3 of diethyl ether, adding this solution to 90 grams of dry alumina, and stirring until the ether had evaporated and the mixture was dry. Hypoiodous acid is reported to be the sole species responsible for the iodination of phenols(9); hence, this material would be expected to be an excellent hypoiodous acid adsorbent if the rate of iodination is fast compared to the residence time of the hypoiodous acid in the bed.

Both copper zeolite in the sulfide form and 4-iodophenol on alumina were tested to determine their adsorption efficiencies for hypoiodous acid. In all cases, the bed of test material was preceded by a bed of cadmium iodide on Chromoborb-P to remove elemental iodine. The adsorption efficiency of both materials for hypoiodous acid was greater than 90 percent and for methyl iodide less than one percent. A summary of the adsorption efficiencies for the most promising adsorbents for various iodine species is given in Table I.

TABLE I

ADSORPTION EFFICIENCIES FOR VARIOUS IODINE SPECIES ADSORBENTS

0.5 inch ID x 1.0 inch long bed @ 50 ft/min face velocity

	Adsorption Efficiency (%)		
Species	CdI_2 on Chromosorb-P	4-Iodophenol on Alumina	Cu-Zeolite Sulfide form
I_2	99+	99+	99+
HOI	3-4	96	95
CH_3I	< 0.1	< 1	< 1

The current concept for the sampler arrangement and the specific iodine species to be adsorbed by each component is shown in Figure 1.

Pilot Plant Scale Testing of the Particulate-Iodine Sampler: As part of the LOFT support program, the Contamination-Decontamination Experiment (CDE) has been operated to provide test atmospheres for the development of various samplers, including the P-I sampler. Tests have been conducted using short-cooled, irradiated fuel pins(10) and with single isotopes of xenon and iodine(11). In CDE Tracer Run 10, where the injected fission product species was predominantly elemental iodine, with about 2 percent methyl iodide as an impurity, 24 P-I samplers were suspended inside the CDE vessel, as shown in Figure 2. To isolate the

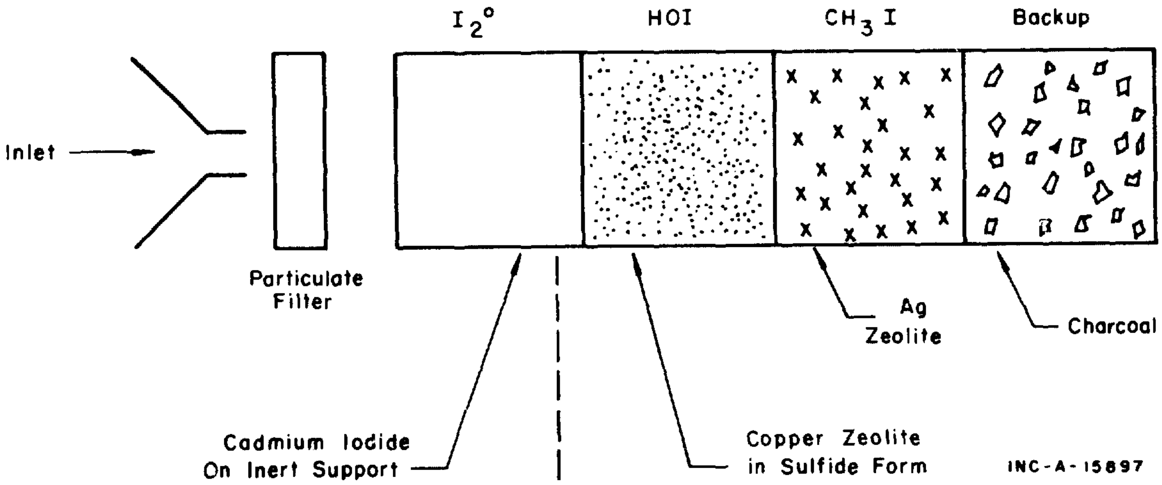


Fig. 1 Particulate Iodine Sampler Concept

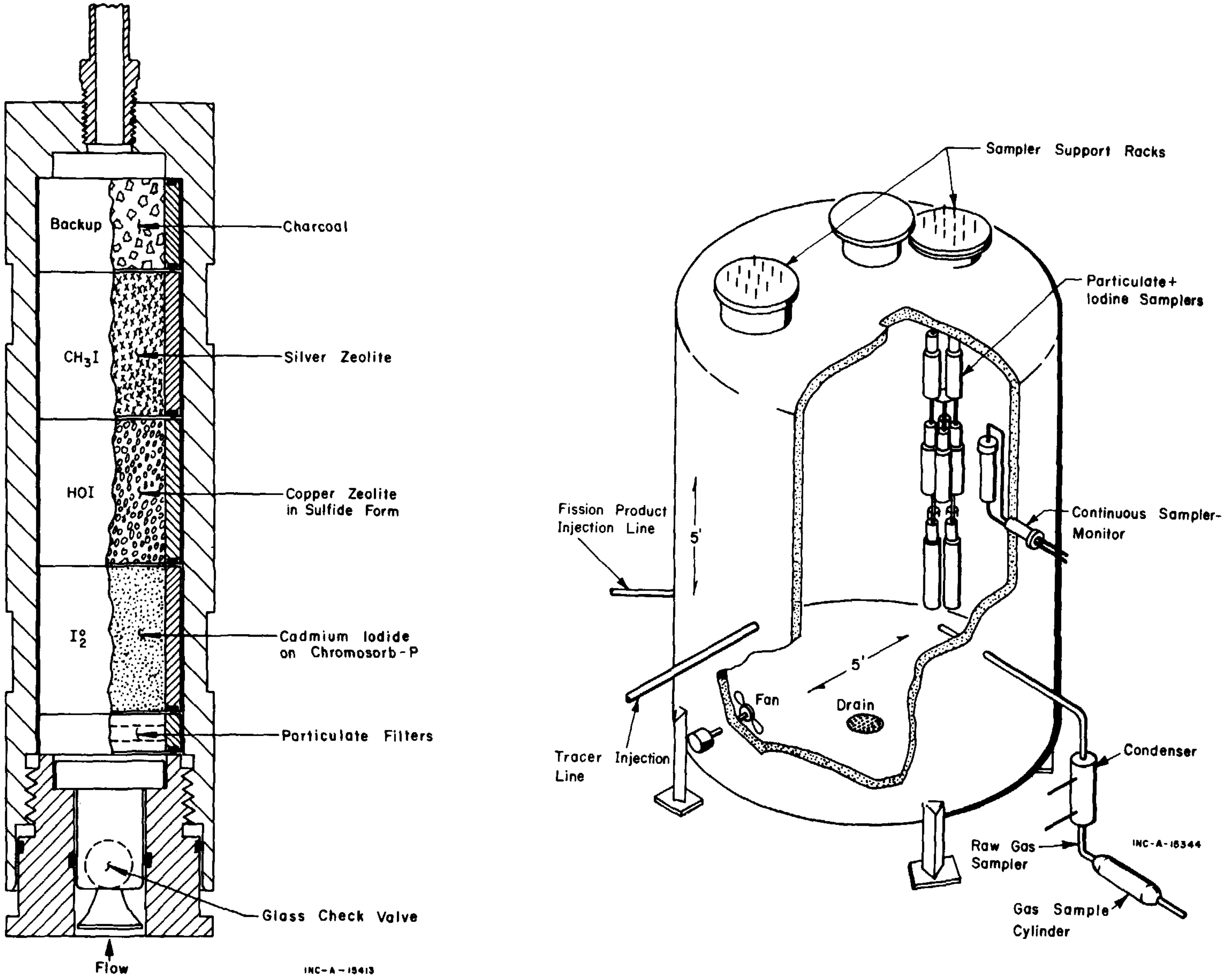


Fig. 2 Particulate Iodine Sampler as Installed in CDE

sampler components from the CDE atmosphere during the test, the glass check valve was pressurized with argon.

Following the run, the P-I samplers were removed from the CDE vessel and disassembled. The interior of the glass check valve for each of the samplers was leached to obtain the I-131 activity adsorbed on the check valve during sampling; the adsorbent train from each sampler was gamma scanned to determine the qualitative distribution of the I-131 activity on each bed; and each individual bed was gamma counted to give quantitative data for total iodine and species differentiation. Based on the activity in the samples, the flow through the samplers, and the specific activity of the iodine injected, the concentration, in $\mu g/M^3$, of the various species was calculated.

The iodine species differentiation data for the samplers in Tracer Run 10 are shown in Figure 3. The total iodine values are based on the sum of all iodine on the sampler components and in the inlet leach. The elemental idoine values are based on the sum of the activities in the inlet leach, the particulate filters, and the cadmium iodide bed. The distribution of activity on the two particulate filters of each sampler indicated that no significant iodine activity was associated with particles, and that the activity on the filters was due to plateout of gas phase elemental iodine.

Prior to the injection of the iodine species into the CDE vessel, 12 of the samplers were saturated with steam and became water-logged. These steam-saturated samplers provided total iodine and elemental iodine concentration data but did not adequately separate the hypoiodous acid from the methyl iodide. The problems associated with the check valves in the CDE tests will be avoided in the LOFT series by the use of a different hardware concept shown in Figure 4.

As stated, each of the samplers was gamma scanned to give a qualitative distribution of the activity adsorbed on each bed of the sampler. Two scans, one representative of an early sample in the run and one of a later sample, are shown in Figure 5.

Scan A, the three-minute sample, shows activity on the particulate filters, a sharp band at the front edge of the cadmium-iodide bed, a broadband on the copper-zeolite bed, and a sharp band on the silver-zeolite bed. Scan B, the 60-minute sample, after the iodine washout, shows minor activity on the filters and the cadmium-iodide bed, a very broadband on the copper-zeolite bed, and a sharp band on the silver zeolite bed. All of the particulate-iodine samplers that had been saturated with steam prior to the run showed very poor adsorption profiles on the copper-zeolite bed as indicated by the failure of activity to be reduced to background before the end of the bed (dashed curve, Scan B). The copper-zeolite beds from samplers on the dry rack showed better adsorption profiles; however, nearly all showed some activity breakthrough onto the silver-zeolite bed. No apparent correlation exists between breakthough and flow rate or any other

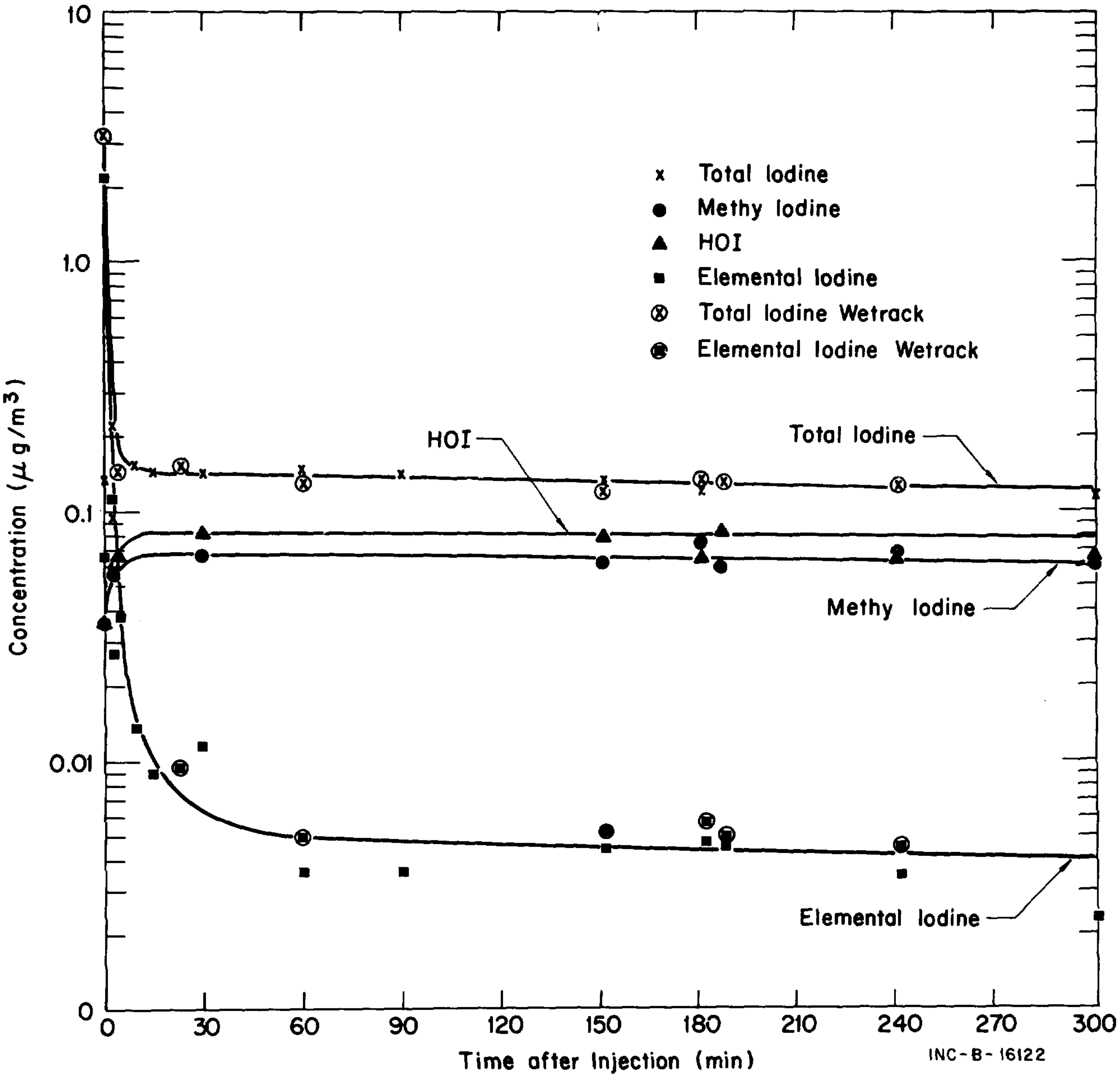


Fig. 3 Particulate-Iodine Sampler Species Differentiation in CDE Tracer Run 10

LOFT SEQUENTIAL PARTICULATE-IODINE SAMPLER

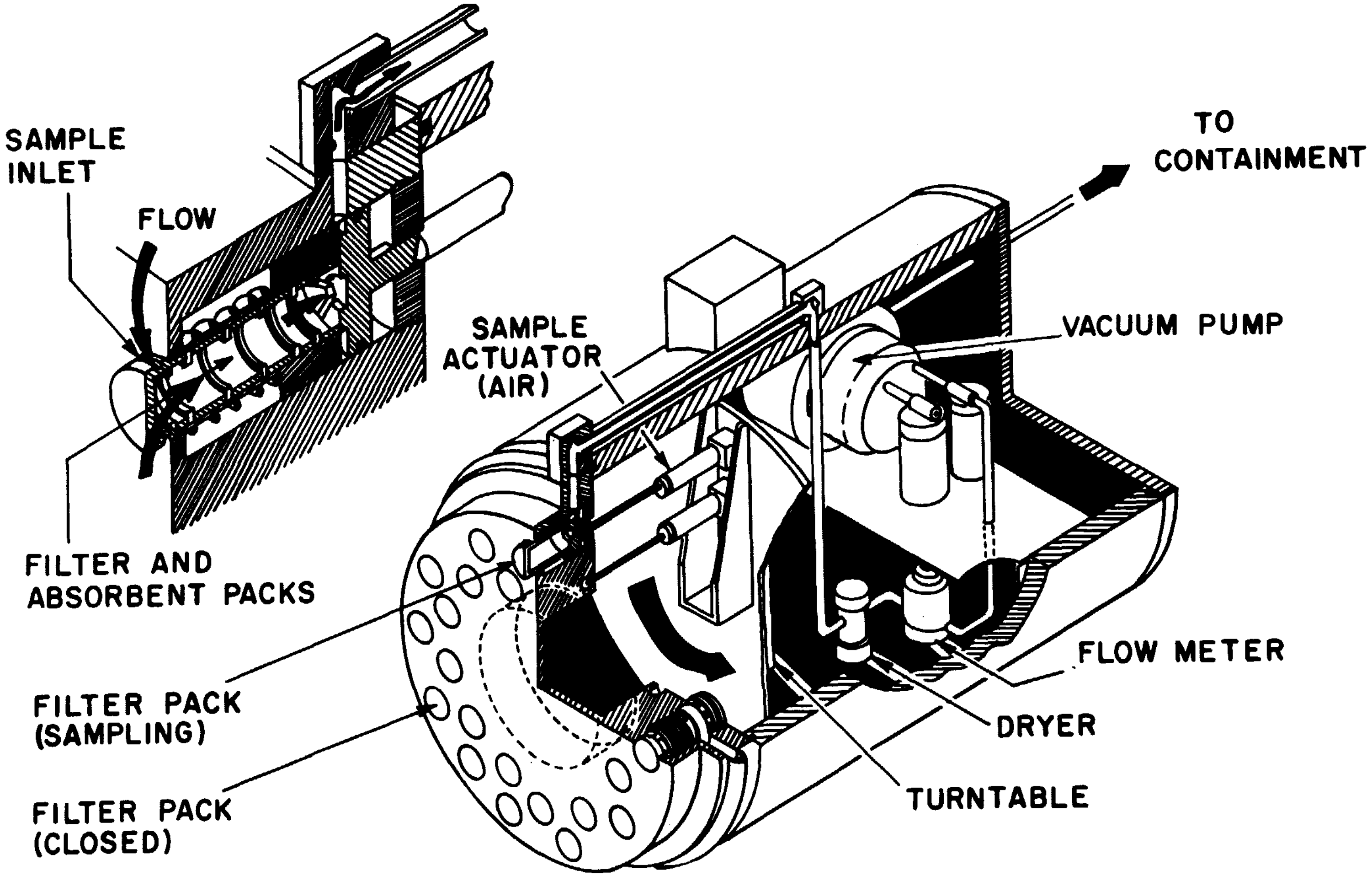


Fig. 4 LOFT Sequential Particulate-Iodine Sampler

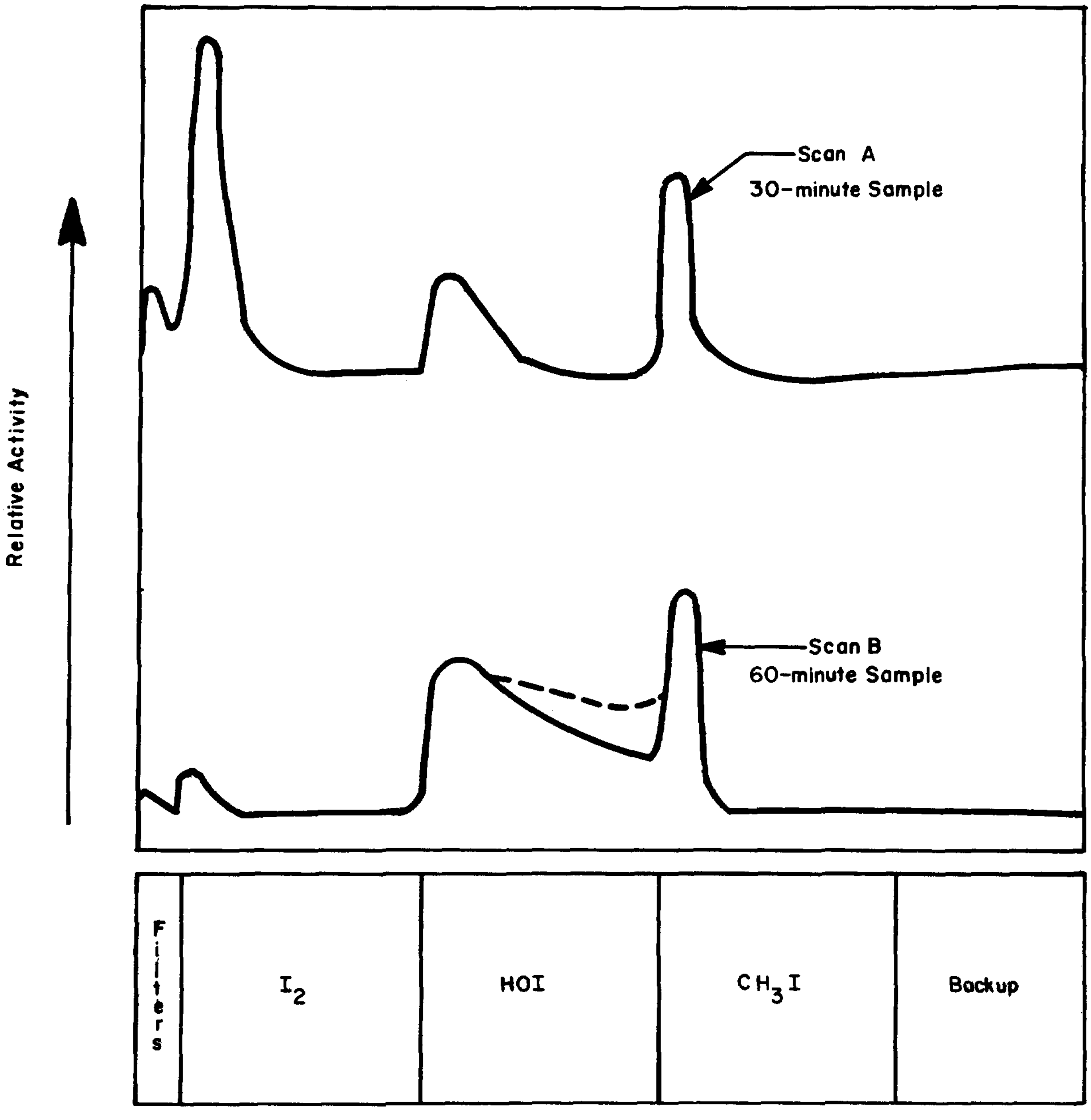


Fig. 5 Gamma Scans of Particulate-Iodine Sampler Components -- CDE Tracer Run 10

variable. The incomplete adsorption of hypoiodous acid by the copper zeolite results in an apparent high value for the concentration of methyl iodide.

To verify the design characteristics of the developed sampler, gas bomb samples of the CDE vessel atmosphere were taken at various times during the run, and the organic iodide content of the samples was determined by gas chromatography and gamma counting(12). No significant I-131 activity was detected which would indicate the presence of any volatile organic species other than methyl iodide. A comparison of the methyl iodide concentrations obtained from the raw gas bombs and from the P-I sampler is shown in Figure 6. Tracer Run 10 was the first large scale test of the copper zeolite and cadmium iodide adsorbents in the P-I samplers. The overall agreement between the two sampling systems, the P-I and raw gas, for methyl iodide is the best obtained to date.

The initial and essentially constant methyl iodide concentration, as measured in the raw gas samples, indicates that methyl iodide was present in the injected iodine source. The low methyl iodide values of the first samples from the P-I samplers indicate inhomogeneity of the vessel atmosphere early in the run. As discussed previously, the P-I sampler values for methyl iodide were high because of breakthrough of the hypoiodous acid onto the methyl iodide adsorbent.

<u>Particulate Filter Studies</u>: Several F-700[a] HEPA filters in series are presently being used for the P-I sampler. This type of filter adequately retains particulate fission products as indicated by their performance in test atmospheres produced by melting short-cooled, irradiated fuel pins(10); however, gas phase elemental iodine is also partally adsorbed. Several different types of HEPA filter materials have been tested(8), but all show partial adsorption of gas phase elemental iodine. The use of fluorocarbon membrane filters has been suggested. While the iodine adsorption problem is less serious, other investigators(2) have shown that the penetration of aerosols is too high to be tolerated.

Currently, the relative amounts of iodine bound to particles and that in the gas phase are estimated by the use of a series of filters. All of the iodine bound to particles is retained on the first filter of the series along with a fraction of the gas phase elemental iodine. The second and third filters in the series adsorb only gas phase iodine; and through extrapolation,the amount on these filters can be used to estimate the amount of elemental iodine adsorbed on the first filter.

Summary and Conclusions

Based on experimental data obtained in the laboratory and in the CDE facility, the concept of using selective specific adsorbents to

---

[a] Product of Flanders Filters, Inc, Riverhead, N.Y.

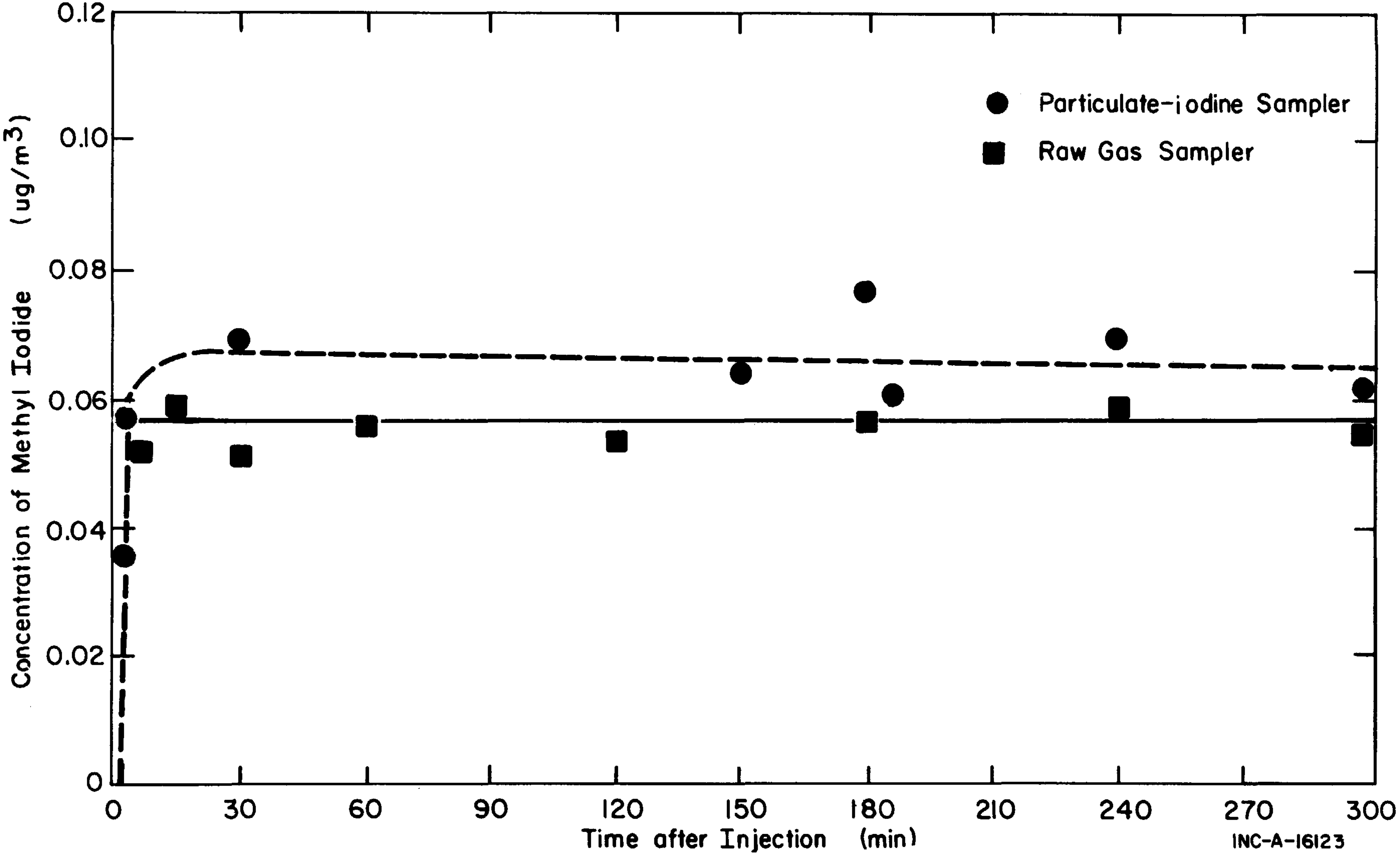


Fig. 6 Comparison of Particulate-Iodine Sampler and Raw Gas Methyl Iodide Concentrations

differentiate the airborne iodine species shows considerable promise. To improve the performance of the sampler, additional studies are necessary in the areas of particulate iodine discrimination and hypoiodous acid discrimination.

The possible ambiguity, as to the amount of iodine bound to particles and that in the gas phase which could arise from the undesired adsorption of gas phase iodine by the particulate filters, can be resolved by the use of several filters in series. The search for a better filter material is continuing.

Laboratory studies are in progress to establish the best means of eliminating the incomplete adsorption of hypoiodous acid by the copper-zeolite bed. Four approaches are being pursued: (a) decreased particle size of the copper zeolite, (b) increased bed length, (c) more complete copper exchange in the zeolite structure, and (d) use of a different basic zeolite.

The P-I sampler, as presently proposed, must be operated such that the sampler components do not become water-logged. Satisfactory operation of the sampler has been obtained in the laboratory and in the CDE vessel using 100 percent relative humidity atmospheres; however, if steam is allowed to condense in the samplers, species differentiation will not be complete. Conversely, if the samplers are overheated to prevent condensation, changes in the chemical state of the airborne iodine in the sample may occur.

Although the present concept of the P-I sampler is not an ideal arrangement, the sampler has shown that it will probably meet the design requirements for LOFT. Further refinements and additional testing are required to insure satisfactory performance under all conditions expected in the LOFT program.

References

(1) W. S. Megaw and F. G. May, The Behavior of Iodine Released in Reactor Containers, S. Nucl. Engrg., Parts A/B, 16 427 (1962).

(2) S. D. McCormack, Maypack Behavior in the Containment Systems Experiment--A Penetrating Analysis, BNWL-1145, August 1969, p. 3.

(3) L. F. Parsly, Jr., Experience with Maypacks in the Nuclear Safety Pilot Plants, ORNL-TM-2044, Feb. 1968, p. 2.

(4) W. E. Browning, Jr., and R. D. Ackley, "Characterization of Radioactive Iodine Compounds by Diffusional Deposition," Nuclear Safety Program Semiannual Progress Report, June 30, 1963. ORNL-3484.

(5) R. E. Adams, R. L. Bennett, W. E. Browning, Jr., Characterization of Volatile Forms of Iodine at High Relative Humidity by Composite Diffusion Tubes, ORNL-3985, August 1966, p. 4.

(6) R. L. Bennett, W. H. Hinds, and R. E. Adams, Development of Iodine Characterization Sampler for Application in Humid Environments, ORNL-TM-2071, May 1, 1968, p. 18.

(7) R. E. Adams, W. H. Hinds, and R. L. Bennett, "Development of Samplers and Aerosol Generators," Nuclear Safety Programs Annual Progress Report for Period Ending December 31, 1968, ORNL-4374, June 1969, p. 120.

(8) J. H. Keller, F. A. Duce, and F. O. Cartan, Retention of Iodine on Selected Particulate Filters and A Porous Silver Membrane Being Considered for the LOFT Maypack, IN-1078, May 1967, p. 10.

(9) V. Cofman, The Active Substance in the Iodination of Phenols, J. Chem. Soc., 115 (1040-9), 1919.

(10) W. A. Freeby, L. T. Lakey, and D. E. Black, Fission Product Behavior Under Simulated Loss-of-Coolant Accident Conditions in the Contamination-Decontamination Experiment, IN-1172, January, 1969.

(11) R. L. Nebeker, L. T. Lakey, W. P. Palica, J. H. Keller, D. E. Black, and R. E. Schindler, Containment Behavior of Volatile Fission Products in the CDE Under Simulated LOFT Conditions, IN-1394, September 1970.

(12) J. H. Keller and G. W. Webb, "Gas Chromatography Studies Applications," Analytical Chemistry Branch Annual Report Fiscal Year, 1969, R. C. Shank, Manager, IN-1316, September 1969, p. 118.

Work performed under Contract AT(10-1)-1230
U. S. Atomic Energy Commission
Idaho Operations Office

DISCUSSION

MERZ: Do you have any information on the absorption of HI on the cadmium iodide? Would you expect that to be indistinguishable from elemental?

KELLER: Yes, we feel that the HI will be retained on the cadmium iodide. We have not done tests in hydrogen rich atmospheres.

DETERMINATION OF THE INTERPARTICLE VOID VOLUME IN PACKED GRANULAR BEDS FROM AEROSOL BREAKTHROUGH CURVES*

Dwight W. Underhill
Parker C. Reist
Ronald Hurley

Harvard School of Public Health
665 Huntington Avenue
Boston, Massachusetts 02115

ABSTRACT

Accurate measurement of the interparticle void volume is required for understanding the mass transfer phenomena which take place in packed granular beds. For many beds, conventional measurement techniques are unsatisfactory because of inaccuracies or because they may alter the bed in some way. Here it is shown that the interparticle porosity of a packed bed may be determined accurately from the breakthrough curve of a flowing stream of aerosol. This method uses the statistical moments of the aerosol breakthrough curve. From the zeroth moment, a rate constant is found which describes the rate of aerosol removal by collisions between the aerosol particles and the granules in the packed bed. The analysis proceeds by using this collision rate factor to remove the effect of aerosol loss from the breakthrough curve data. Then from the normalized breakthrough curves obtained in this manner the first and second statistical moments are calculated. The interparticle porosity is determined directly from the first statistical moment. The second statistical moment, used in combination with the first statistical moment, determines the effective interparticle diffusion coefficient. Breakthrough curves obtained from beds of Raschig rings and Berl saddles were analyzed by this method and compared to results determined from conventional porosity measurement techniques.

1. Introduction

Packed granular beds are commonly used for the removal of air pollutants. The efficiency of these beds depends in part on two interparticle characteristics: the interparticle

---

*The work reported upon herein was performed under terms of Contract AT (30-1) 841 between Harvard University and the U.S. Atomic Energy Commission; and the U.S. Public Health Service Air Pollution Training Grant #5 T01 AP 00003-09.

porosity and the interparticle diffusion coefficient. In one other paper* given at this conference, equations were derived showing the effect of these parameters on bed performance. In this paper we report a new physical procedure for measuring these two interparticle parameters.

The usual method for measuring flow patterns is to inject an inert material and follow its movement downstream. For example, to measure the interparticle flow patterns in a packed bed, we could inject a pulse of an inert gas and follow its elution through the bed. But if the bed consists of a very porous packing such as charcoal, there could be as much intraparticle as interparticle porosity, and the assumption that the holdup time of an inert tracer was solely due to interparticle effects would be in gross error.

In order to measure the effects of the interparticle void volume, we must select a tracer material which will either not enter the intraparticle spaces, or if it does, react and be retained. One tracer which meets this criterion is a fine aerosol. First, aerosol particles have low diffusion coefficients and so are unlikely to diffuse into intraparticle spaces and if an aerosol particle does enter an intraparticle micropore, it has a very high probability of colliding with a surface and being permanently retained by van der Waals forces. This paper reports the use of aerosol breakthrough curves to measure the interparticle porosity and diffusion coefficient in packed beds.

2. Mathematical Analysis

2.1 Mass Balance. The differential equation for the mass balance of aerosol at a distance x from the inlet of a packed bed at a time, t, is

$$\frac{D\partial^2 C}{\partial x^2} - \frac{V\partial C}{\partial x} - \varepsilon\alpha C = \frac{\varepsilon\partial C}{\partial t} \tag{1}$$

---

*Analysis of Concurrent Adsorption and Chemical Reaction in Packed Beds.

where

$\frac{D\partial^2 C}{\partial x^2}$ = increase in aerosol particles from diffusion

$-\frac{V\partial C}{\partial x}$ = increase in aerosol particles from convection

$-\varepsilon\alpha C$ = loss of aerosol particles by collision

$\frac{\varepsilon\alpha C}{\partial t}$ = net gain in aerosol particles in the interparticle space at a distance x from the bed inlet at time, t.

and

C = concentration of particles in the interparticle space at a distance, x, and time, t
D = interparticle diffusion coefficient, cm^2/sec
t = time following introduction of pulse of aerosol, sec
V = superficial velocity, cm/sec
x = distance from inlet, cm
α = rate constant for aerosol attachment, sec^{-1}
ε = interparticle porosity, cc void volume/cc bed volume

2.2. Exact Solution. An exact solution of Equation 1, assuming a unit pulse (or delta function) input of aerosol at time, t = 0 is

$$C(t) = e^{-\alpha t}\left\{\frac{x}{2\sqrt{\pi D t^3/\varepsilon^3}}\, e^{-\frac{(x - \frac{Vt}{\varepsilon})^2}{4Dt/\varepsilon}}\right\} \qquad (2)$$

By trial and error, a best fitting curve to Equation 2 can be used to estimate the unknown parameters, α ε and D. In this procedure the three unknown parameters are varied sequentially and the theoretical curve thus obtained compared with the experimental data points using a least squares technique, until optimum values for the unknown parameters are obtained.

2.3 Calculation by Moment Analysis. Analysis by moments, which also is exact, allows a solution to be obtained by varying only a single parameter. The first step in this analysis is to take the Laplace transform of Equation 1 with respect to time, converting it from a partial to an ordinary differential equation.

$$\frac{Dd^2\bar{C}(s)}{dx^2} - \frac{Vd\bar{C}(s)}{dx} - \varepsilon(s+\alpha)\bar{C}(s) = 0 \qquad (3)$$

Then solving for $\bar{C}(s)$, the transformed solution gives:

$$C(s) = e^{-\left[\left(\sqrt{V^2 + 4\varepsilon D(\alpha+s)} - V\right)x/2D\right]} \qquad (4)$$

If the function, $\bar{g}(s)$ is defined as

$$\bar{g}(s) \equiv \mathcal{L}\left[e^{\alpha t}c(t)\right] = \bar{C}(s-\alpha) \qquad (5)$$

then

$$\bar{g}(s) = e^{-\frac{\left(\sqrt{V^2 + 4s\varepsilon D} - V\right)x}{2D}} \qquad (6)$$

The nth ordinary moment of g(t) defined by

$$M_n = \int_0^\infty t^n \, g(t) \, dt \qquad (7)$$

is from one of the elementary properties of the Laplace transform, equal to

$$M_n = (-1)^n \lim_{s \to 0} \frac{d^n}{ds^n} g(s) \tag{8}$$

so that

$$M_0 = 1 \tag{9}$$

$$M_1 = \frac{\varepsilon x}{V} \tag{10}$$

$$M_2 = \frac{2\varepsilon^2 xD}{V^3} + \frac{\varepsilon^2 x^2}{V^2} \tag{11}$$

Equations 10and 11 are used below to analyze the interparticle flow patterns of a packed bed.

2.4. Analysis of Experimental Data to Give Interparticle Porosity. In order to determine ε from a C(t) curve, we need only to find the appropriate value of α such that

$$\int_0^\infty e^{\alpha t} C(t)dt = 1. \tag{12}$$

Then from Equations 7 and 10

$$\varepsilon = \frac{V}{x} \int_0^\infty te^{\alpha t} C(t)dt. \tag{13}$$

This method of analysis appears to be quite straightforward. As long as all values of C(t) are positive (and by definition they must all be positive) there is only one possible value for α.

Pulses of aerosol are not required for this analysis. If F(t) is the elution curve obtained from passing an aerosol-free gas through a bed in which a constant input has been passed for a long time up to time t = 0, then

$$C(t) = \frac{-\frac{d}{dt}(F[t])}{C_o} \qquad (14)$$

where

C_o = the input concentration of aerosol.

2.5. Calculation of the Interparticle Diffusion Coefficient. The interparticle flow patterns are responsible for the spreading of the pulse (or front) of aerosol as it passes through the bed. From Equations 10 and 11, the effective diffusion coefficient is given by

$$D = \frac{Vx}{2}\left\{\frac{M_2}{M_1^{\,2}} - 1\right\} \qquad (15)$$

The effective diffusion coefficient in packed beds is usually found to be a linear function of the carrier gas velocity, viz,

$$D = \varepsilon\gamma D_m + \lambda_p d_p V \qquad (16)$$

where

γ = the tortuosity factor for interparticle diffusion, dimensionless

D_m = the coefficient for molecular diffusion of the aerosol, cm^2/sec

λ_p = the coefficient for eddy diffusion, dimensionless

d_p = the mean diameter of particles in the bed.

In finding D as a function of V, the fundamentals of the effect of flow patterns in packed beds may be determined.

For an aerosol at linear velocities of the order of 1 cm/sec passing through bed granules of about 1 cm diameter, $\lambda_p d_p V >> \varepsilon\gamma D_m$, and

$$\lambda_p \simeq D/d_p V \qquad (17)$$

3. Experimental Procedure

Figure 1 is a schematic diagram of the experimental apparatus. Condensation nuclei originating in the laboratory compressed air system were used for the test aerosol. Even though these nuclei do vary somewhat in size, we believed that with their low and fairly equal diffusion coefficients they would behave similarly to a homogeneous cloud. To eliminate concentration fluctuations the test aerosol was passed through a 11,000 liter mixing tank prior to use.

Aerosol concentrations were measured continuously with a General Electric condensation nuclei counter and data were read out on an x-y recorder. Nuclei concentrations upstream of the column were determined at the beginning and the end of each run and compared for consistency. If the values were the same, it was assumed that the aerosol concentration was constant throughout the test.

Each run consisted of passing filtered air through a packed column having a volume of about 5 liters until equilibrium conditions were established downstream of the bed, then passing nuclei through the bed until a new equilibrium was reestablished downstream. The breakthrough curve of the aerosol was plotted on the x-y recorder. At this point clean air was passed through the bed once more until the initial equilibrium level was reached, thus producing a flushing curve for the bed. This curve was also plotted using the x-y recorder. Throughout the course of each run flow through the bed was maintained at a constant value.

Table 1 lists essential characteristics of the two packing materials used in the tests and Figure 2 shows the recorder output of a typical run.

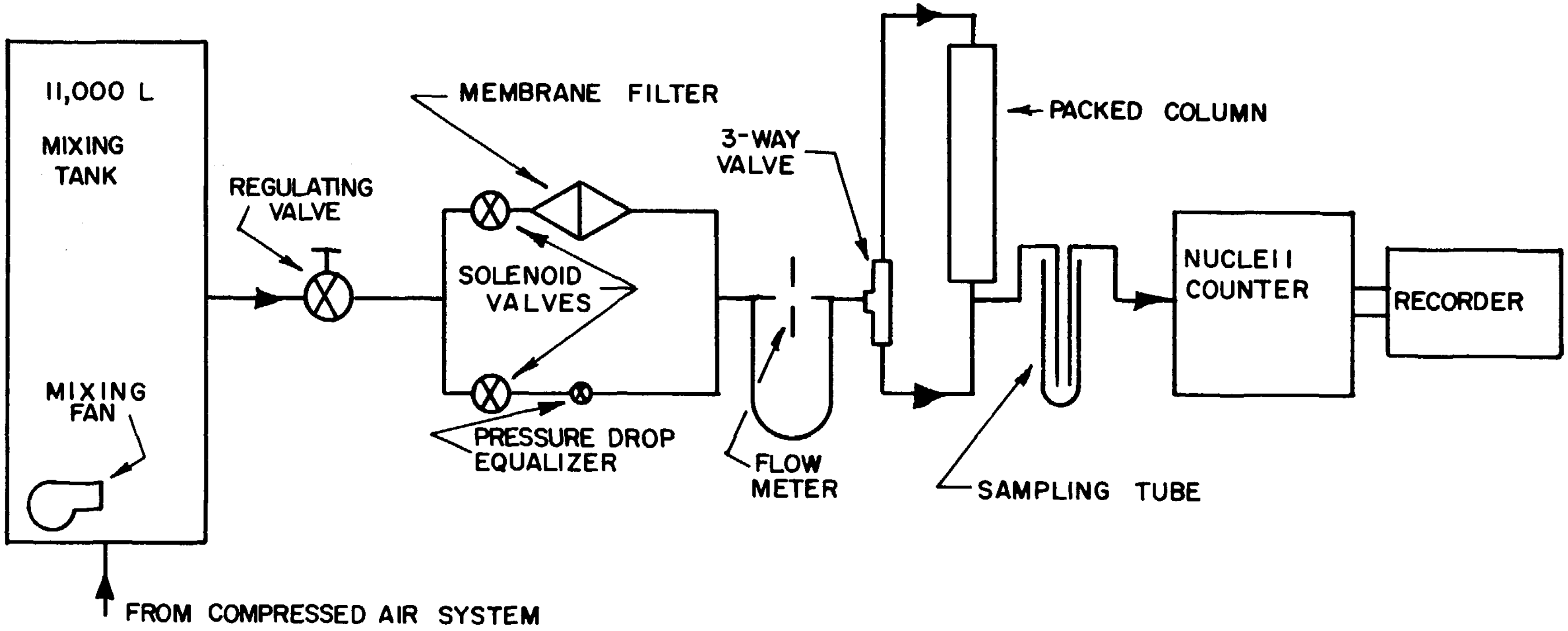


FIG. 1 - SCHEMATIC DIAGRAM OF APPARATUS

TABLE 1

Characteristics of Bed Packing Materials

Type	Size Range	Characteristic Size cm	Typical External Porosity	Conventionally Measured Porosity, %
Rachig Rings	ℓ = 1 cm, d_o = 1 cm, d_i = 0.5 cm	1.0	67(1)	60.2(2)
Beryl Saddles	ℓ = 0.7 cm	0.7	65(1)	65.4(2)

Notes: (1) Perry, J.H., *Chem. Eng. Handbook*, 4th Ed., Pages 18-28, McGraw-Hill (1963).

(2) Measured by filling packed column with water.

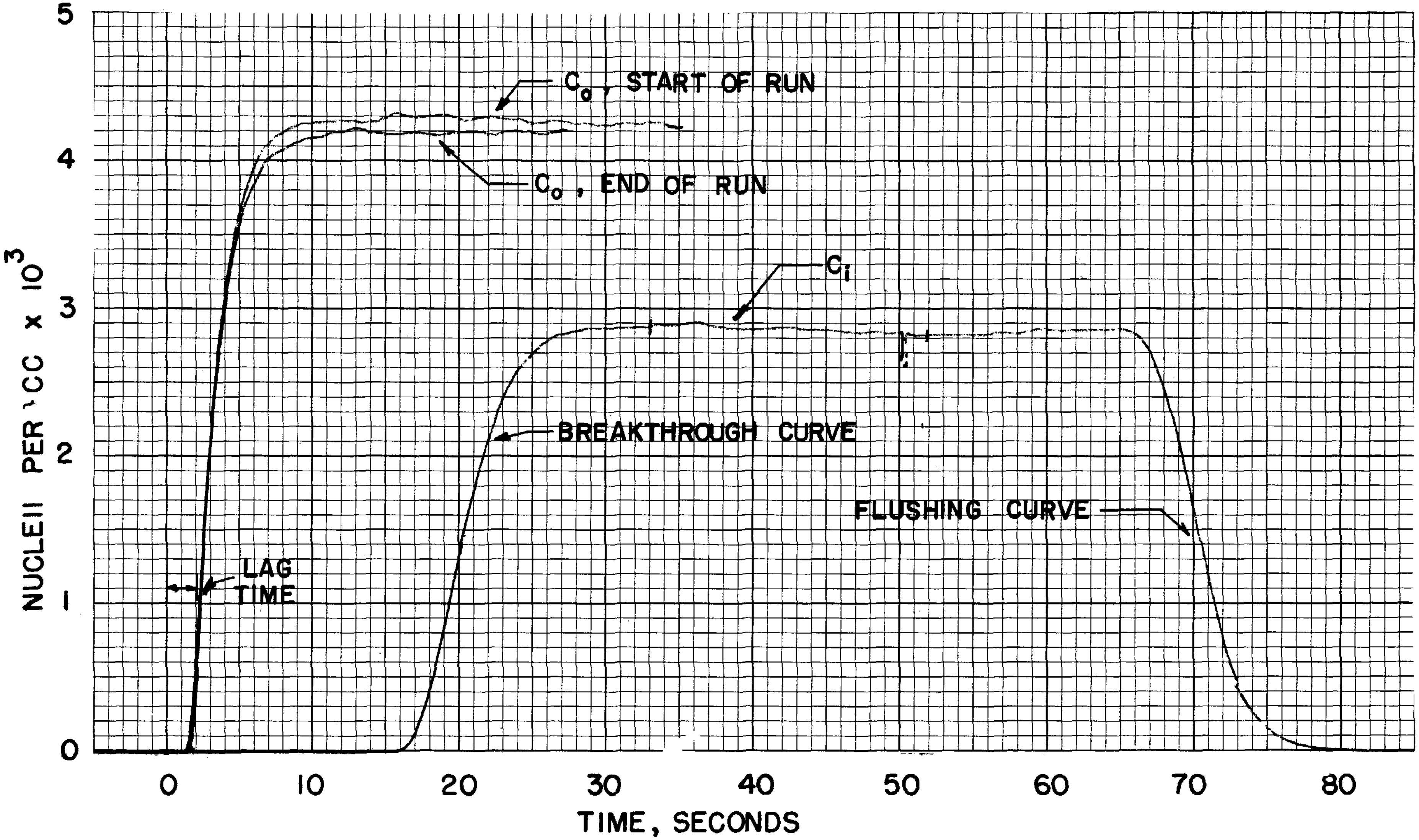


FIG. 2 - TYPICAL OUTPUT FROM NUCLEII COUNTER

As can be seen from Figure 2, when the nuclei bypass the column a characteristic breakthrough (or flushing) curve is also produced. This effect, the so-called "lag time" was also eliminated from our raw data by subtraction, as noted on Figure 2. In addition, background nuclei levels were also subtracted from the raw data.

For an ideal column, the breakthrough curve, $y(t)$, and flushing curve, $z(t')$ are related as

$$z(t') = y(\infty) - y(t) \tag{18}$$

where t and t' represent respectively the time after starting to add nuclei to the column and the time after a flow of clean air is initiated through the column.

Thus we considered the best estimate of column behavior to be the average of $z(\tau)$ and $y(\infty) - y(\tau)$.

Differences between successive data points of the "best estimate" flushing curve were then computed and a value of α calculated such that Equation 12, cast in the difference notation

$$\Sigma_{i=1}^{n} e^{\alpha t_i} C(t_i)\Delta t = 1 \tag{19}$$

was satisfied.

Using this value of α and the measured $C(t_i)$, the first and second moments, M_1 and M_2 could be determined from the difference equations.

$$M_1 = \Sigma_{i=1}^{n} t_i e^{\alpha t_i} C(t_i)\Delta t \tag{20}$$

and

$$M_2 = \Sigma_{i=1}^{n} t_i^2 e^{\alpha t_i} C(t_i)\Delta t. \tag{21}$$

Finally, the interparticle porosity was computed from Equation 10 and the effective diffusion coefficient from Equation 15.

4. Results

The average porosity of Berl saddles packed in a cylindrical column, as estimated from four runs at different velocities through the bed, was determined to be 67.0% with a standard deviation of 4.2%. This value compares favorably to the reported value of 65% as given by Perry(1) and also agrees with the bed porosity of 65.4% which was determined by measuring the amount of water necessary to fill the packed bed.

Good agreement with reported data was also found for Raschig rings. With five runs at different velocities we found an average porosity of 68.4% with a standard deviation of 1.6%, whereas Perry(1) gave a porosity of 67% for the same size rings. When, however, we attempted to confirm this measurement using a water filling technique, we only found a porosity of 60.2%, significantly less than the value measured using the method of moments. One possible reason for this discrepancy lies in the nature of the Raschig rings. Since they pack as randomly oriented cylinders, some cylinders will be horizontal, and when the bed is filled with water, it is conceivable that air bubbles may be trapped, making the overall bed porosity appear lower. With the Berl saddles air trapping should not be observed.

Figure 3 is a plot of the measured bed porosity as a function of the Reynold's number, defined as

$$R_e = \frac{\varepsilon V d}{\nu} \tag{22}$$

where

d = the characteristic grain diameter of the Berl saddles or Raschig rings
ν = the kinematic viscosity.

From this figure it may be concluded that in accordance with theory, the measured values of porosity

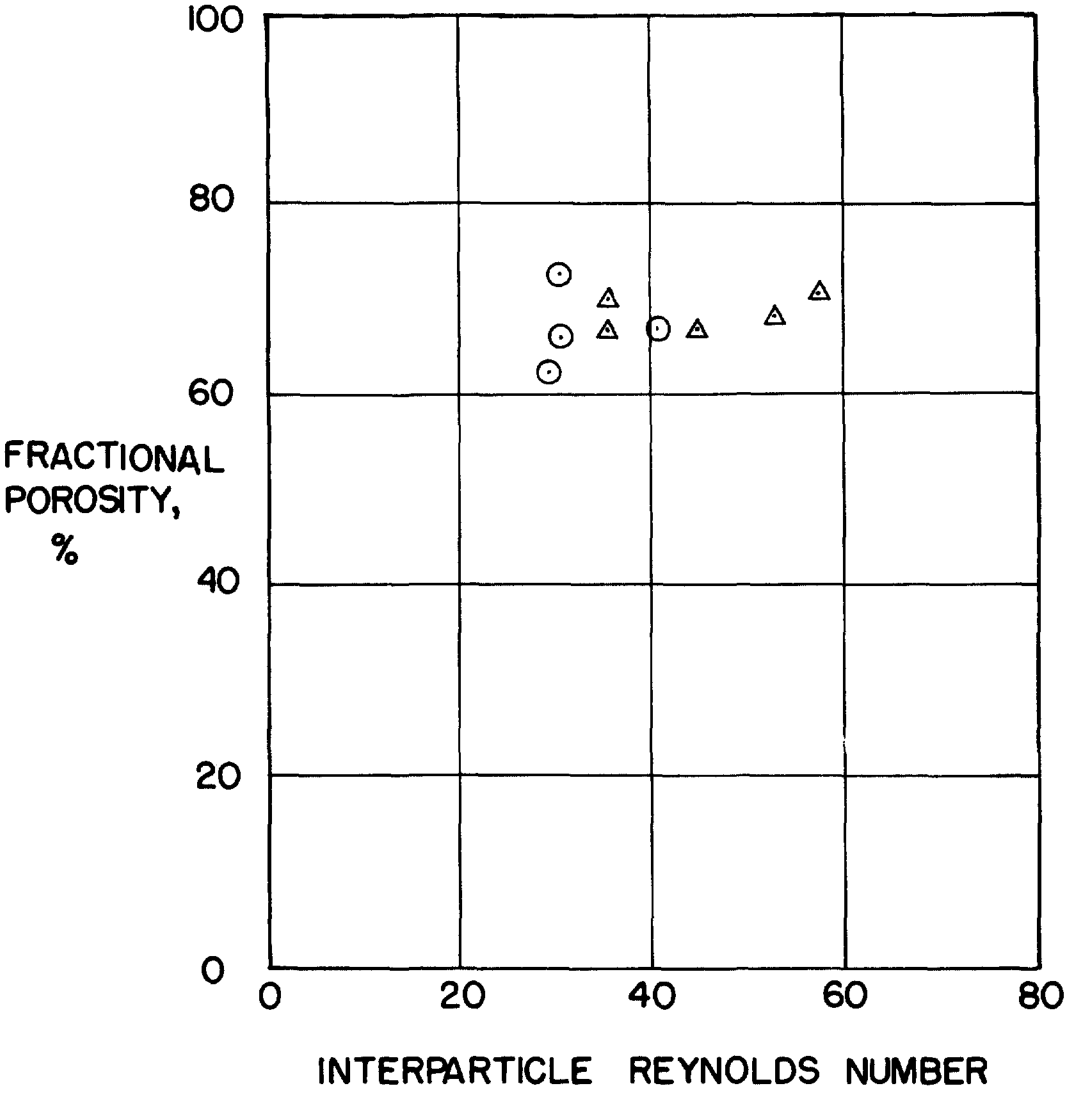


FIG. 3 - POROSITY AS A FUNCTION OF REYNOLDS NUMBER
(○ - BERYL SADDLES, △ -RACHIG RINGS)

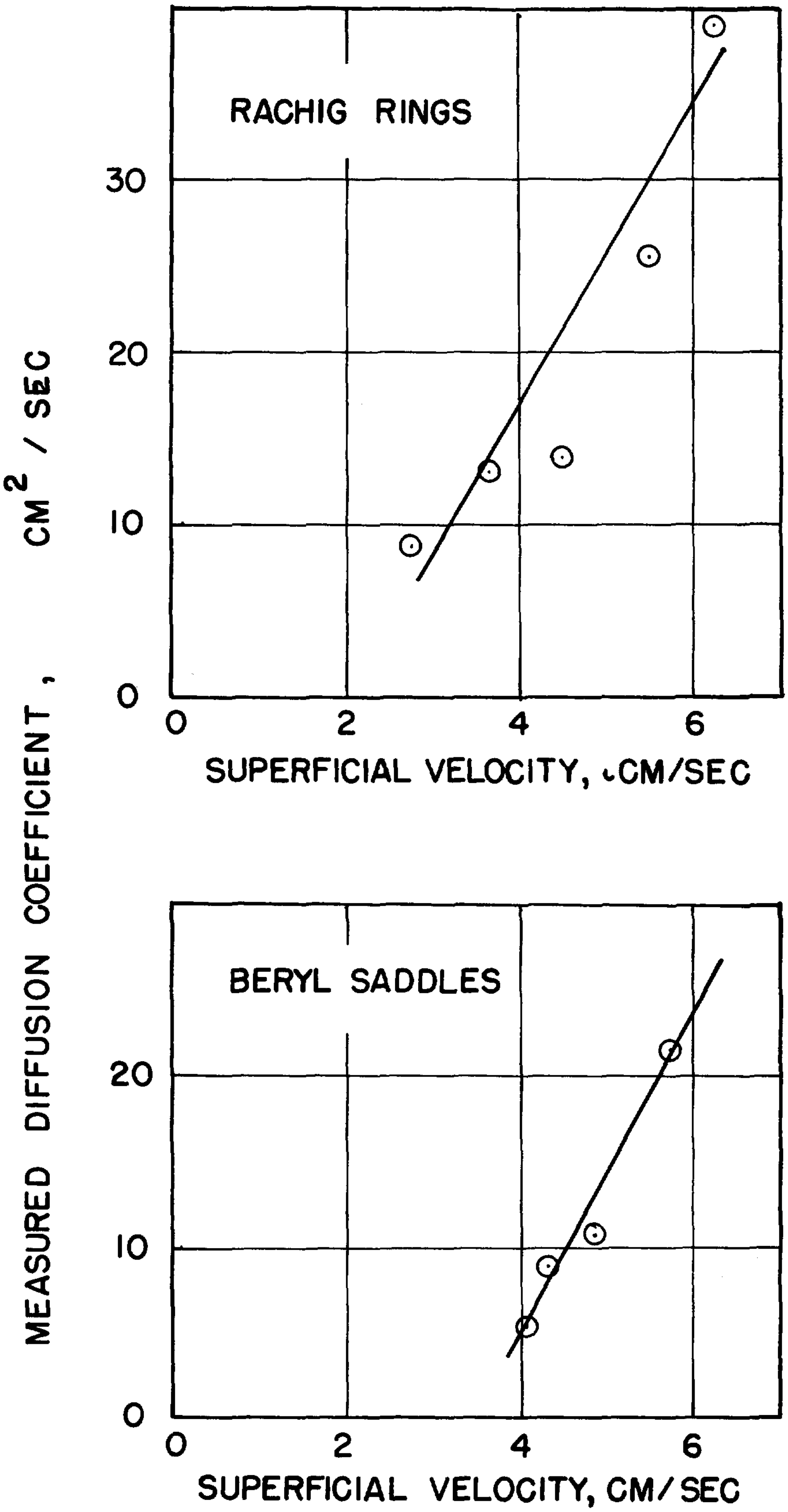


FIG. 4 - MEASURED DIFFUSION COEFFICIENTS AS FUNCTIONS OF VELOCITY

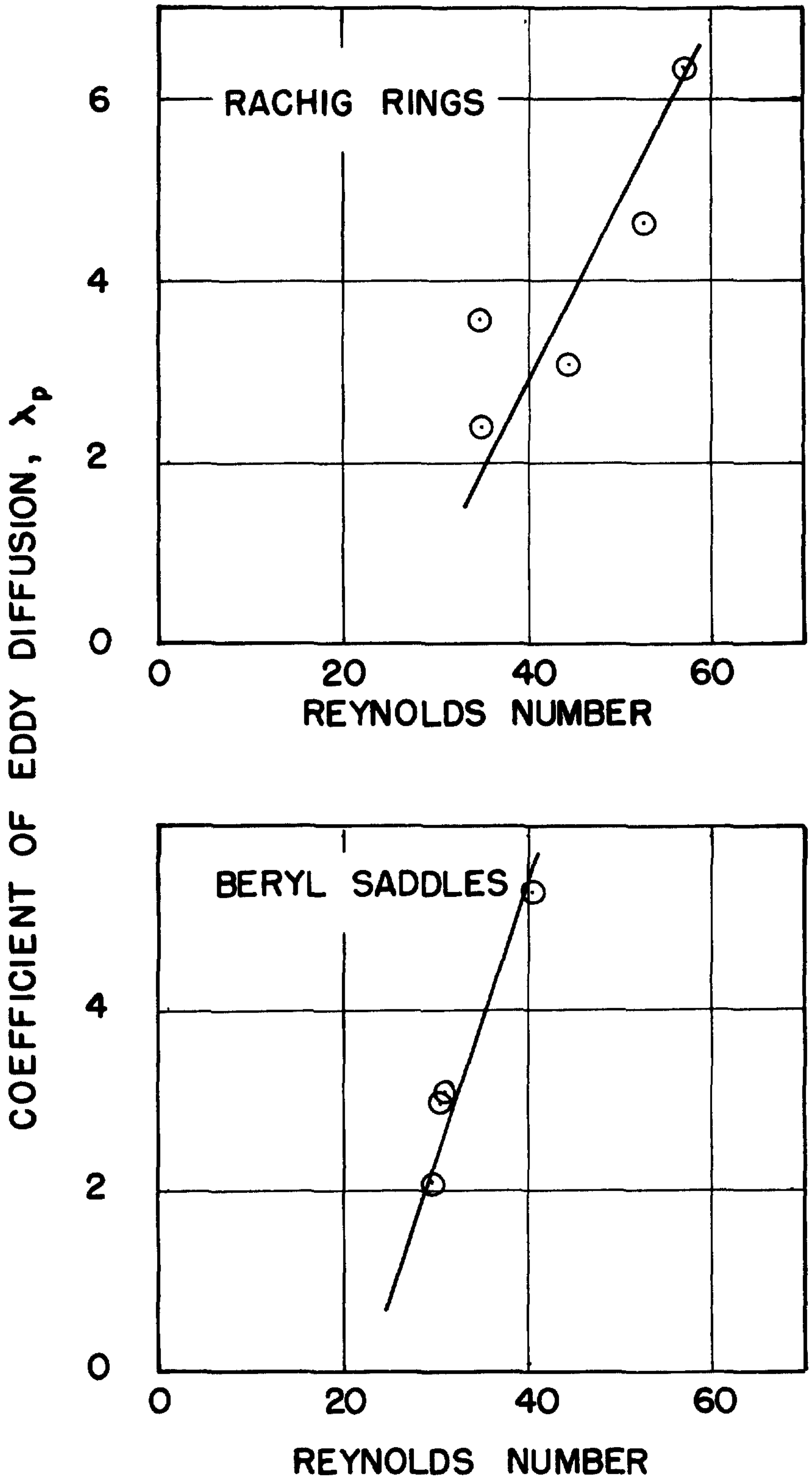


FIG. 5 - COEFFICIENT OF EDDY DIFFUSION AS A FUNCTION OF REYNOLDS NUMBER

have very little, if any observed dependence on aerosol velocity through the bed.

Figure 4 gives a plot of diffusion coefficients as a function of superficial velocity. As mentioned earlier, the effective diffusion coefficient describes spreading of the front of the aerosol as it passes through the bed. This effective diffusion coefficient is made up of a part which results from molecular diffusion of the aerosol particles and a portion resulting from eddy diffusion of the aerosol particles. In our experiments, eddy diffusion predominates. Figure 5 gives the coefficient of eddy diffusion, calculated from the expression

$$\lambda_p = \frac{L}{2d_p}\left\{\frac{M_2}{M_1^2} - 1\right\} \qquad (23)$$

plotted as a function of the interparticle Reynolds number. All runs were at velocities transitional between laminar flow, $Re < 1.0$, and bulk turbulent flow, $Re > 100$. In this intermediate region, λ_p is seen to be a function of Reynolds number, and not a constant as it is commonly assumed to be in laminar flow. More accurate measurements of λ_p as a function of Reynolds number should permit improved calculation of the overall efficiency of adsorption beds.

REFERENCE

1. Perry, R.H., Chilton, C.H. Kirkpatrick, S.D., Eds., CHEMICAL ENGINEERS' HANDBOOK, 4th Ed., McGraw-Hill Book Co., Inc. (1963).

DISCUSSION

CRAIG: Just a very simple one concerning this last slide of yours. How do you define Reynolds number here?

UNDERHILL: This Reynolds number is calculated from the kinematic viscosity, ν ; the interparticle velocity, v_i ; and the characteristic grain diameter, d, is the most difficult to determine. For the Raschig rings, both the height and diameter was one centimeter and this distance was used as the characteristic diameter; for the Berl saddles we used the average of several measurements in different directions.

CRAIG: What is your equation for the Reynolds number?

UNDERHILL: Equation 21 in the paper. There is a misprint in the preprint. The factor, d, should be defined as the characteristic grain diameter, not as the bed diameter.

KOVACH: I have two questions for you. One is would you consider that because of the large number of particles that you had in the bed what you are measuring is not really eddy diffusion. Generally, in most experimental data it is shown that the eddy diffusion coefficients become high at small particle sizes, and small interparticle volumes. The second question is your experimental method is somewhat dependent on aerosol particle sizes and also the particle size in the bed, because you can get to the point where you develop a stationary efficiency front which doesn't appear to move with time. At least for some aerosols of polystyrene and 0. 3 DOP we will be presenting data tomorrow where we obtained a stable efficiency in packed bed for aerosol removal, and with considerable length of time. We didn't see any movement. So we didn't get any breakthrough as such. It appears that we had a somewhat stationary front in the adsorbent bed.

UNDERHILL: In answer to your questions, I believe that we did measure eddy diffusion in these experiments and that we did not observe stationary fronts as might be caused by a nonlinear isotherm. A nonlinear isotherm implies interaction between aerosol particles and this just did not take place at the concentrations we had in the bed. In regard to your experiments we have some experiments which we didn't report here in which we passed a very fine aerosol through a bed of charcoal. This experimental work was completed just as I was leaving for this conference. The results we had were quite puzzling until we discovered a calibration error in one scale of the aerosol analyzer. This scale was not used for the data reported here. The data we obtained from the charcoal beds were maddeningly reproducible, but obviously in error. We were getting interparticle porosities of the order of 80%, when we knew the true value to be about 40%. We believe that once the aerosol analyzer is recalibrated we will get accurate results for the charcoal beds.

KOVACH: What are your bed dimensions?

UNDERHILL: Our bed was contained in a 3-1/2 inch diameter tube about 3 feet tall.

DEVELOPMENT OF A CONTINUOUS SAMPLER-MONITOR FOR THE LOFT CONTAINMENT ATMOSPHERE

R. E. Schindler, R. R. Hammer, D. E. Black, L. T. Lakey

Idaho Nuclear Corporation
National Reactor Testing Station
Idaho Falls, Idaho

ABSTRACT

A Continuous Sampler-Monitor (CSM) has been developed for the LOFT Integral Test Program. During the LOFT, the CSM will remotely sample and determine the airborne noble gas, total iodine, and organic iodide concentrations and will monitor changes in total activity in the LOFT containment atmosphere. In the current CSM, a 2 liter/min. stream of the atmosphere is continuously drawn into a scrubber where the elemental iodine and most of the particulate fission products are washed into a stream of basic-thiosulfate scrubbing solution; the noble gases, organic iodides, and hypoiodous acid remain in the gas stream. The scrubbed gas stream and the scrubbing solution flow in a common line to a sampling station located outside the containment building where they are separated. The gross activity levels of the separated streams are monitored, and samples of each stream are analyzed to determine the concentrations of individual nuclides in the containment atmosphere.

In tests conducted with low concentrations of iodine or xenon in an 86-ft^3 vessel under simulated Loss-of-Coolant Accident atmospheric conditions, the CSM performed satisfactorily. Xenon values from the CSM were representative within 4 percent of xenon concentrations in the containment atmosphere. The CSM total iodine values were accurate to at least 50 percent, and the CSM organic iodide values to within 30 percent when corrected for the methyl iodide absorbed in the scrubbing solution. The gross activity monitors provided reasonable gross activity records.

Introduction

A Continuous Sampler-Monitor (CSM) has been developed to determine fission product concentrations in the containment building atmosphere during the LOFT (Loss of Fluid Test) Integral Test Program(1,2). The LOFT is an engineering scale demonstration of engineered safeguard systems for use in the unlikely event of a reactor Loss-of-Coolant

Accident (LOCA). In the LOFT, the coolant will be released from a 55 MW pressurized water reactor and the operation of engineered safeguard systems demonstrated(1). The atmosphere in the 300,000 ft^3 LOFT containment building following the coolant blowdown will consist of an air-steam atmosphere containing a short-cooled fission product mixture released from overheated fuel pins. If the fuel pin damage is limited to cladding failure, the fission-product mixture will consist mainly of the noble gases and their daughters, and lesser quantities of the radioiodines as elemental iodine vapors, organic iodides, iodine adsorbed on particulates, and hypoiodous acid vapors. Particulate fission products--e.g. cesium, tellurium, and molybdenum--would be present if the fuel pins overheat sufficiently to melt or vaporize.

Samples provided by the CSM during the LOFT will be analyzed to determine the noble gas, total iodine, and organic iodide concentrations in the containment atmosphere. The CSM will also continuously monitor and record the gross activity levels in the containment atmosphere.

The CSM performance met the LOFT criteria in a series of evaluation tests conducted under simulated LOCA conditions. However, the development and testing program was terminated before the performance of the CSM could be refined or rigorously demonstrated. The CSM system and the performance in the evaluation tests are described in the following sections. Additional details are reported elsewhere(3).

Although developed specifically for the LOFT, the CSM might be adapted for monitoring off-gases from a reprocessing plant handling short-cooled fuels or other operations where monitoring radioiodine concentrations in the presence of noble gas nuclides is necessary.

CSM Design

The CSM uses a scrubber located in the containment building to continuously and remotely sample the atmosphere. The fission products are separated into a liquid and a gas stream, which leave the containment building together, then are separated outside the containment building.

Elemental iodine vapor cannot be transported in a gas stream through long lines, because it deposits on the wall of the sampling line. The CSM minimizes iodine deposition by removing elemental iodine from the gas stream with a scrubber located inside the containment building at the point of sampling. A continuous sample of the containment atmosphere is drawn into a 2-in. OD by 12-in. long "Teflon" scrubber (shown in Figure 1) by a pump located outside the containment building and connected to the scrubber by 3/8-in. stainless steel tubing. The atmosphere sample enters the vertical scrubber through three ports at the top of the scrubber and is washed by a fine mist of scrubbing solution. Iodine and most of the particulate-associated fission products are absorbed by the scrubbing solution, leaving noble gases, organic iodides, hypoiodous acid, and some particulates in the gas stream. The gas sample stream and the scrubbing solution flow sequentially from the outlet at the bottom of the scrubber through stainless steel tubing to a cooler located outside the containment building. Excess moisture is removed from the gas in the cooler. After being cooled, the gas and the scrubbing solution flow to a pot where the liquid is separated from the gas. As shown in Figure 2, the scrubbing solution and gas then flow separately to gross activity monitors and sampling stations.

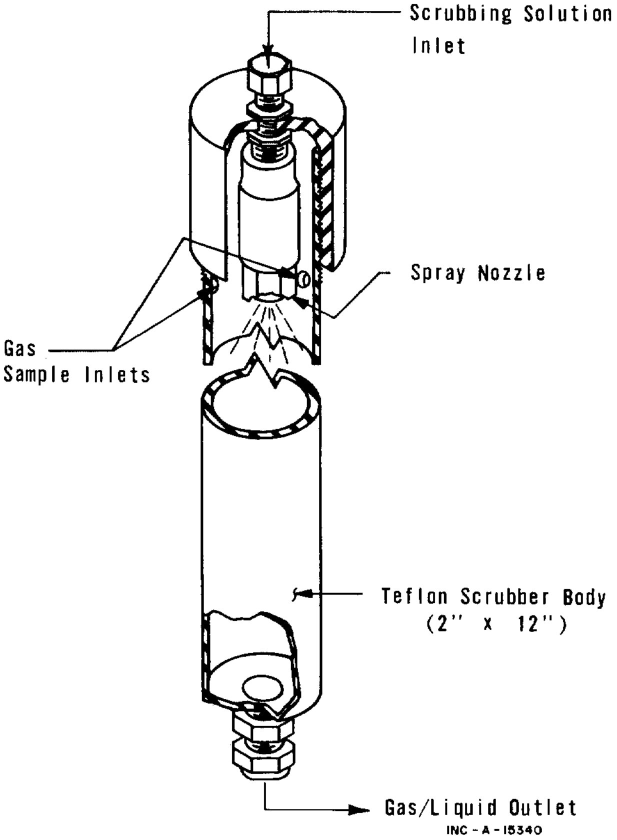


Fig. 1 Cut-a-way view of CSM scrubber.

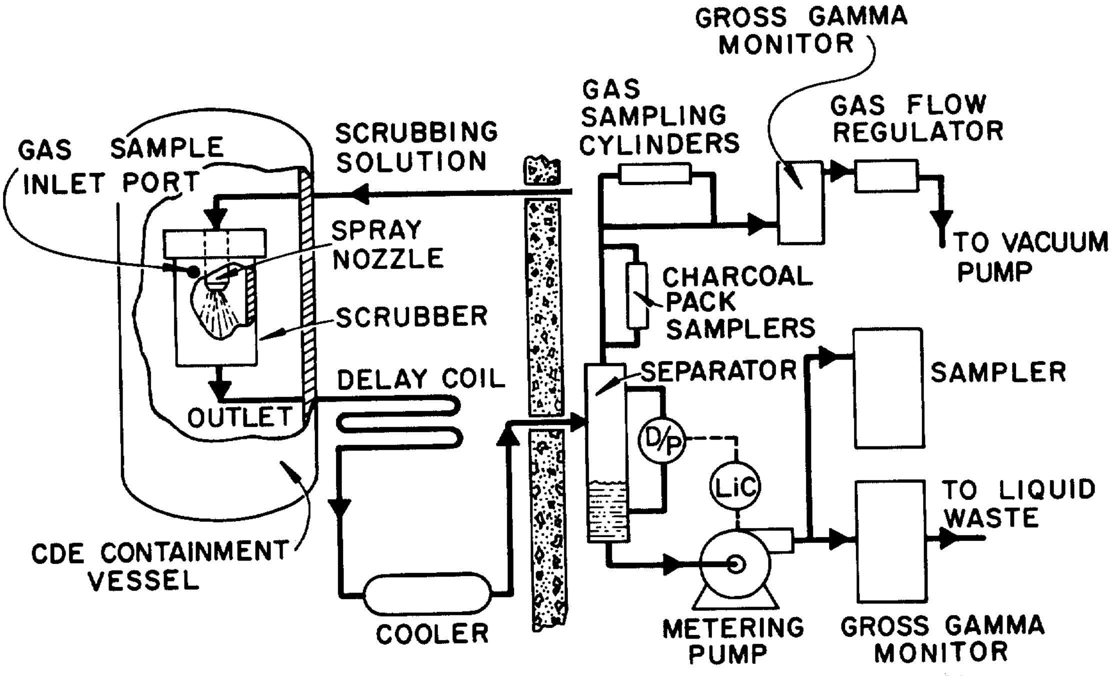


Fig. 2 Simplified flowsheet of Continuous Sampler-Monitor

The atmospheric sample flow is controlled by a system located downstream of the gas sampling station which maintains a constant mass flow of dry air. This gas flow control system maintains a constant volumetric gas flow rate into the scrubber when the air and steam in the containment building are well mixed. A vacuum pump downstream of the gas flow control system maintains the pressure difference which drives the gas flow. A liquid-level control system--consisting of a differential-pressure transmitter, a controller, and a variable-speed metering pump--maintains the required liquid level in the separator pot.

The concentrations of individual nuclides in curies per unit volume of containment atmosphere are determined from the analyses of two gas stream samples and a liquid stream sample. The samples and the analyses required are listed in Table I.

TABLE I

CSM SAMPLES

Effluent Stream	Sample Form	Analyzed By	Analyzed For
Liquid	Bottle	Gamma-Ray Spectrometry	Total Iodine
Gas	Sorbent Pack	Gamma-Ray Spectrometry	Total Iodine
Gas	Gas Sample	Gas Chromatometry Followed by Gamma-Ray Spectrometry	Noble Gases and Organic Iodides

The total activity of each iodine nuclide in the CSM liquid stream is determined by analysis of liquid samples collected intermittently in small bottles and analyzed by gamma-ray spectrometry. The total iodine concentration in the CSM gas stream is determined by analysis of small charcoal packs (Barnebey-Cheney Type 727 charcoal) through which a known volume of gas stream is diverted. The total iodine concentration in the containment vessel is calculated by multiplying the iodine concentration in the liquid stream by the liquid-to-gas-flow ratio and adding this value to the total iodine concentration in the gas stream.

The concentrations of light organic iodides (methyl, ethyl, and propyl iodides) and noble gases in the CSM gas stream are determined by analysis of gas samples collected intermittently in gas sample cylinders which are flow-purged with the gas being sampled. The light organic iodide or xenon fraction in the gas sample is separated and purified by chromatography*, then collected in charcoal beds, and finally analyzed by gamma-ray spectrometry.

Evaluation of CSM

The CSM was evaluated with low concentrations of individual nuclides as xenon, methyl iodide or an iodine mixture containing mostly elemental iodine under simulated LOCA atmosphere conditions.

The performance of the CSM was evaluated by comparing CSM concentrations with those from other atmosphere samplers. For total iodine concentrations, the CSM values were compared with those from the Particulate and Iodine (P-I) Sampler. The P-I Samplers (see Figure 3) are "Maypack" type cartridges consisting of a series of filters and sorbent beds which collect particulate fission products and volatile iodine species. The current arrangement of sorbent beds in the P-I Sampler consists of a glass fiber filter to collect particulates, a bed of cadmium iodide adsorbed on "Chromasorb-P" to collect elemental iodine vapors, a bed of copper zeolite to collect hypoiodous acid vapors, a bed of silver zeolite to collect methyl iodide, and a bed of impregnated charcoal as a backup trap. The noble gas and organic iodide samples from the CSM were compared with gas samples taken directly from the containment vessel. The latter were drawn through a short length of tubing and a condensor into gas sample cylinders with the Raw Gas Sampler (shown in Figure 4) or the Filtered Gas Sampler (a modification of the Raw Gas Sampler). The organic iodide or xenon concentrations of the containment atmosphere samples were then determined by the chromatographic technique described earlier.

The evaluation tests were conducted under simulated LOCA atmosphere conditions in the Contamination-Decontamination Experiment (CDE)(4). The 86-ft^3 CDE vessel, which is shown in Figure 4, was pressurized with steam to 22 psig and the aerosol generated by sweeping xenon, elemental iodine, or methyl iodide into the containment vessel. Following the injection, the vessel was cooled over a five-hour period and sampled.

---

*The organic iodides and xenon were separated from the inorganic iodine species by a Beckman GC-5 chromatograph with a 0.25-inch diameter column of Porapak Q preceded by a silica gel plug to retain inorganic iodides. The xenon samples were separated with a 14-ft long column operated at 25°C with a 50 ml/min flow of helium carrier gas. The organic iodide samples were separated in a 4-ft long column operated at 150°C with a 100 ml/min flow of helium carrier gas.

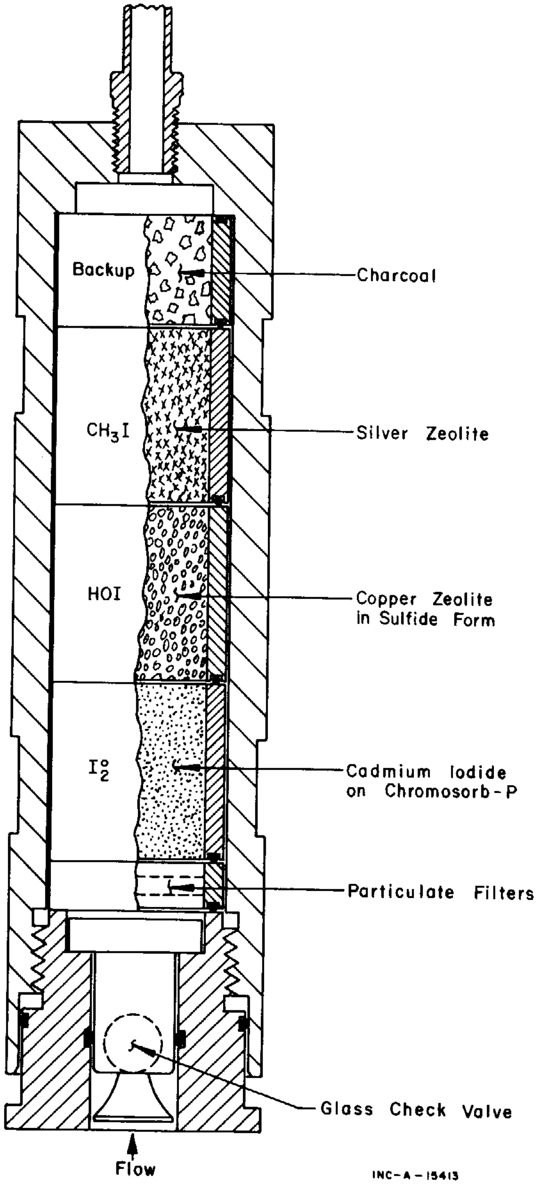


Fig. 3 Particulate and Iodine Sampler

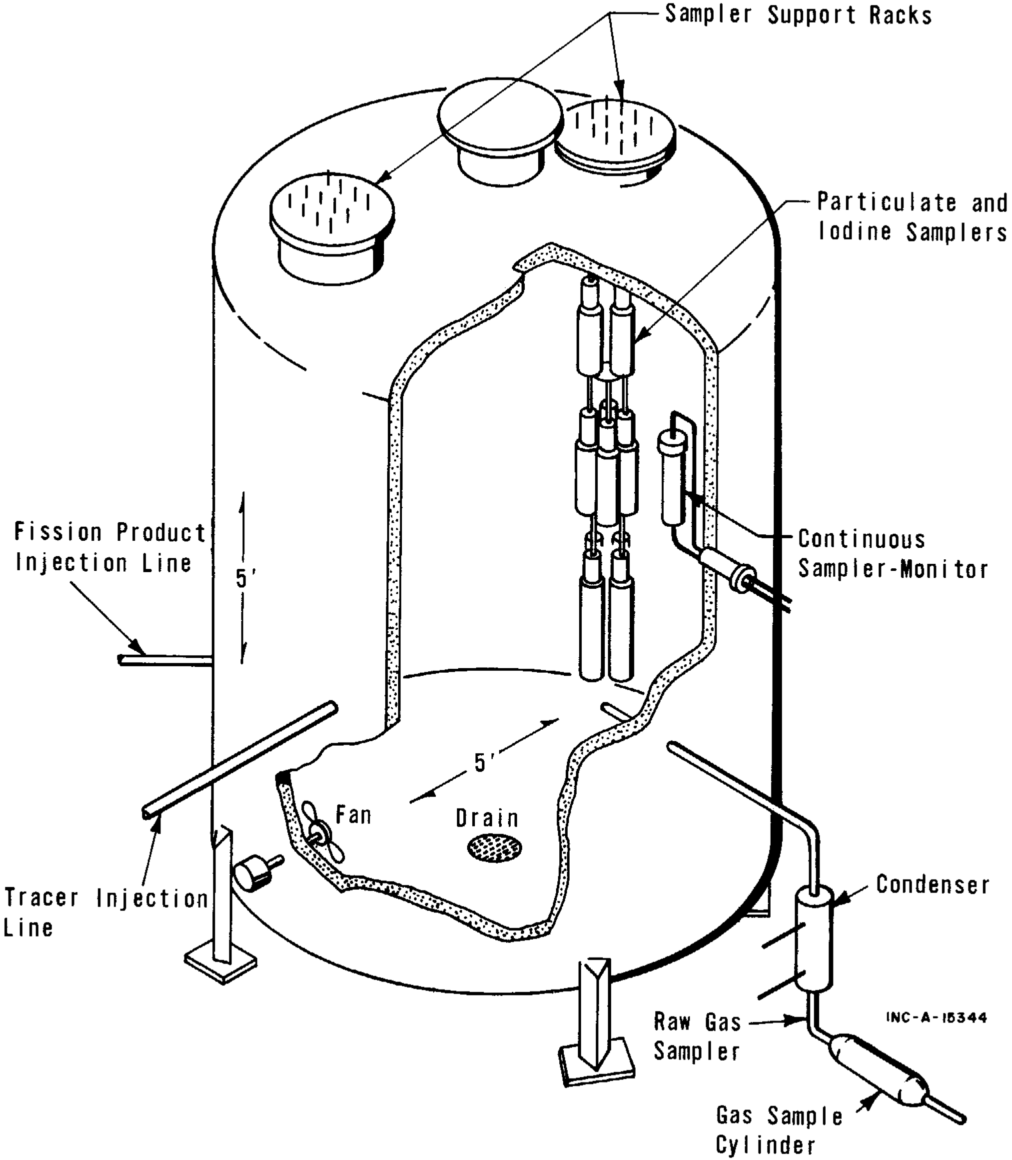


Fig. 4 Cut-a-way view of CDE showing sampler locations

The methods used to prepare the injection source and the general fission product behavior noted for the three types of tests are summarized in Table II. Additional data were collected in laboratory tests.

TABLE II

SUMMARY OF EVALUATION RUNS

Run Type	Total Initial Iodine Concentration ($\mu g/M^3$)	Source Preparation	Fission Product Airborne Behavior
Xenon-133	70	Received as ampule of xenon	Essentially constant after injection
CH_3I-131	0.6 to 4.0	Reaction of dimethyl sulfate with sodium iodide	Slow decrease after injection--half-time(a) of ∿ 1 day
Elemental Iodine-131(b)	0.054 to 7.1	Oxidation of NaI with molten $K_2Cr_2O_7$ and cold trapping of I_2 vapors	Rapid washout of elemental iodine

---

(a) Half-time is the time for the airborne concentration to decrease to half its previous value.

(b) The "elemental" iodine also contained small amounts of organic iodides and hypoiodous acid vapors.

In each of the CDE elemental iodine runs, there was a rapid washout--2/3 to 3 min half-time--of 80 to 95 percent of the iodine initially injected. The elemental iodine released was removed within 5 or 10 min of injection by absorption in the condensing steam and deposition on the walls. Following the initial rapid washout, the total airborne iodine concentration decreased slowly over the rest of the run leaving from 5 to 15 percent of the injected iodine airborne at the end of the run. The iodine remaining airborne after the initial washout consisted essentially or organic iodides and hypoiodous acid vapors. The organic iodides apparently were formed as an impurity during preparation of the iodine injection source. Essentially all the hypoiodous acid was formed within one minute after injection; it is not known whether it was formed before, during, or immediately after injection.

CSM Performance

The operating parameters--i.e. the scrubbing solution composition and the gas and liquid flow rates--affect the distribution of the fission product forms between the gas and liquid streams. In general, higher fractions in the gas stream are obtained with higher gas sampling rates and less reactive solutions. Numerous tests were required to find a scrubbing solution composition that would rapidly absorb elemental iodine and prevent its deposition in transport lines, while leaving most of the organic iodides in the gas phase. Satisfactory performance was obtained with a solution containing 1 M sodium hydroxide and 0.007 to 0.01 M sodium thiosulfate concentrations, a solution flow of 110 ml/min, and a 2 liter/min gas sampling rate.

The CSM performance in the evaluation tests is presented in the following sections according to objective.

1. Noble Gas Sampling

The noble gases--xenon and krypton--present few sampling problems. Because they are inert and sparingly soluble, they remain predominantly in the scrubbed gas stream. In the xenon tests, the average xenon concentrations from the CSM, determined by summing the xenon concentrations in the liquid and the gas streams, agreed within 4 percent of the average values from the Raw and Filtered Gas Samplers. The results from a typical CDE xenon run are shown in Figure 5. The xenon concentrations in the scrubbing solution at the 210 ml/min gas sampling rate agreed reasonably well with those calculated from existing solubility data(5). At the recommended 2000 ml/min gas sampling rate, the fractions of xenon and krypton absorbed in the scrubbing solution should be negligible--about 1 percent of the total xenon and 0.5 percent of the total krypton in the sample stream.

2. Total Iodine Sampling

The CSM performance for total airborne iodine (total of all chemical species and physical forms) was evaluated in the CDE "elemental" iodine runs. There were significant differences in the sampler performance in the various runs. In two runs, the total concentrations from the CSM

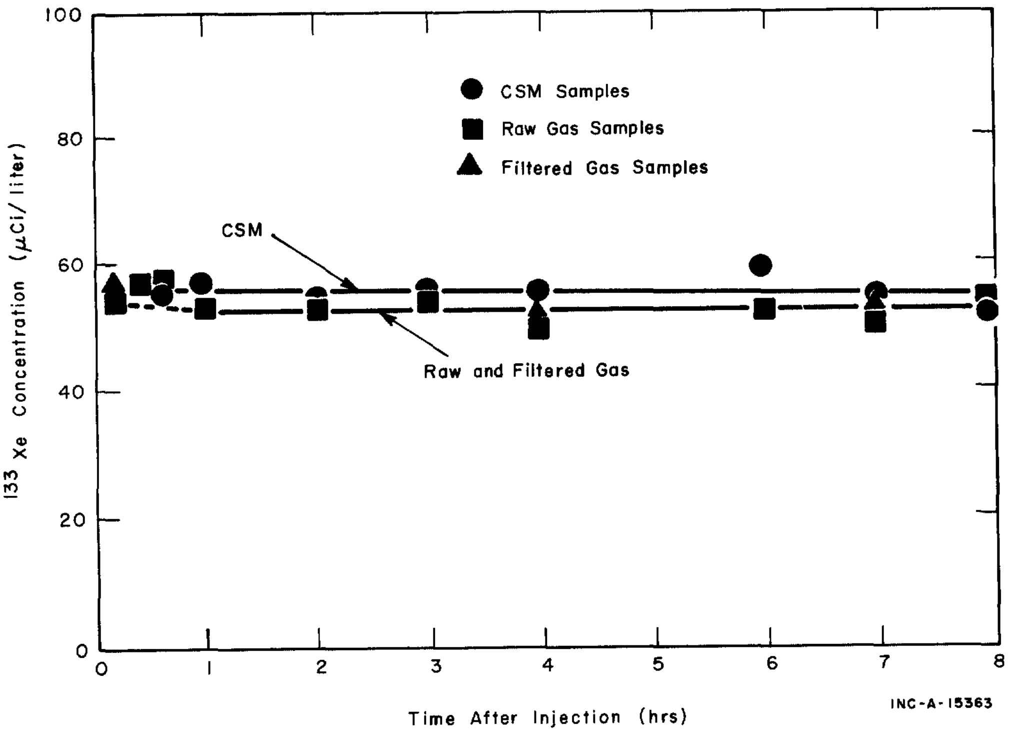


Fig. 5 Xenon-133 concentration in CDE containment atmosphere during CDE Tracer Run 2.

and P-I Samplers agreed within 10 percent. Figure 6 shows the results of one of these runs. In two later runs, the total iodine concentration from the CSM at the two different gas sampling rates, and from the CSM and P-I Sampler differed significantly. These differences are illustrated in Figure 7. The results of the CDE elemental iodine runs indicate that the CSM provides total iodine concentration values accurate at least to within ± 50 percent of actual values.

The separation of organic and inorganic iodides by the CSM was complicated by the presence in the CDE containment atmosphere of a volatile, unreactive iodine species which has tentatively been identified(6) as hypoiodous acid. The total iodine concentration values from the CSM are not affected as long as the total iodine concentrations in both the gas and liquid streams are measured. However, two gas stream samples must be taken--one for total iodine and one for organic iodide--as well as a liquid stream sample, to determine both total iodine and organic iodide concentrations with the CSM.

Hypoiodous acid and organic iodides were determined to be the major components of the CSM scrubbed gas stream by sampling with P-I type sorbent beds. A comparison of the hypoiodous acid concentration in the containment vessel and in the CSM scrubbed gas indicates that about half was absorbed by the liquid stream. The relative effects of solubility and chemical reaction cannot be determined from this data. Preliminary laboratory tests on scrubbing an iodine vapor, believed to be hypoiodous acid, indicate this species is slightly more soluble than methyl iodide but that it does not react appreciably with thiosulfate solutions or bases.

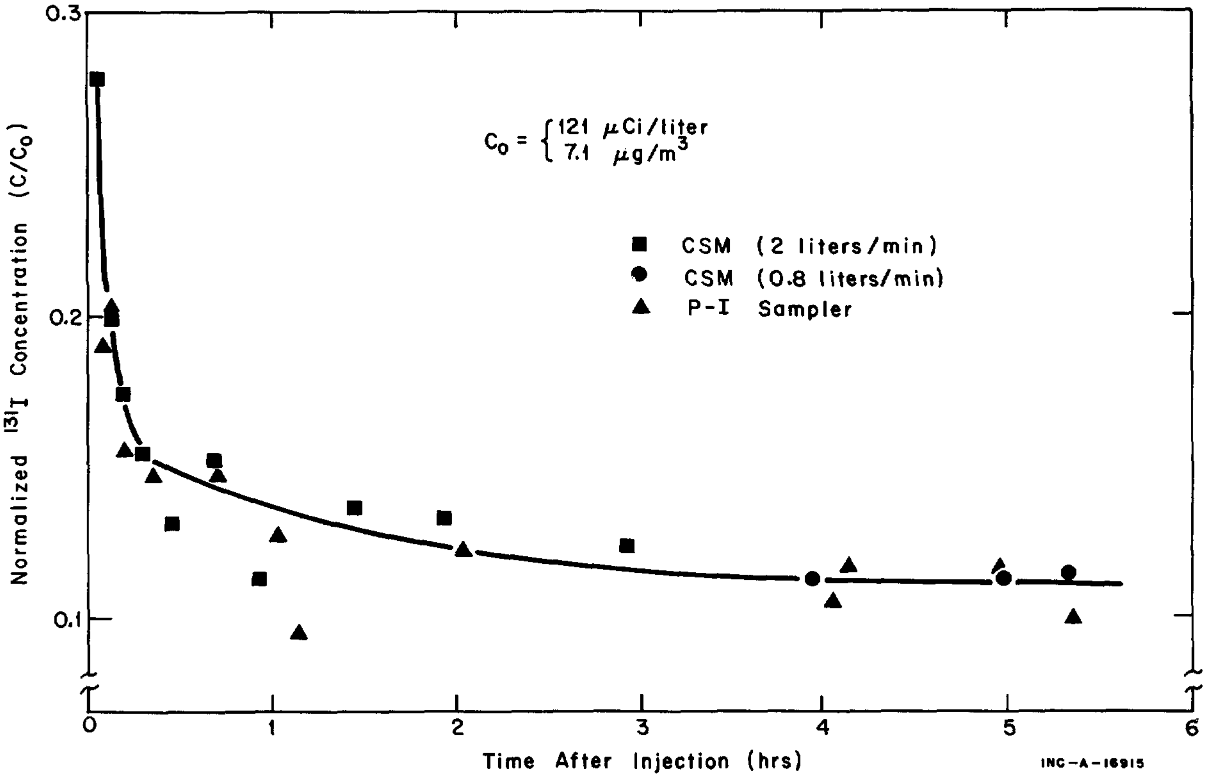


Fig. 6 Iodine-131 concentration in CDE containment atmosphere during CDE Tracer Run 6.

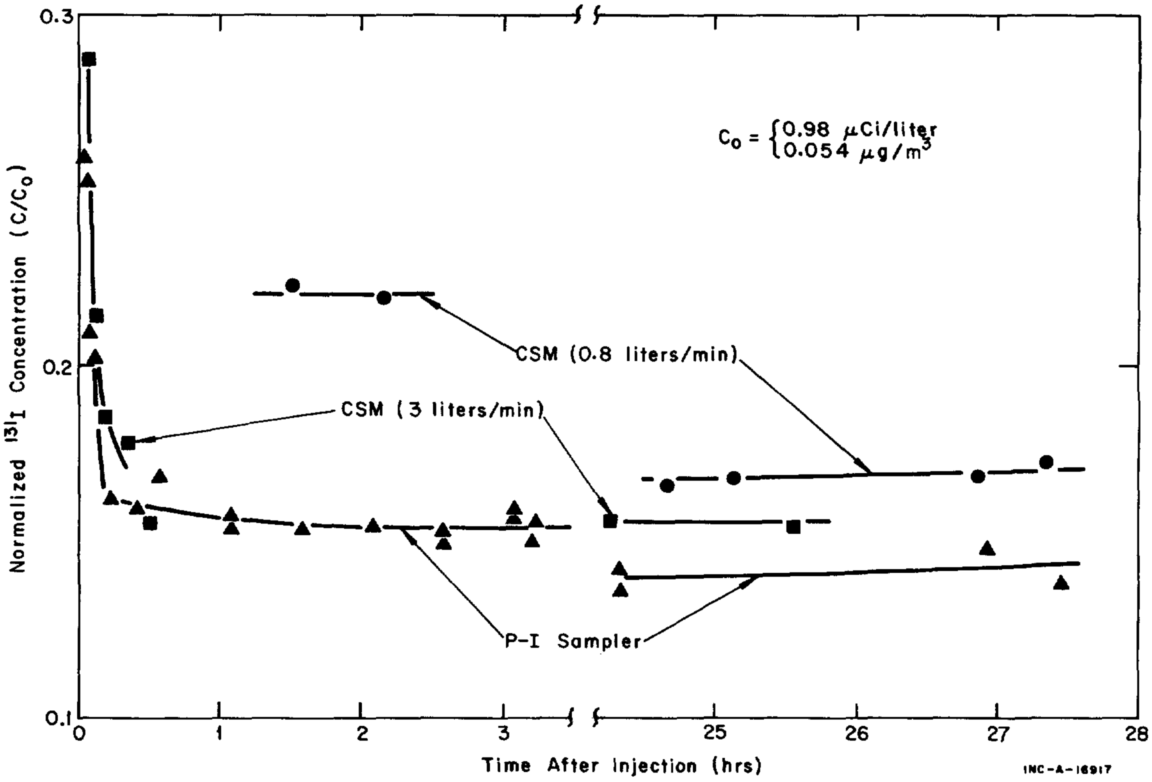


Fig. 7 Iodine-131 concentration in CDE containment atmosphere during CDE Tracer Run 11.

The scrubbing efficiency of the CSM for particulates has not been determined for the current CSM design but appears to depend on the particle size. In laboratory tests(3) with fluorescein dust, a previous version of the scrubber effectively scrubbed particles larger than 0.2 micron diameter, but most of the finer particles remained in the scrubbed gas stream. However, the CSM design and operating conditions have changed since the earlier tests. The net effect of these changes has not been determined.

3. Organic Iodide Sampling

The organic iodide concentrations can be determined by correcting the concentrations of the CSM gas stream samples for the fraction of the organic iodides absorbed by the scrubbing solution. The absorption of methyl iodide by a solution is affected by: the scrubbing solution composition, the temperature, the gas-to-liquid flow ratio, and the gas sampling rate (affects gas-liquid contact time). Laboratory tests and published reaction rate constants(7) show that methyl iodide reacts with sodium thiosulfate solutions more rapidly than with sodium hydroxide solutions. The sodium thiosulfate concentration in the scrubbing solution, therefore, must be low to prevent excessive methyl iodide absorption.

In organic iodide tests at the recommended CSM operating conditions, the scrubbing solution absorbed from 10 to 50 percent of the methyl iodide in the entering gas stream. The results of a typical CDE run for these conditions are shown in Figure 8 where the ratio of the methyl iodide concentration in the CSM scrubbed gas samples, C, to the methyl iodide concentration in the containment atmosphere, C_A, (as determined by analysis of raw gas samples) is plotted against time after injection. The increase in C/C_A during the run appears to be a result of the decrease in the containment (and the scrubbing solution) temperature during the run. The high initial temperature resulted in a more rapid reaction rate in the scrubbing solution.

For convenience, an average correction factor $C/C_A = 0.7 \pm 0.2$ can be used in place of the actual correction factor which varies with temperature. The error introduced by this simplification is less than 30 percent.

The laboratory tests(3) show that ethyl iodide reacts more slowly than methyl iodide with both thiosulfate and hydroxide ions. No reaction with the hydroxide ion and only a slight reaction with the thiosulfate ion was observed for ethyl iodide. Stearic hinderance is the probable reason for the slower reaction rate of ethyl iodide. The slow reaction rate of ethyl iodide (and probably other heavy organic iodides) means that ethyl iodide will be easier to sample with the CSM than methyl iodide. It also infers that containment sprays will be less effective for ethyl iodide than for methyl iodide.

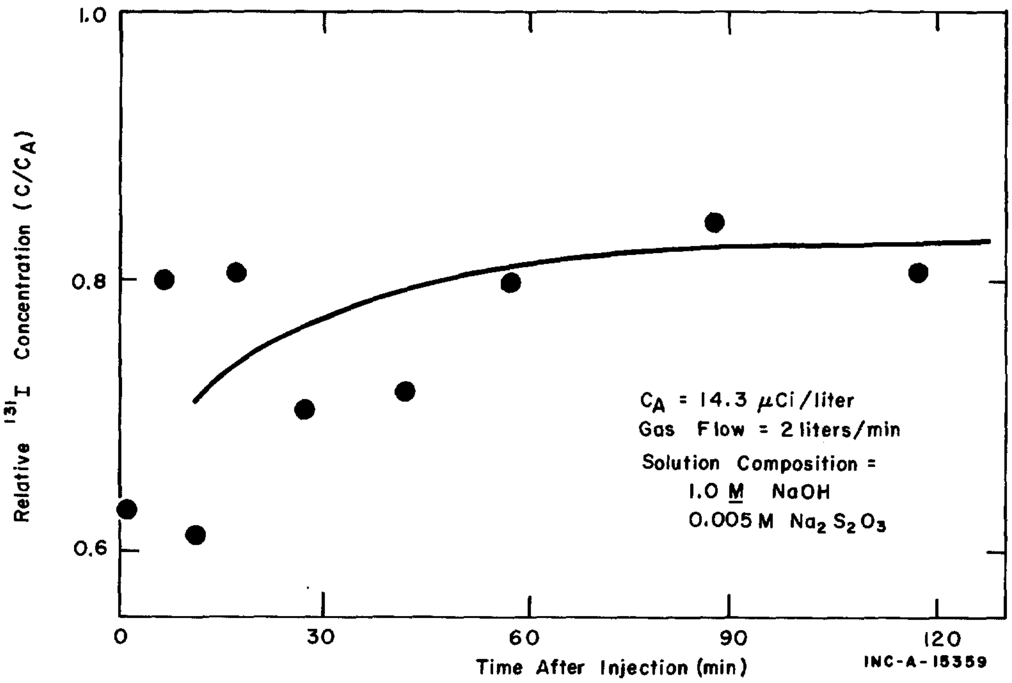


Fig. 8 Relative methyl iodide concentration in the CSM scrubbed gas stream during CDE Tracer Run 8.

4. Gross Activity Monitoring

Gross activity monitors are located on both the scrubbing-solution and scrubbed-gas streams. The gross activity traces provided by these monitors in the CDE runs agrees with the behavior expected. Typical responses of the gross-activity monitors to an iodine release in CDE are shown in Figure 9. (The gaps in the gas stream trace were a result of gas samples taken upstream of the gross-activity monitor.) Both monitors showed an initial time lag of 2 to 5 minutes (required for iodine to travel through the CSM lines), followed by a rise to the maximum reading over a period of about 2 minutes. This extended rise was probably a result of backmixing in the lines, Following the peak activity, the liquid stream monitor reading decreased by a factor of five with a 2 minute half-time as it followed the iodine washout from the containment atmosphere. The gas stream monitor showed a constant level because it monitored organic iodides and hypoiodous acid whose concentration remained essentially constant.

Conclusions

A prototype CSM was tested in the 86-ft^3 CDE vessel under atmospheric conditions simulating those anticipated in a reactor LOCA with tracer-level

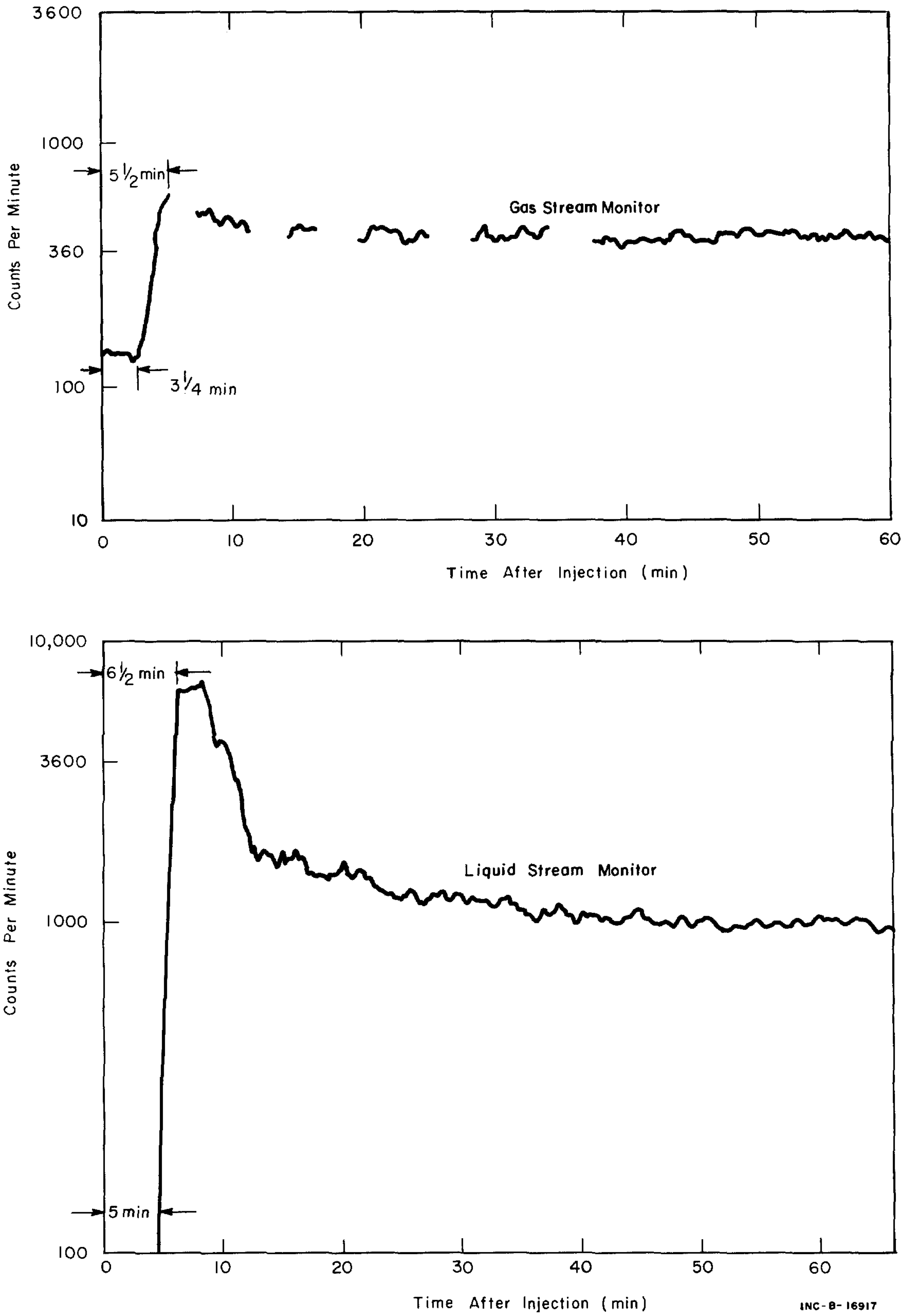


Fig. 9 Response of the CSM gross activity monitors to an iodine release--CDE Tracer Run 10.

releases of xenon, methyl iodide, and an iodine mixture consisting initially of elemental iodine mixed with small amounts of organic iodides and hypoiodous acid. Satisfactory results, summarized in the following statements, were obtained at the recommended operating conditions of a sampling rate of 2 liters/minute and a solution containing 1 M sodium hydroxide and 0.007 to 0.01 M sodium thiosulfate.

1. The CSM scrubbed gas stream provides noble gas samples representative within 5 percent; only a small fraction--less than 1 percent--is absorbed by the scrubbing solution.

2. The total iodine content of both the CSM gas and liquid streams must be determined and added to obtain total airborne iodine concentrations from the CSM. These values are accurate at least to within ± 50 percent.

3. The concentrations of organic iodides in the containment atmosphere can be determined by correcting the concentration values obtained by chromatographic analysis of CSM gas stream samples for the fraction of organic iodides absorbed by the scrubbing solution. For convenience, an average correction factor can be used in place of the actual correction factor which varies with temperature. The error introduced by this simplification is less than 30 percent.

4. The gross activity monitors on the CSM gas and liquid streams provide gross activity traces which agree with the behavior expected. A correction must be applied for the 3- to 5-minute time lag which occurs in transporting the sample streams through the long sample lines.

References

1. K. A. Dietz, (ed.), LOFT Engineered Safety Systems Investigations, IDO-17258 (1969).
2. D. H. Walker, et al, LOFT Integral Test Program, IDO-17258K (April 1969).
3. R. E. Schindler, et al, Development of a Continuous Sampler-Monitor for the LOFT Containment Atmosphere, IN-1309 (June 1970).
4. W. A. Freeby, et al, Fission Product Behavior Under Simulated Loss-of-Coolant Accident Conditions in the Contamination-Decontamination Experiment, IN-1172 (January 1969).
5. Handbook of Chemistry and Physics, 35th Ed., Chemical Rubber Publishing Co., Cleveland, 1953, p. 1611.
6. F. O. Cartan, et al, Evidence for the Existence of Hypoiodous Acid as a Volatile Iodine Species Produced in Water-Air Mixtures, paper presented at the Tenth Air Cleaning Conference, New York, August 21, 1968.
7. L. C. Schwendiman, et al, The Washout of Methyl Iodide by Hydrazine Sprays--Final Report, BNWL 935 (November 1968) p. 5, p. 27.

DISCUSSION

PARKER: Bob, when you started I think you implied that your monitor would discriminate between hypoiodous acid and other iodine forms, but with the thiosulfate in the scrub solution, do you really believe that?

SCHINDLER: In this sampler hypoiodous acid is neither fish nor fowl. It's split about half and half between the gas and liquids stream. It's included in the total iodine value by including it in the total iodine concentrations from the gas and liquid streams which are added to provide the total airborne iodine concentration value. But this CSM does not distinguish chemical species, at least between the hypoiodous acid and the other species.

PARKER: One more point. Do you expect a significant plate-out problem in the transfer line for solids, or fission products other than iodine and the rare gases?

SCHINDLER: The loss due to deposition of solid fission products would depend pretty much on whether they're soluble in the solution. The highly soluble ones like cesium we would have no trouble with. Fission products like ruthenium and molybdenum will deposit heavily.

APPLICATION OF THE CONTINUOUS SAMPLER MONITOR (CSM) AS A HAZARD EVALUATION INSTRUMENT

R. J. Schultz

Idaho Nuclear Corporation
National Reactor Testing Station
Idaho Falls, Idaho

ABSTRACT

The practical applications of the Continuous Sampler Monitor (CSM) in the LOFT Integral Test Program and the possible use of the CSM in the nuclear power industry are discussed in this paper. The unique features that the CSM provides for gathering information concerning the conditions and radioactivity levels in the containment atmosphere following a loss-of-coolant accident (LOCA) are described. These unique features are: (1) whole air sample remotely taken from the containment vessel atmosphere, (2) real time activity profile of airborne fission products, and (3) rapid measurements of activities to below 0.05 $\mu Ci/ft^3$ of containment atmosphere. These features make the CSM valuable as a conventional instrument for monitoring nuclear power plant containment atmosphere. During normal plant operations the CSM can be operated without scrubbing solution as a constant air monitor with remote sampling capabilities. In the event of a massive spillage involving radioactive material, loss-of-coolant accident, or any event leading to the release of fission products to the containment atmosphere, the scrubber system can be activated and the sampler used for hazard evaluation. The hardware to be used in LOFT and the adaptations that will render the instrument usable for industry are also described.

The data obtained from the CSM's during the LOFT tests are to be used both for analytical model evaluation and hazards evaluation. The specific functions of the LOFT CSM's are: (1) to continuously monitor the activity present in the containment vessel atmosphere for operational control, and (2) to provide samples of the containment vessel atmosphere as a function of time for detailed analysis of radionuclide behavior.

The development of the Continuous Sampler Monitor as a sampling device for the LOFT Integral Tests is described in the paper submitted by Dr. R. E. Schindler entitled, "Development of a Continuous Sampler-Monitor for the LOFT Containment Atmosphere".

Introduction

The mission of the LOFT Integral Test Program is threefold:

(1) To evaluate the adequacy of analytical models to predict: (a) the accident response of large power reactors, (b) the performance of engineered safety systems, and (c) the margins of safety inherent in the performance of safety systems

(2) To identify any unexpected events or thresholds that are exhibited in the response of either the plant or the engineered safety systems and develop subsequent analytical techniques

(3) To provide experience in the development of standards and in the application of RDT standards and codes generally applicable to pressurized water reactors.

The specific objectives of the LOFT Integral Test Program place the emphasis on determining the performance of emergency core cooling systems (ECCS) under loss-of-coolant accident conditions because failure of the ECCS to perform its intended function poses the largest uncertainty concerning the ability to prevent harmful releases of fission products to the public(1). Since the injection of emergency core coolant does not eliminate the possibility of fission product release from the fuel and hence leakage from the containment, containment safety systems are used to reduce the amount of fission product leakage. To complete the evaluation of power reactor response to a loss-of-coolant accident, the LOFT Integral Test Program includes investigation of containment safety systems and fission product behavior.

The LOFT tests provide the only immediately foreseeable opportunity to represent the thermal response for the entire loss-of-coolant accident with nuclear fuel and with a core that has most of the characteristics of cores of large nuclear power plants. In the area of fission product behavior, the LOFT integral tests are the only immediately foreseeable means of determining the partition of released fission products among the emergency core coolant, the primary system surfaces, and the containment system under conditions of a loss-of-coolant accident with application of plant safety systems. The safety systems to be employed by the LOFT integral test system are an emergency core coolant system and a pressure reduction spray system using a base-borate solution. A halogen and particulate recirculation filtration system, which contains water separators, HEPA filters, and charcoal adsorbers, is to be employed for final containment vessel atmosphere cleanup after the pressure of the containment vessel atmosphere returns to ambient pressure.

The purpose of the fission product program being conducted in conjunction with the LOFT-ECC test series is to obtain data for determining the adequacy of analytical models for predicting the radiological consequences resulting from the fission products released in a loss-of-coolant accident.

Specific objectives of the fission product studies in the LOFT tests are to:

(1) Provide experimental data for determining the capability of analytical models for:

   a. Predicting the magnitude and composition of the fission product source that reaches the containment atmosphere in a LOCA in which an emergency core cooling system is applied and predicting the magnitude of the source in the containment atmosphere as a function of time

   b. Predicting the capability of containment safety systems to perform their intended function of removing the fission product source from the containment atmosphere.

(2) Determine whether unexpected events or thresholds, not accounted for in the models for predicting fission product behavior in a LOCA, appear in the integral nuclear tests in which engineered safety features are applied.

LOFT Continuous Sampler Monitor System

The Continuous Sampler Monitor, as described by Dr. R. E. Schindler, was developed specifically for use in the LOFT Integral Test Program(2). The CSM plays a dual role in the LOFT tests. It will be used to obtain fission product behavior data and to access the fission product concentration levels in the containment vessel test chamber for test operations following the simulated LOCA blowdown.

In fulfilling the role of a hazard evaluation instrument the CSM will provide the following types of information:

(1) Fission product concentration in the containment atmosphere during the conduct of the test. This information will assist in assessing the magnitude of the downwind radiological hazard following either a test or an unplanned LOCA. In this assessment the dispersion factors obtained from the existing meteorological conditions and the leak rate are applied to the airborne fission product concentration obtained from the CSM in order to calculate the off-site release.

(2) The fission product concentration in the containment atmosphere following the application of pressure reduction sprays and recirculation filtration systems to insure that the levels of radioactive gaseous waste are below the limits specified in 10 CFR 20(3,a) before the rare gases are exhausted to the atmosphere.

(a) Local site regulation applying to release of radioactive gases is "ID Handbook Prevention, Control and Abatement of Air and Water Pollution", ID Manual Appendix 0510, January 17, 1969.

(3) The airborne fission product concentration, by nuclide, prior to personnel reentry into the containment vessel for sample retrieval or maintenance. The level of respiratory protection required before personnel reentry into the containment vessel can be determined from the CSM output.

For both the fission product behavior information and the hazard evaluation work, five continuous sampler monitors are to be used in LOFT. Four of the CSM's are of the type described by Dr. Schindler (that is, scrubber type systems) and the fifth is a raw gas sampler that draws a stream of sample gas from the containment vessel atmosphere but does not employ a scrubber solution to fix the iodine and particulates.

The four scrubbing CSM units are to be located in the containment vessel as shown in Figure 1. Two samplers are to be located on swinging booms on opposing walls on the north-south axis. These instruments, which are 38 feet above the test chamber floor, can be located any predetermined distance from three to twelve feet from the vessel wall. One sampler is to be located at the center of the vessel dome above the pressure reduction spray rings and 95 feet above the containment vessel test chamber floor. The fourth sampler is to be near the test chamber floor as near the center line of the vessel as possible. The four CSM's will yield information concerning the homogeneity of the fission product source throughout the containment vessel atmosphere as a function of time.

The raw gas sampler is to be located near the blowdown nozzle. This sampler is to be used to obtain the first indication of fission product release to the containment vessel atmosphere.

A Sequential Particulate-Iodine Sampler (the LOFT "Maypack" type sampler) is to be used in conjunction with each CSM to obtain samples for posttest analysis for accurate differentiation of iodine chemical states or constituents for iodine species measurements. The iodine differentiation sampling was discussed in detail by J. H. Keller in a paper entitled, "A Selective Adsorbent Sampling System for Differentiating Airborne Iodine Species"(a). Three types of atmospheric data will be available (CSM gamma traces, CSM grab samples, and Sequential Particulate-Iodine Sampler total and differential iodine data) for use in determining the buildup and depletion of the fission products in the containment vessel atmosphere. Figure 2 shows a graphic display of the sequential particulate iodine and CSM data interplay.

The LOFT CSM systems will employ three grab sampling stations; two for obtaining liquid- and gas-phase samples from the four scrubbing CSM's and one for sampling the raw gas stream. The stations for the scrubbing CSM's are to be equipped to take simultaneous samples from any two CSM's at any given time. Both gas bombs and adsorber pack samplers are to be taken at the gas sampling station. The station for sampling the raw gas sample stream is to be provided with grab sampling facilities and delay coils for noble gas daughter product analysis.

(a) J. H. Keller et al., "A Selective Adsorbent Sampling System for Differentiating Airborne Iodine Species", presented at the 11th USAEC Air Cleaning Conference.

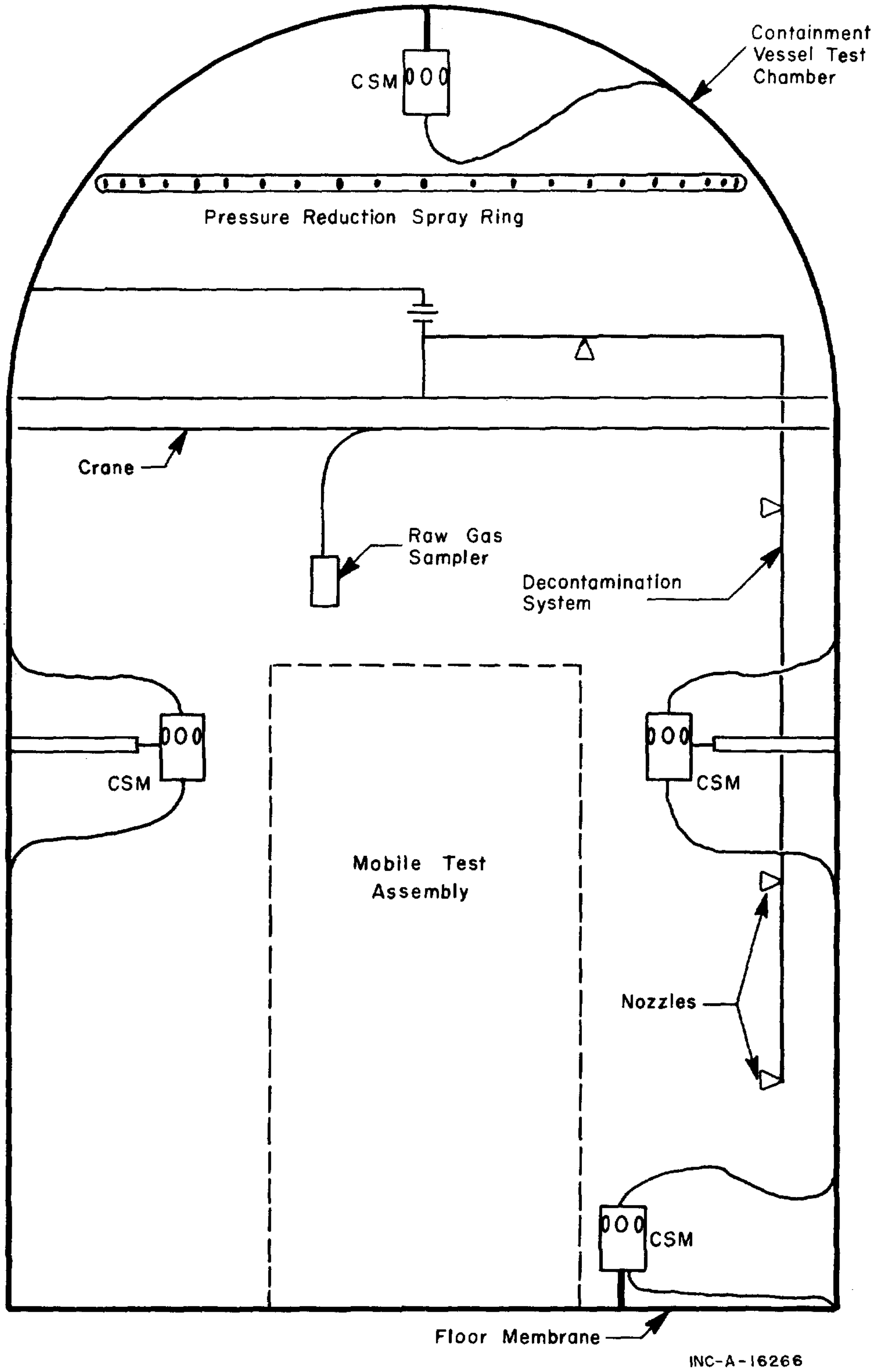


FIGURE 1 LOFT CSM LOCATIONS

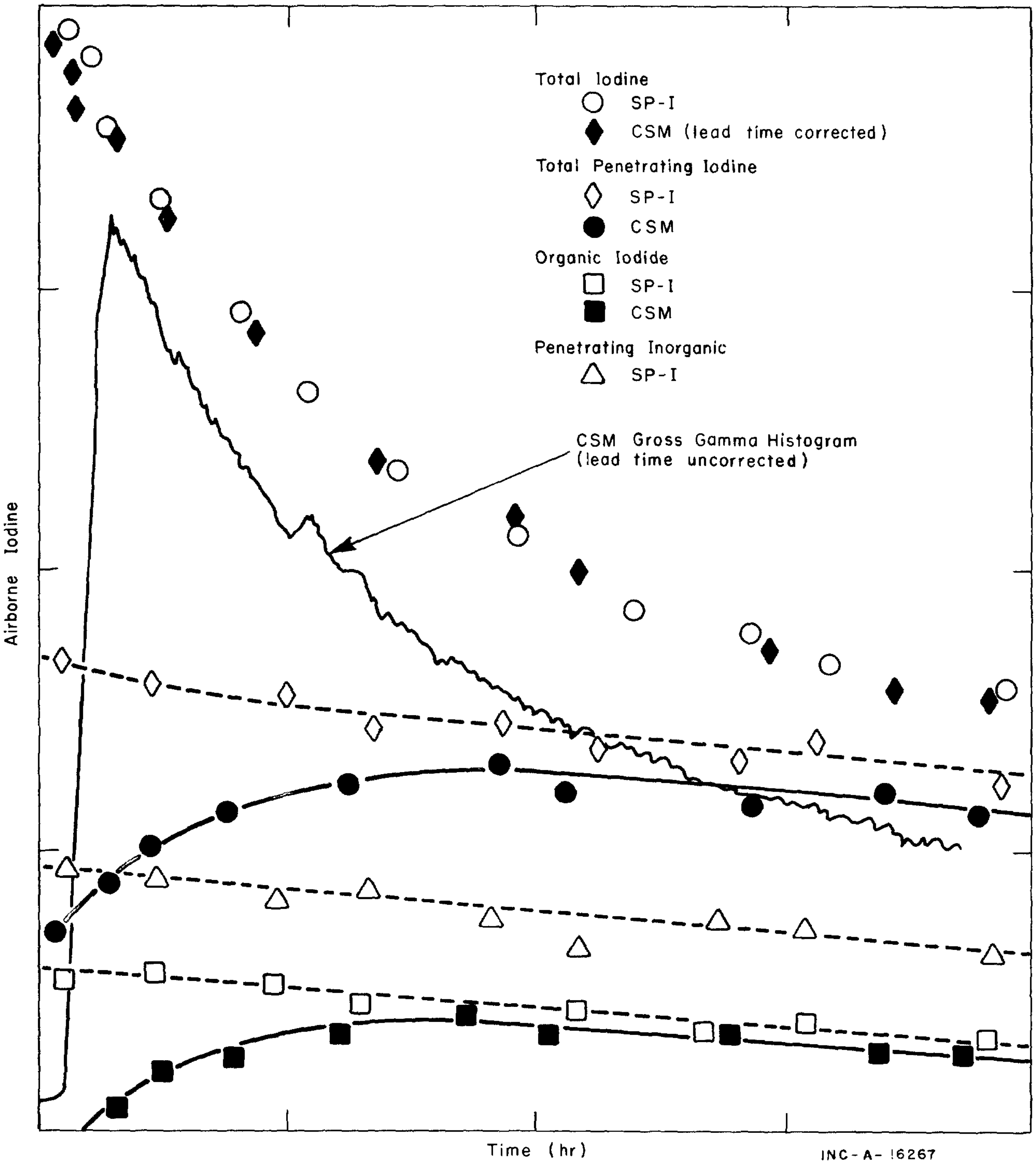


FIGURE 2 CSM-SP-I DATA INTERPLAY

The analytical system for the LOFT CSM's is to consist of four germanium-lithium (GeLi) gamma ray detectors and amplifiers coupled through four analog-to-digital converters to a small digital processor. This system will thus collect data simultaneously from four different analyses. In addition to the four detector systems, the digital processor will collect data from gross gamma monitors and from flow sensors. The data system will provide output that can be reduced further by the acquisition system itself, by auxiliary small processors, or remotely by an IBM-360 computer. The complete LOFT fission product data system consists of:

(1) A 16K central processing unit

(2) A disk and interface

(3) A magnetic tape storage unit and teletype

(4) An oscilloscope display

(5) A control panel.

A schematic diagram of the data system is shown in Figure 3. Not explicitly shown in the diagram is a minimum of four levels of priority interrupt and extended arithmetic capabilities.

CSM for Industrial Hazards Evaluation

In the event of a major atmospheric radioactivity release in the containment vessel of a power reactor, several types of information are needed rapidly to determine the existence or severity of the potential off-site hazard resulting from airborne activity contained within the structure.

The foremost questions and the corresponding information needed to access the potential hazard are:

(1) Levels of airborne contamination present in the containment atmosphere

(2) Buildup or depletion rate in the atmosphere

(3) Isotopic composition of the activity suspended in the atmosphere

(4) Predominate chemical species of iodine present in the atmosphere

(5) Atmospheric composition in the containment vessel.

A CSM system will yield at least qualitative and in most cases quantitative information in these areas.

In applications of the continuous sampler monitor as a hazards evaluation instrument for industrial use, the unit should be a combination scrubber type CSM and a raw gas sampler. This type of instrument will yield maximum monitoring and sampling capabilities with a minimum expenditure.

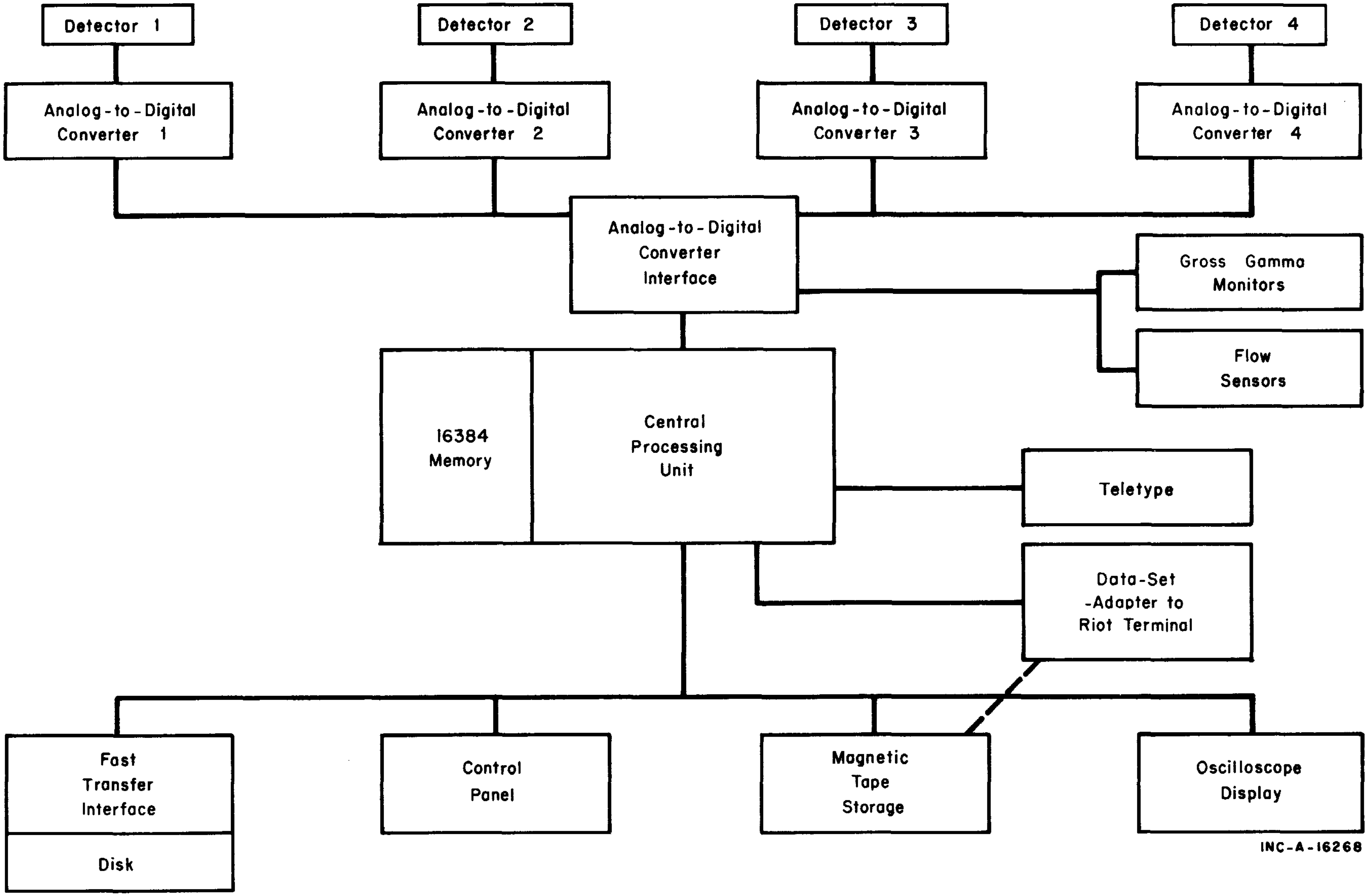


FIGURE 3 FISSION PRODUCT DATA PROCESSING SYSTEM

The concept of using a combination CSM raw-gas unit for monitoring the containment vessel is shown in Figure 4.

The flow pattern for the system is divided into two segments; a raw gas segment and gas-liquid scrubber segment.

(1) Raw Gas Segment. The containment vessel atmosphere is drawn into the open end line, transported from the containment vessel through the stainless steel line, passed through the heat exchanger, through the gamma monitor, and to the sampling station junction. At the junction,the gas stream can either be directed to the sample station, for collection of a grab sample, and then to the flow controlling assembly or the sampling station can be bypassed and the gas stream directed without interruption to the flow controller. After passing through the flow controller, the gas stream can either be vented to the atmosphere through the stack, pumped back into the containment vessel, or passed through a halogen and particulate removal filtration system, depending upon the facilities available. The heat exchanger would only be used following an accident in which the containment vessel atmosphere is at elevated temperature and consists of a steam-air mixture.

(2) Gas-Liquid Scrubber Segment. Solution for the scrubber system is supplied from the storage tank by gravity flow. The pressure is then increased to approximately 550 psig by the pressure pump. The scrubber solution then enters the containment vessel and is atomized in the scrubber head by the nozzle. The containment vessel atmosphere is drawn into the scrubber head, through side-wall ports directly below the nozzle, where the first gas-to-liquid contact is made and the major removal of the reactive fission products from the gas stream is accomplished. The scrubber liquid and gas pass as two-phase flow through the exit line by means of gravity and then leave the containment vessel. After leaving the containment vessel, the liquid and gas phases flow through the heat exchanger to the separator where the gas and liquid phases are separated into the scrubbed gas phase and the scrubber liquid phase.

The gas stream is taken from the top of the separator and is directed through the gas gross-gamma monitor. The gas then can be directed either to the sampling station or disposed of in the same manner as the effluent of the raw gas.

The liquid stream is drained from the bottom of the separator by a pump and flow controller. The liquid then flows by the gross-gamma monitor and is either dumped to hot waste or directed to the sample station where grab samples can be obtained.

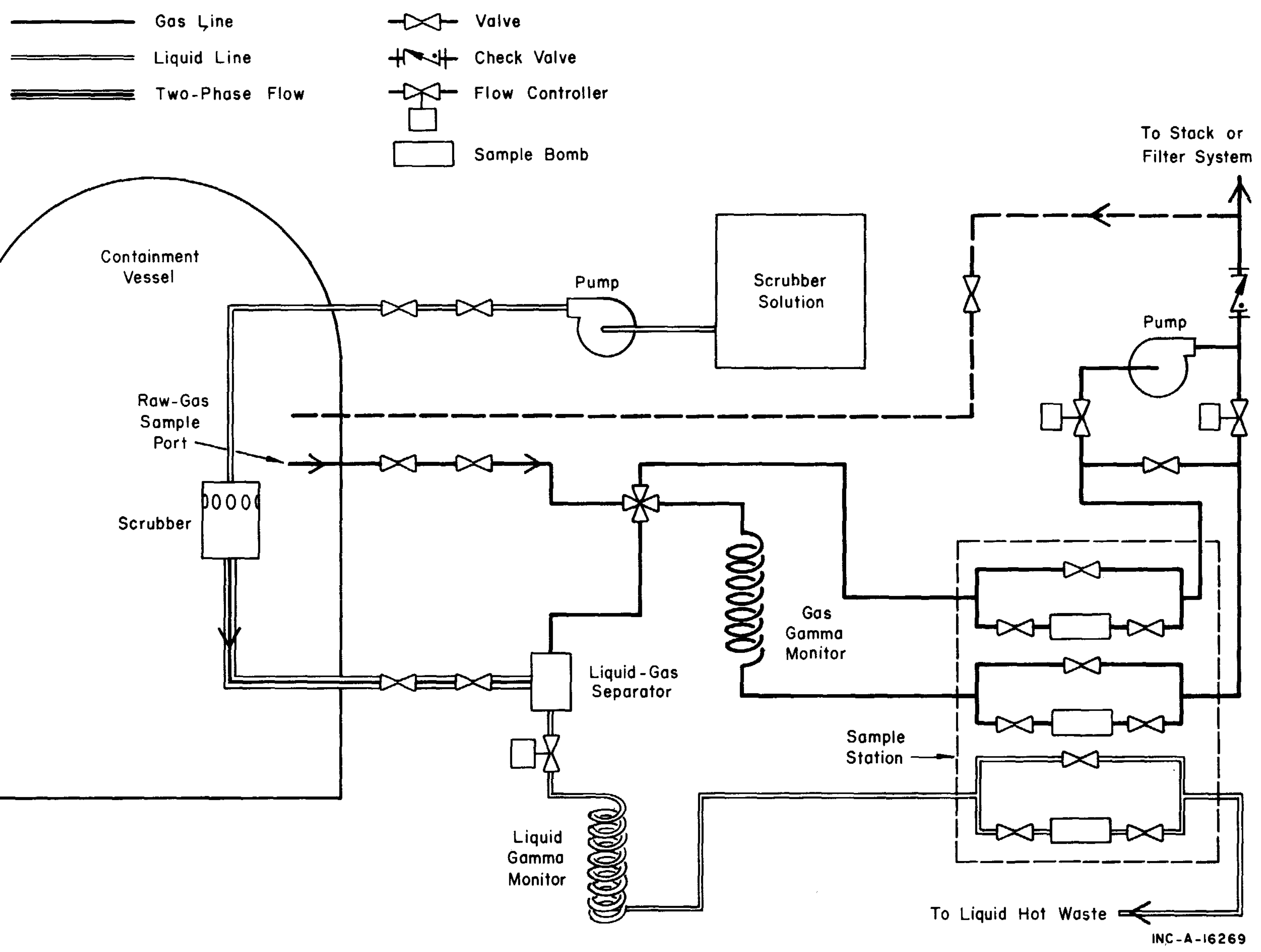


FIGURE 4 CONCEPTUAL DESIGN FOR LARGE PRESSURIZER WATER REACTOR--CSM

The raw gas portion of the system will be in continual operation and will therefore serve as a constant air monitor (CAM) with remote sampling capabilities. Air will be drawn out of the containment vessel at any selected flow rate up to 50 liters/minute, passed by a gross-gamma monitor, and disposed of by means available at the particular facility. The gross-gamma monitor output can be recorded directly on a strip chart recorder with an audible alarm in parallel to signal when preset limits have been exceeded, or the output can be processed through a data acquisition system that is programmed to scan the output periodically and alarm when the predetermined activity level (count rate) is exceeded. Either system will maintain a permanent record of the relative activity in the containment vessel atmosphere such that all releases will be recorded.

When a signal is received that indicates the containmenc vessel atmospheric activity levels have increased, two operations are to be initiated in regards to the sampling instrument. The first operation is to initiate the scrubber solution pump, to enable iodine sampling to be accomplished. The second operation is to obtain both a gas bomb and a charcoal (or filter) pack sample from the raw gas line. The samples obtained are to be analyzed to determine the isotopes present that caused the alarm. The isotopic composition in many cases may indicate the source of the airborne activity. A gross analysis of the first raw gas sample is expected to take about five minutes, at which time information is expected to be available from the gross-gamma monitors on the scrubber portion of the instrument that will yield both total activity per unit volume of the containment vessel atmosphere and the relative iodine activity.

Following collection and analysis of grab samples from both the liquid and gas lines, a complete assessment of the hazard can be made.

The specific activity of the liquid samples can be obtained by counting the activity of the liquid bomb in a precalibrated geometry and correcting for the air volume contacted by the amount of liquid analyzed.

Two types of samples will be collected from the gas phase portion of the system. The first sample will be a small gas bomb and the second a differentiating adsorber pack sample. The gas bomb can be counted in a precalibrated geometry to determine the specific activity of the noble gases and the iodine present. This sample later will receive more detailed analysis by chromatography(4). The adsorber pack can be split into four basic elements (the particulate filter, the elemental iodine adsorber, the HOI adsorber, and the organic iodide adsorber) and radiometrically analyzed. From this analysis, the amount of organic iodide present in the containment vessel atmosphere can be determined.

Depending upon the analytical facilities and data processing equipment available for analyzing the samples and data, the complete process for accurately determining the overall potential hazard present in the containment vessel is expected to be complete within 30 minutes following the first indication of radioactive release to the atmosphere. Once the isotopic makeup of the two sample streams is identified, monitoring the containment vessel airborne activity by means of the two gross-gamma monitors becomes more meaningful. Grab samples will then be taken periodically or when abnormalities appear on the gross-gamma monitors.

The sensitivity of the instrument, for all nuclides, cannot be defined at this time as it depends upon the isotopic makeup of the sample, the equipment available for analysis, and the abundance of the isotope of interest. For the LOFT CSM and associated data system, calculations show that reactive iodine (I_2) levels can be determined to below 0.05 μCi/ft^3, or 0.1 Ci airborne I_2 in a typical PWR containment vessel (2x10^6-ft^3 volume). The limit of sensitivity for unreactive iodine can be increased by at least an order of magnitude by passing the gas stream through the in-line adsorber pack and obtaining an integral sampler over a limited period.

During operation of the scrubber portion of the CSM, the raw gas system may be either deactivated by isolating it from the system or left in continuous operation by continuing flow and exhausting the effluent gas through the plant filtration system. The raw gas sampler can be used to collect grab samples for monitoring the elemental constituents in the containment vessel. These samples give the plant operator a means of collecting samples for monitoring the hydrogen buildup in the event metal-water reaction takes place, and for monitoring hydrogen buildup from corrosion of metal surfaces by caustic spray solution.

This paper has described a continuous sampler monitor, its operation, and its application in determining the level of radioactivity in a reactor containment structure under normal reactor operating conditions and under accident conditions as a hazards evaluation instrument. In application of the continuous sampler monitor as a hazards evaluation instrument for industrial use, a unit that is a combination scrubber and raw gas sampler is the most economical and versatile. The instrument and method of operation discussed will yield the maximum monitoring and sampling capabilities with minimum equipment expenditure and minimum amount of contaminated liquid waste.

References

1. J. Dugone, D. E. Solberg, and D. H. Walker, "LOFT Integral Test Program", IDO-17258K, April 1969.

2. R. E. Schindler, et al., "Development of a Continuous Sampler-Monitor for the LOFT Containment Atmosphere", IN-1309, June 1970.

3. Title 10, Council of Federal Regulations, Part 20, "Standards for Protection Against Radiation".

4. R. C. Shank, Manager Analytical Chemical Branch, Annual Report FY-1969, IN-1316 (September 1969) pp 117-119.

Work performed under Contract AT (10-1) - 1230 U. S. Atomic Energy Commission, Idaho Operations Office.

DISCUSSION

OWEN: You described how sensitive the instrument was, how insensitive is it? How high a concentration can you measure with such a device, can it go up several orders of magnitude?

SCHULTZ: The insensitivity, or more descriptive, the range of operation for the monitoring portion of the system is dependent upon the type of gross gamma monitor selected for use. Flowthrough detectors can be used for low level work whereas flowby detectors can be used for high level monitoring. For the old LOFT-U Test we were planning to cover approximately five decades on the gross gamma monitors, in the LOFT/ECC Tests we are expecting a much lower level of activity so we are not planning on spanning that many orders of magnitude.

PARKER: My question is mainly this: have you considered the interference you may get from the short lived daughters of the kryptons? I recall in the old homogeneous reactor off gas system we were overwhelmed by the rubidiums when we were looking for xenon. We couldn't see anything but rubidium activity and unless you have an optimized gas release compositio based on those isotopes which have taken a long time to diffuse, so that short lived kryptons are at a minimum you may have the same problem. It may require a hold up point where you let the radioactive krypton decay a while before you look at the residual activity.

SCHULTZ: We have thought of this George, and in our on-line gas monitoring we have no protection as far as the short-lived kryptons masking the other activity on the gross gamma monitor. It is just going to be there and is going to read quite high. Very early we will have to obtain our on-line data from the liquid monitor which will contain the majority of the iodine and very small amounts of krypton. As far as the gas portion, qualitative data will be obtained from grab samples which will be taken and analyzed by the chromatograph to get methyl iodide concentrations.

PARKER: I do recall that there was a question pending for the two gentlemen from Savannah River by the representative from Chalk River. He was interested in comparing service life of a charcoal bed, and I believe he told me that he would take time tomorrow in the open session to comment a little bit. If he is still here would he care to say anything?

EDWARDS: In Dr. Evans' paper "Effect of Service on Retention of Iodine by Activated Charcoal" the curves that were shown were very similar to ones I have produced from three years of tests on charcoal filters at CRNL. I believe his curves indicate a rapid decrease in efficiency after 4 years whereas the filters at CRNL were only used 6 to 10 months before beginning to show a loss in iodine retention capability. The iodine retention efficiency decreased in a few months from 99.9+% to between 98 and 60%.

Just before coming to this Conference I received an analysis of the contaminants found in a batch of charcoal from a filter which had been removed after 18 months' service and also from the same charcoal that had been stored unused in a drum. The mass spectra and the gas chromatogram indicated that a large number of compounds was present, but only the most predominant were identified. The volume of gas desorbed from the used charcoal at 550°C was about 87 cc/g. The major components (amongst at least 30 present) were identified as CO_2, NO, SO_2, CH_4, C_2H_6, C_3H_8 and $CH_2ClCHCl_2$. The unused charcoal desorbed 17.6 cc/g of gas comprised principally of CO_2 and H_2O. These contaminants are similar to those reported by Dr. Evans.

I have made a series of tests on a total of 12 filters since the beginning of this program. The charcoal filters are installed downstream of roughing and HEPA filters, in the ducts from the Universal Cells. Each is rated at 1000 cfm and operated at an air flow of just under 1000 cfm. Each contains 55 lbs. of Barnebey-Cheney No. 513 charcoal, -10 + 20 mesh.

Each test was made using approximately 4 mCi of iodine-131 with 50 mg. of iodine as carrier. The iodine was oxidized by dripping the iodine mixture into a warm solution of H_2SO_4 and KIO_3, (from which the iodine was sparged with a stream of air and introduced into the duct). Samples were obtained from both before and after the charcoal filters. The iodine was collected on "May Packs" made up of four treated 100 mesh copper screens, one fiberglass paper (GF/A), one charcoal impregnated paper (ACG/B) and a 45 mm diameter 30 mm deep bed of -18 + 35 mesh activated charcoal. The nominal face velocity was 30 cm/s for all components of the sampler. The screens were pretreated with hydriodic acid no more than 12 hours before use. In over 25 tests, 97 to 99% of the iodine collected was on the copper screens on the upstream samples and 50 to 98% of the iodine on the downstream samples was on the copper screens and about 1.5% was on the charcoal paper. In contrast, when the iodine came from ruptured fuel, samples taken both upstream and downstream of the charcoal filter had 30 to 50% of the iodine on the copper screens and 50 to 20% on the charcoal paper.

I believe Dr. Parker's question also referred to some remarks I made about tests on the iodine losses in the reactor exhaust duct system. These tests were just completed before this Conference so I only had a brief look at the results. This duct system carries 25000 cfm of air a distance of 1/2 a mile from the two reactors to the stack. It is interesting to note that when the same iodine generating system was used the "May Pack" samples from several points along the duct showed about 65% of the iodine collected on the copper screen and about 30% on the carbon paper. The majority of the iodine was lost between the point of introduction and the first sampling point. A small percentage was lost in the HEPA filters and very little was absorbed on the remaining 1/2 mile of duct. There are no charcoal filters in this system.

KELLER: I would like to know what the approximate relative humidity of your duct work air samples are in your high flow ducts.

EDWARDS: I have not measured the humidity in the ducts. I assume the air in the ducts from the cells is the same as the building atmosphere. This is just air drawn from outdoors, passed through roughing filters and heated when necessary.

The air supplied to the reactors is conditioned to 75°F and 50% RH. However, I have noticed moisture on samples taken near the end of the 1/2 mile duct. This may be caused by the cooling of the air along the duct which is exposed above ground and is not insulated.

PARKER: If I recall Charcoal No. 513 is an untreated charcoal which would make your performance data resemble the Savannah River data in that they are similar charcoals. Theirs was No. 416. I really don't know what exact difference that implies. At Oak Ridge a test program has discovered deterioration in charcoal beds being tested mainly with methyl iodide and the loss of efficiency has been embarrassing; like 40% in less than a year. These deterioration problems are not too well understood there. Do you have any feeling of what is happening in your case?

EDWARDS: Yes, I believe Barnebey-Cheney No. 513 is untreated charcoal. I don't know the cause of the deterioration but as the contaminants are similar to those reported by Dr. Evans, I expect the cause is the same even though ours deteriorate quite a bit more rapidly. I might add that on one occasion I checked the efficiencies of two charcoal filters before and after a cave clean up. There was no detectable difference after the cell was put back into operation. In a cave clean up we use steam, detergents and solvents.

ANALYSIS OF ATMOSPHERIC GASES

Frederick B. Johns and Richard E. Jaquish
Technical Services
Southwestern Radiological Health Laboratory

U. S. Department of Health, Education, and Welfare
Public Health Service
Environmental Health Service

ABSTRACT

The Southwestern Radiological Health Laboratory collects and analyzes radionuclides which occur in the gaseous state in the environment. A variety of samplers are used depending upon the type of gas being sampled. The mixtures of gases are separated in the laboratory using low temperature adsorption and gas chromatograph techniques. After separation, the quantity of radioactivity is determined by counting. The gases routinely sampled and analyzed are xenon, water vapor, krypton, carbon dioxide and radon.

Introduction

The Southwestern Radiological Health Laboratory has the capability of collecting and analyzing samples for radionuclides which occur in the gaseous state in the environment. Radionuclides which are found in the environment and are of significant health importance include tritium (^{3}H), carbon-14 (^{14}C), radon-222 (^{222}Rn), and the isotopes of xenon, krypton and argon. A list of the nuclides of interest and their properties is found in Table 1.

Sampling for radioactive gases is usually from the atmosphere but with recent Plowshare projects to stimulate natural gas fields with nuclear explosives, the analysis of radioactive gases in natural gas is of interest.

Sampling Equipment

Air sampling and analysis procedures are very much interrelated; the purpose of sampling is to collect only gases of interest, thereby increasing the sensitivity of the method. Based on this criterion, several sampling devices have evolved.

A. Freezing Traps - water for tritium analysis.

This device consists of two glass traps immersed in dry-ice acetone (DIA) slush. Air is passed through at a flow rate of three to six liters per minute. To check on collection efficiency, data are collected at the same time on the humidity in the ambient air.

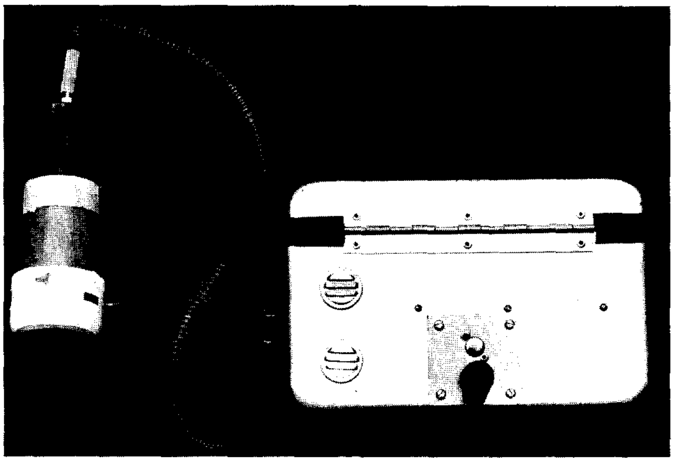
Table I

RADIOLOGICAL PROPERTIES OF GASES

NUCLIDE	BOILING POINT °C	HALF-LIFE	TYPE OF DECAY	ENERGY (MeV) AND ABUNDANCE	
Tritium ^{3}H	100 (as water)	12.262a	β-	0.0186	MAX
Carbon ^{14}C	-78.6 (as carbon dioxide)	5730a	β-	0.156	MAX
Argon ^{37}Ar	-185.7	35.1d	EC	x-rays	
^{39}Ar		269a	β-	0.565	MAX
^{41}Ar		1.83h	β-	2.49	MAX
			γ	1.293	(99%)
Krypton ^{85}Kr	-152	10.76a	β-	0.67	MAX
			γ	0.514	(0/41%)
^{85m}Kr		4.4h	β- (77%)	0.82	MAX
			γ	0.150	(74%)
				0.305	(13%)
^{87}Kr		76m	β	3.8	MAX
			γ	0.403	(84%)
				0.85	(16%)
				2.57	(35%)
^{88}Kr		2.80h	β-	2.8	MAX
			γ	0.166	(7%)
				0.191	(35%)
				0.36	(5%)
				0.85	(23%)
				1.55	(14%)
				2.19	(18%)
				2.4	(35%)
Xenon ^{127}Xe	-107	36.4d	EC,γ X-rays,	0.058	(1.4%)
				0.145	(4.2%)
				0.172	(22%)
				0.203	(65%)
				0.375	(20%)
^{133}Xe		5.27d	β-	0.346	MAX
			γ	0.081	(37%)
^{135}Xe		9.14h	β-	0.92	MAX
			γ	0.250	(91%)
				0.61	(3%)
Radon ^{222}Rn	-61.8	3.8229d	α	5.49	

Figure 1 - Freezing trap in field installation

Figure 2 - Small molecular sieve sampler as currently used.



B. Molecular Sieve Sampler - water for ^{3}H and carbon dioxide for ^{14}C analysis

Molecular sieves have the unique property of selectively absorbing atoms or molecules based on their diameter. This feature is used in the molecular sieve samplers. Two sampling devices are used. A large sampler containing 2000 grams of 13x molecular sieve operating at a flow rate of 120 liter/minute is used in an aircraft or in semi-permanent installations. A small portable sampler is also used which contains 200 grams of molecular sieve and operates at a flow rate of 15 liters per minute.

C. Aerial Grab Sampler - xenon and krypton analysis

This sampling device is installed in the sampling aircraft. Air is pumped for thirty seconds from outside the airplane into a 30-liter plastic bag. The air in the bag is then pumped by means of a compressor into a steel gas bottle that has been previously evacuated. The volume of air is determined by weighing the evacuated bottle before and after it has been filled. Approximately 0.3m^3 of air is collected as a sample for analysis for xenon and krypton.

D. Cryogenic Sampler - xenon and krypton analysis

This device utilizes a cannister of molecular sieve 5A immersed in liquid nitrogen at 12 psig (giving a temperature of -182 $^{\circ}$C) to absorb xenon and krypton, although water vapor and carbon dioxide are also quantitatively collected. Air is pumped through the sampler and a dry gas meter measures the sample volume. The initial flow rate of 1250 liters per minute gradually decreases due to the freezing out of the water and carbon dioxide to a flow of 70 liters per minute. Average collection is 1.5 to 4m^3.

E. Radon Sampler - radon-222 analysis

Two types of sampler are used to collect radon gas in air:

1. An integrated sampler consists of a small pump, Figure 7, which fills a plastic bag with a volume of 30 liters. The sample, collected over a 24-hour period, includes all gases in air although radon is the nuclide of interest.

2. A grab sample for radon consists of a 2-liter gas bottle through which air is pumped until seven or eight volume changes of air in the bottle occur. This collection is made at atmospheric pressure for five to ten minutes.

F. Natural Gas

Natural gas is collected in 8-liter steel gas bottles which are evacuated to a pressure of 10^{-4}mm of mercury prior to use. In the field, the

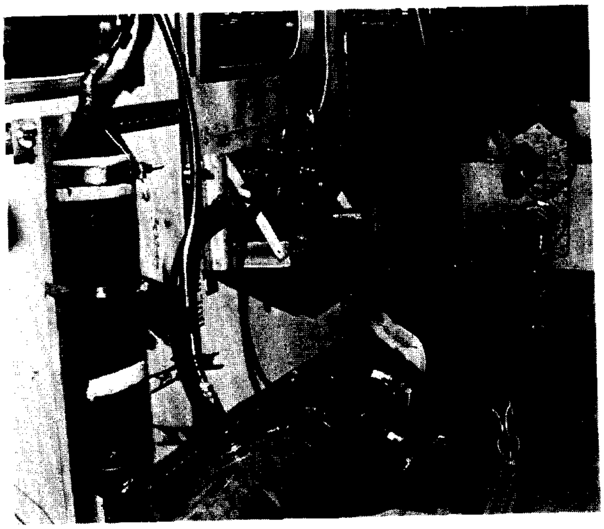


Figure 3 -
Large molecular sieve sampler configured for aerial sampling.

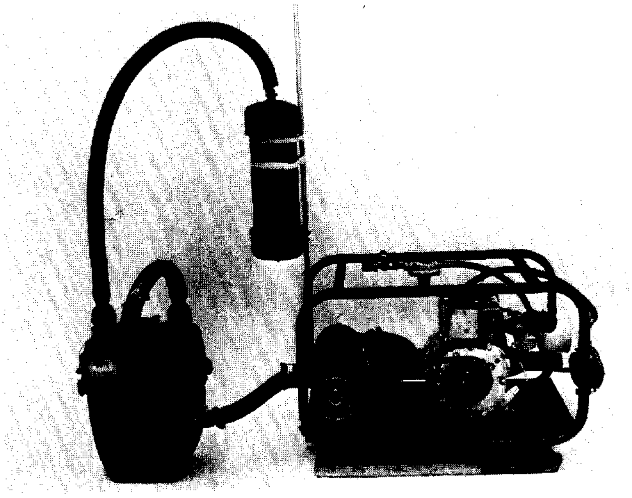


Figure 4 -
Large molecular sieve configured for ground sampling.

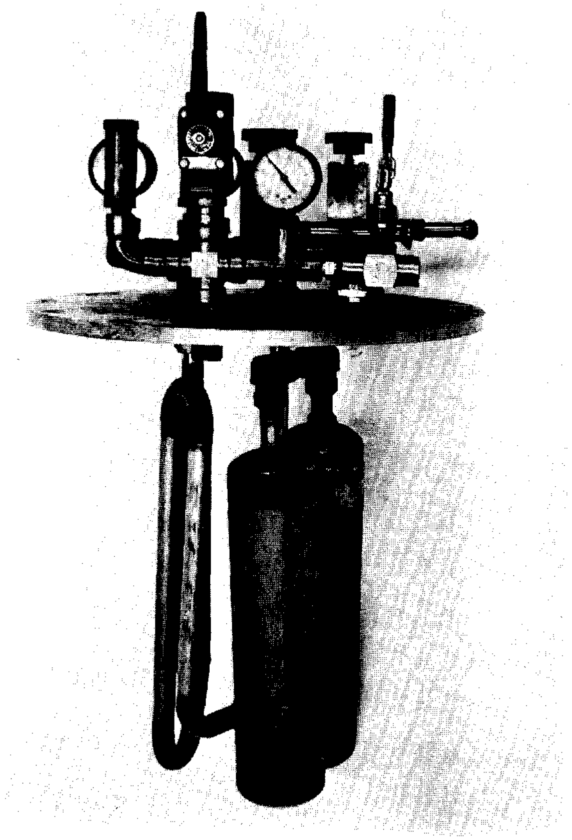


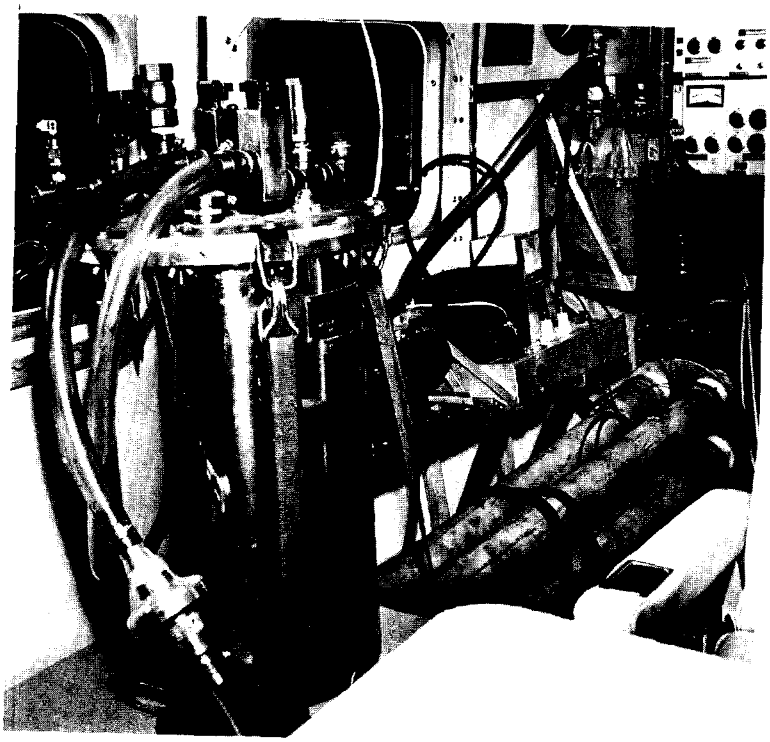
Figure 5 -

Disassembled cryogenic sampler

Figure 6 -

Cryogenic sampler

installed in aircraft.



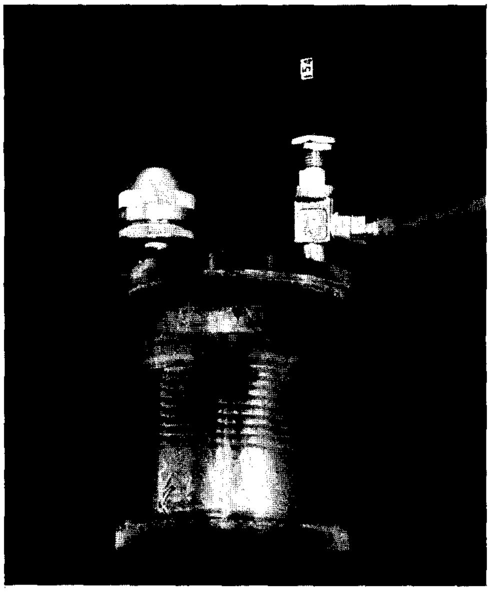
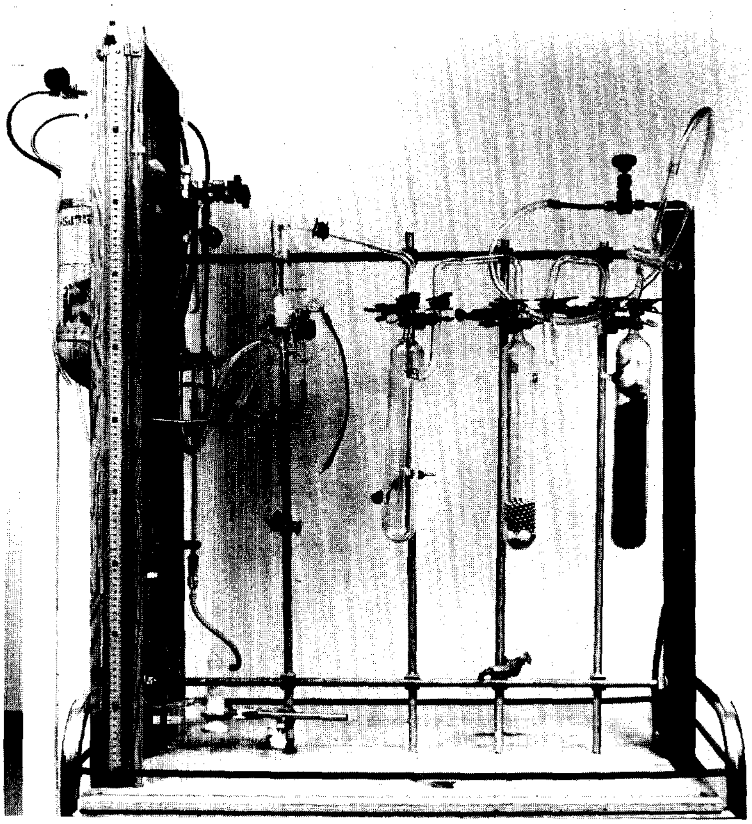


Figure 7 - Pump used for integrated radon sampling.

Figure 8 - Combustion and collection apparatus for natural gas analysis.



bottle is attached to the high pressure gas line. The valve is opened to allow gas to enter the bottle. The pressure is not allowed to exceed 1000 psi. The bottle is emptied and refilled eight times, then, under pressure, is returned to the laboratory. Before analysis, a measured volume of the natural gas sample is ignited with excess oxygen, Figure 8. Water vapor is collected and the remaining products of combustion and noble gases are introduced into the gas analysis apparatus.

Separations

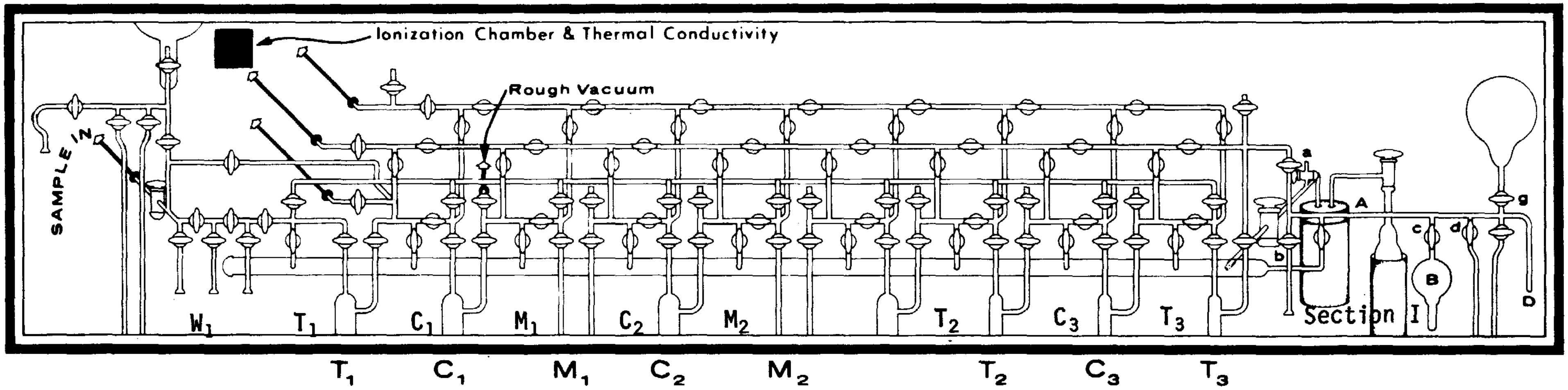
A. Water and Carbon Dioxide

The collected gases from the molecular sieve, cryogenic and aerial grab samplers and products of combustion from natural gas are introduced into the separation apparatus, Figure 9, by a combination of heat and helium purge. In all cases, the water vapor is collected in the steel ball trap (T_1) at liquid nitrogen (LN) temperature. A portion of the carbon dioxide, xenon and krypton is also collected in the steel ball trap and the remainder on the charcoal in C_1 at LN temperature. When only tritium and carbon-14 analyses are to be conducted, T_1 is heated to approximately 30 °C to melt the water and vaporize the carbon dioxide. The water is refrozen on the steel balls at -80 °C with DIA and the carbon dioxide is transferred to C_2. This step is repeated until all of the carbon dioxide is transferred. The water is distilled into a receiver at W_1. Oxygen and nitrogen are removed from C_1 by purging with helium at DIA temperature. The carbon dioxide is desorbed from C_1 at 350 °C and transferred to T_2 of LN temperature with a helium carrier gas. After removing the helium in T_2 (by vacuum), the trap is allowed to come to room temperature and the carbon dioxide transferred to Section 1 for volume measurement. The water, after distillation, and the carbon dioxide are prepared for liquid scintillation counting as described in Part IV below.

B. Xenon and Krypton

When analysis for xenon and krypton is to be performed, known volumes of xenon and krypton carrier are added to T_1 and C_1. T_1 is then heated to 30 °C and refrozen with DIA and the xenon, krypton and carbon dioxide transferred to C_1. The water is distilled to W_1. After the oxygen and nitrogen on the charcoal in C_1 are removed by purging with helium at DIA temperature, heat is applied to C_1 and the gases of interest are transferred to the molecular sieve colum (M_1) which is at LN temperature. The temperature of the molecular sieve column is raised to wet ice temperature (0 °C) which will elute the krypton more rapidly than the xenon. The thermal conductivity cell and the ionization chamber indicate the elution of the various gases. After krypton has passed through the column to C_3, the temperature of the column is raised to boiling water temperature (100 °C) to speed the removal of the xenon. The xenon is transferred to T_3 and the temperature is raised to 350 °C to remove the carbon dioxide to T_2. The xenon is then transferred to Section 1 by heating T_3. The recovered volume is determined for yield determination and a portion of the xenon is then transferred to a counting cell for subsequent beta and gamma counting.

Figure 9 - Schematic, Natural Gas Separation Apparatus



W_1 - Water Trap

T_1 - Steel Ball Trap

C_1 - Charcoal

M_1 - Molecular Sieve (5A)

T_2 - Steel Ball Trap

C_2 - Charcoal Trap

T_3 - Empty Trap

The krypton is transferred to Section 1 in the same manner prescribed for the xenon. The volume is determined and the gas transferred to a counting cell.

For the determination of krypton in air at environmental levels the procedure is modified. A one cubic meter sample without krypton carrier is first passed through a copper oxide furnace to burn any organic gases or hydrogen that may be in the sample. Part of the oxygen and nitrogen is removed by purging the C_1 trap at DIA temperatures with helium. The C_1 trap is heated to 200 $^{\circ}$C and the gas passed through a copper furnace followed by a titanium furnace to remove the traces of oxygen and nitrogen. The krypton is collected on the M_1 trap at LN temperature and then eluted to the C_4 trap (a small 8 inch by 2 mm trap not shown on Figure 9) at LN temperature. The helium is removed by evacuation and the volume of krypton measured and transferred to a liquid scintillation counting vial.

The carbon dioxide is transferred to Section 1.

C. Radon

When radon-222 analysis is required from the cryogenic sample, a portion of the xenon is transferred to an alpha scintillation counting cell for radon-222 determination. The radon remains with the xenon fraction. Radon in natural gas is determined by direct transfer of the natural gas to an alpha scintillation counting cell. The cell is then alpha counted. Radon in air is determined by adsorbing the radon in a known volume of air on charcoal and then desorbing with helium into an alpha scintillation counting cell.

Counting

Tritium is determined by liquid scintillation counting. A measured volume of sample water is transferred to a liquid scintillation counting cell containing the scintillator cocktail. (1) Since gamma-emitting nuclides interfere with the tritium counting, all water samples are gamma scanned and when gamma emitters are present, the water is redistilled with holdback carriers. All samples are counted on the liquid scintillation spectrometer for a minimum of 100 minutes. (See Table II). Carbon-14 is also determined by liquid scintillation counting. A known volume of carbon dioxide is reacted with NaOH solution. $Ba(OH)_2$ is added to precipitate $BaCO_3$. Five grams of $BaCO_3$ are gelled with Cab-O-sil* and toluene based liquid scintillation cocktail. The mixture is counted on a liquid scintillation counter.

*Trade Name Packard Instrument Co.

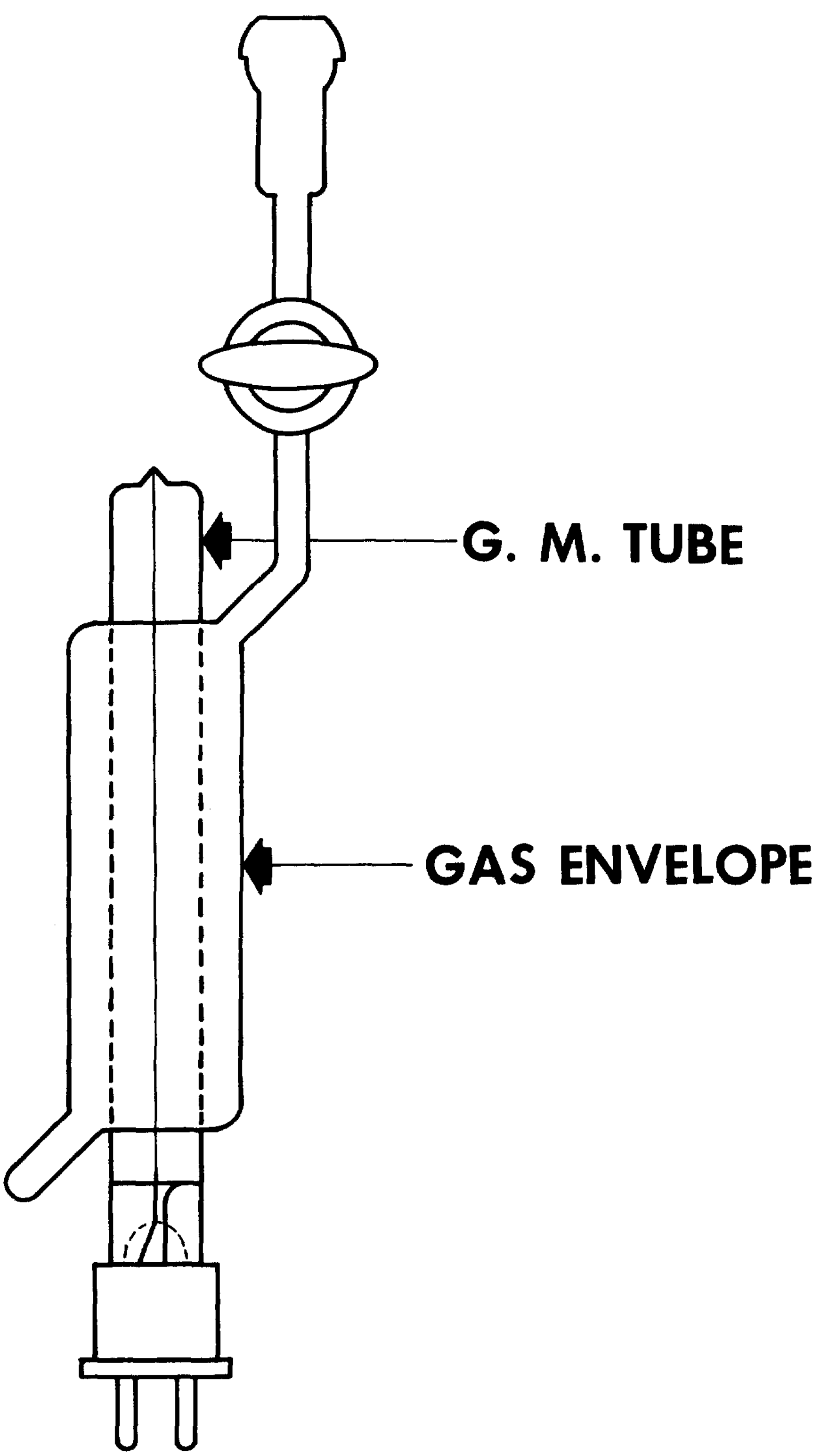


Figure 10. Gas Envelope Geiger-Mueller Tube

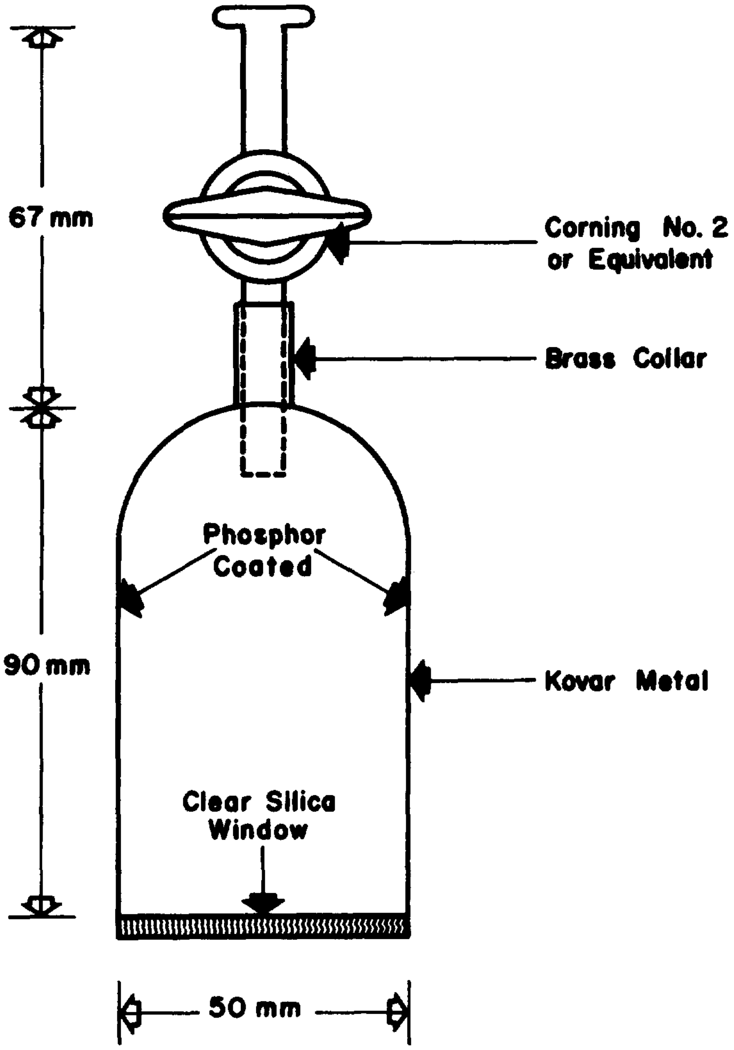


Figure 11. Radon Scintillation Cell

TABLE II

MINIMUM DETECTABLE CONCENTRATION (MDC)

	AIR	NATURAL GAS
Tritium	0.4 pCi/ml H_2O collected[a]	1 pCi/liter
Carbon-14	0.02 pCi/ml CO_2 collected	20 pCi/liter
Xenon and Krypton	100 pCi/total sample	100 pCi/total sample
Radon	0.04 pCi/liter	0.04 pCi/liter

[a] = based on 5 ml sample counted for 100 minutes

The radioxenon and krypton are counted by two methods. If gamma emitting isotopes of these gases may be present a portion of the sample is gamma scanned for isotopes identification and relative concentration. Krypton-85, argon-37 and argon-39 are counted by liquid scintillation counting. (2) An alternate method to liquid scintillation counting is the use of a gas envelope Geiger-Mueller tube.

Radon-222 is determined by alpha counting the radon gas in a scintillation counting cell, Figure 11, the interior surface of which is coated with ZnS. The counting cell containing 125 ml of gas is placed on a photomultiplier tube for scintillation counting. The counting time is usually 60 minutes

REFERENCE

1. A. A. Moghissi, H. L. Kelley, J. E. Regnier, M. W. Carter. Low-Level Counting by Liquid Scintillation I. Tritium Measurement in Homogeneous Systems. International Journal of Applied Radiation and Isotopes, Vol. 20, pp 145-156. Pergamon Press. (1969)

2. R. E. Shuping, C. R. Philips, A. A. Moghissi. Low-Level Counting of Environmental Krypton-85 by Liquid Scintillation. Analytical Chemistry, Vol. 41, pp 2082-2083. (1969)

BIBLIOGRAPHY

Breck, D. W. and Smith, J. V. Molecular Sieves. Scientific American. (January 1959)

Linde Molecular Sieves Non-hydrocarbon Materials Data Sheets. Union Carbide Corporation.

Momyer, F. F. The Radiochemistry of the Rare Gases. National Academy of Sciences, Nuclear Science Series.