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**DETERMINATION OF LOW SPECIFIC ACTIVITY ^{129}I
OFF-GAS CONCENTRATIONS BY GC SEPARATION AND
NEGATIVE IONIZATION MASS SPECTROMETRY**

SEPTEMBER 1983

Idaho Falls, Idaho 83401

EXXON NUCLEAR IDAHO COMPANY, Inc.

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**DETERMINATION OF LOW-SPECIFIC-ACTIVITY IODINE-129 OFF-GAS
CONCENTRATIONS BY GC SEPARATION AND NEGATIVE
IONIZATION MASS SPECTROMETRY**

by

S. J. Fernandez
R. A. Rankin
G. J. McManus
R. A. Nielsen
J. E. Delmore
F. A. Hohorst
L. P. Murphy

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ABSTRACT

This document is the final report of the laboratory development of a method for determining the specific activity of the ^{129}I emitted from a nuclear fuel reprocessing plant. The technique includes cryogenic sample collection, chemical form separation, quantitation by gas chromatography, and specific activity measurement of each chemical species by negative ionization mass spectrometry. The major conclusions were that both organic and elemental iodine can be quantitatively collected without fractionation and that specific activity measurements as low as one atom of ^{129}I per 10^5 atoms of ^{127}I are possible.

SUMMARY

Receptor models that predict the environmental impacts of ^{129}I releases from fuel reprocessing plants assume the released ^{129}I is undiluted with stable iodine and in the chemical form most damaging to the target organism. Although this approach will present a conservative limit for ^{129}I releases, it could require unnecessarily large investments in control equipment.

This document is the final report of the laboratory development of a method for determining the specific activity of the ^{129}I emitted from a nuclear fuel reprocessing plant. The technique includes cryogenic sample collection, chemical form separation, quantitation by gas chromatography, and specific activity measurement of chemical species by negative ionization mass spectrometry.

The objectives of the negative ionization mass spectrometer development work were to determine if new ionizers could be used without modification to measure iodine isotopic ratios greater than 10^4 and to determine what type of problems are encountered in the measurement of wide ratio iodine isotopics. The conclusions drawn from this development work were:

- 1) the newly developed ionizers can be used to measure iodine isotopic ratios equal to approximately 10^5 with a precision and accuracy better than 20%;

- 2) the major problem associated with measurement of wide isotopic ratios is thought to be due to iodine contamination effects;

- 3) isotopic ratios as high as 10^5 can be measured on samples as small as 80 ng I.

The development of the GC technique to measure organic and elemental iodine was done in two phases. The first phase used solutions containing the different iodine chemical species. This phase determined optimum column types and operating conditions. The second phase was performed using representative gaseous forms of iodine species and measured minimum detection limits and response. The conclusions of this aspect of the development work were:

- 1) of those tested the better column for separating CH_3I is a 300 cm x 0.3 cm nickel column of 5% SE-30 on Chromasorb W-HP, 80/100 mesh;

- 2) the optimum operating conditions are a column temperature of 100°C and a detector temperature of 310°C ;

- 3) the minimum detection limits for CH_3I and I_2 , respectively were 0.08 ng and 6.0 μg (based on typical blank values);

- 4) no interference with CH_3I at the 0.7 ng level by equal amounts of I_2 was found.

The sample collection technique used a permattube dryer with a NaOH impinger to collect I_2 . The major conclusions of the sampler evaluation were:

- 1) the permattube dryer is sufficient to dry the gas stream;
- 2) no significant fractionation effects for CH_3I and I_2 were determined.

Therefore, the major conclusions of this study are: 1) that isotopic ratios of $^{127}I/^{129}I$ as large as 10^5 can be successfully measured and 2) that both organic and elemental forms of iodine can be collected without fractionation and analyzed by GC and isotope dilution mass spectrometry.

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I. INTRODUCTION

Receptor models that predict the environmental impacts of ^{129}I releases from fuel reprocessing plants assume the ^{129}I is undiluted with stable iodine and in a chemical form most damaging to the target organism (usually man). Although this assumption will present a conservative limit for ^{129}I releases, it could require unnecessary control equipment.

Thyroid dose calculations for ^{129}I releases from DOE facilities are conservative by several orders of magnitude because the dose rate calculation considers only the actual amounts of the radionuclide in the body instead of an assumed state of equilibrium between stable and radioactive isotopes.¹ The conservativeness of this assumption is apparent when one considers the ^{129}I thyroid burden of $3\mu\text{Ci}$ (18 mg ^{129}I) exceeds the total iodine inventory for a standard thyroid (8 mg I).¹ Nevertheless, thyroid dose factors based on this assumption are used to assess the thyroid dose from ^{129}I releases. Assuming 1/16 of all ^{129}I inhaled will be incorporated into the thyroid and eliminated from the body with a biological half-life of 138 days,¹ one derives a thyroid dose factor of $1.5 \times 10^{10} \text{ rem} \cdot \text{m}^3 / \text{Ci} \cdot \text{y}$. This dose factor has been incorporated into

the dose factor file of ALLDOS.² ALLDOS and the computer codes on which it was based, DACRIN³ and PABLM⁴, were used extensively for preparing environmental dose estimates for the Low Level Waste Program at Hanford.

Rather than the 8 mrem/Ci released (maximum individual thyroid dose) predicted by the ALLDOS program for the Hanford site, a much lower dose would have been calculated if the uptake of ^{129}I was adjusted to allow for the stable ^{127}I diluting the ^{129}I at the release point. The purpose of the work described in this report was to develop a technique for measuring the specific activity of ^{129}I releases (or the amount by which the ^{129}I has been diluted by ^{127}I).

To date, the measurement of the specific activity of the ^{129}I emitted from fuel reprocessing plants has been limited by several factors:

- 1) inability to separate ^{129}I chemical species without contamination with stable ^{127}I ;

- 2) inability to measure very low ^{129}I specific activities due to poor mass spectrometric ionization efficiencies ($\ll 1\%$);

- 3) inability to collect and manipulate small ^{129}I samples in the vicinity of ^{129}I sources (such as a nuclear fuel reprocessing plant) without contamination with either stable or radioactive iodine.

Therefore, this study sought to evaluate approaches to eliminate these problems:

- 1) Demonstration of the accurate measurement of $^{127}\text{I}/^{129}\text{I}$ standards by negative surface ionization;

2) Demonstration of gas chromatographic technique to quantitate and separate the iodine in a form suitable for negative ionization mass spectrometry;

3) Demonstration of the ability to collect an unfractionated ^{129}I sample;

4) Demonstration of the ability of an integrated gas chromatography/negative ionization mass spectrometry method to accurately measure specific activities under simulated off-gas conditions.

The results of each step are described in the following sections.

II. MASS SPECTROMETRY DEVELOPMENT

The objectives of the negative ionization mass spectrometer development work were to determine if new ionizers could be used without modification to measure iodine isotopic ratios greater than 10^4 , and to determine what types of problems are encountered in the measurement of wide ratio iodine isotopics.

For this study, three standards (blends) were prepared at different iodine 127/129 ratios. To prepare these standards, pure silver iodide-127^a was dissolved in 28% ammonium hydroxide^a to give a concentration of approximately 0.16 grams iodide per liter of solution. This solution was allowed to equilibrate for several days, checked for isotopic purity by mass spectrometry, and the iodide concentration verified by gas chromatography. One liter of the pure 127I solution was then spiked with 129I to prepare a stock solution with an iodine 127/129 ratio of 590. (The 129I solution had been obtained from the National Bureau of Standards^b and analyzed by mass spectrometry to determine the isotopic composition of the iodine). Aliquots of this stock solution were then volumetrically diluted with pure 127I solution to give two additional standards with iodine 127/129 ratios of 4×10^5 and 2.5×10^7 .

All mass spectrometric measurements were made on a tandem mass spectrometer, a two-stage instrument equipped with a dual detector system (Figure 1). There are differences between using the tandem mass spectrometer to measure iodine by negative surface ionization, and using the "normal" positive ion mode of operation. Specially prepared porous lanthanum hexaboride (LaB₆) filaments, described elsewhere⁵, are used as ionizers. About 3 μ g of AgI is dried from the NH₄OH solution on tantalum side filaments and mounted in a standard AVCO triple filament arrangement.⁶ The ionizing filament is operated at 900-1000°C, or a filament currents from 1.5 to 2.4 amps. With the magnet sectors energized to approximately 5150 gauss, the region was scanned around -9820 volts accelerating potential. This combination of parameters is used to achieve an I⁻ beam strength equivalent of up to 1.6×10^9 counts in 20 seconds for a 3 microgram sample loading.

Both detectors must be used to make measurements at wide-ratios. The pulse counting detector system consists of an EMI type electron multiplier housed within the mass spectrometer vacuum envelope and connected to an EG&G/Princeton Applied Research amplifier/pulse discriminator unit. The signal from the amplifier/discriminator is fed to a Monsanto 10 MHz counter and then to a 32 KByte Raytheon RDS-500 minicomputer system. This detector system is sensitive to a few thousand atoms of iodine and is used to measure the smaller 129 peaks.

The 127 peaks are measured using a Faraday ion collector located between the two magnetic sectors. The ion collector consists of a collector plate which is within the vacuum envelope and connected to a Keithley 642 FET electrometer. Data are output to a strip chart recorder.

^a J. T. Baker, reagent grade

^b National Bureau of Standards, Standard Reference Material 4949

Pulse Counting
Detector
(To Raytheon Computer)

Final
Ion
Collector

1st Stage

2nd Stage

Mid-Sector
Ion Collector

ICPP-A-9080

Figure 1. Tandem Mass Spectrometer Magnet and Detector Arrangement

To use both detectors, the relationship between them must be known. This calibration factor was determined by making 12 measurements of a single peak using both detector systems and then equating the output signals to define the relationship. Table I shows the results of the detector calibration. The pulse counting detector system yielded 2131 ± 263 (std. dev.) counts per second for each division on the chart produced by the Faraday ion collector system.

TABLE I
DETECTOR CALIBRATION

<u>Counts/Sec^a</u>	<u>Chart Disisions^a</u>	<u>Counts/Sec per Division</u>	<u>Range</u>
10,851	5.5	1973	0.1
185,680 ^b	40.6 ^b	4573 ^b	0.1 ^b
266,931	10.4	2567	1.0
141,205	76.0	1858	0.1
91,183	55.1	1655	0.1
406,482	16.9	2405	1.0
395,007	16.8	2351	1.0
1,059,958	51.9	2042	1.0
161,374	71.0	2273	0.1
131,775	59.0	2233	0.1
126,514	61.5	2057	0.1
116,439	57.4	2029	0.1
		Mean =	2131
		Standard deviation =	263

^a All counts and chart readings have been baseline corrected.

^b Point deleted in calculation of mean and standard deviation.

To demonstrate the applicability of the measurement technique, the stock solution ($127/129 = 590$) was analyzed using the pulse counting detector system alone. Subsequently, the 10^5 and 10^7 standard blends were analyzed using both detectors. In making this type of measurement, the 129 mass was measured using the pulse counting detector; the retractable ion collector plate was then inserted, the magnet moved to the 127 mass, and the 127 signal measured with the Faraday ion collection system. The magnet was then returned to the 129 mass, the Faraday system retracted, and the process repeated. This sequence, and the ion collector data processing are done manually. Measurements were made at a number of scale factors, count rates, and percent of scale levels to determine if any effects would be observed from possible differences due to varying counter efficiencies or different ranges.

The stock solution (127/129 ratio of 590), was measured as 590 ± 4.5 using the pulse counting system alone. This demonstrates that iodine at this ratio can be measured accurately and with high precision.

Table II shows the results of the 10^5 blend measurements. In all, 4 filaments were loaded and 36 measurements were made at different times, scale factors and percent of scale levels. Results within a single filament showed a variation from 6 to 39%. The results from filament 1 which showed the 39% relative standard deviation because of a marked change in the measured ratio were not used in the calculation of the final result.

The 10^5 standard, having a makeup value of 4×10^5 , was measured as $(4.0 \pm 0.76) \times 10^5$ overall, or $(3.7 \pm 0.32) \times 10^5$ with filament 1 deleted. For filament 1, these measurements ranged from 3.3×10^5 to 5.1×10^5 . The data presented here clearly demonstrate that ratios on the order of 10^5 can be measured with an accuracy and precision of better than 20%. The 10^5 ratio measurements are summarized in Table III.

The results from the measurements of the 2.5×10^7 ratio blend, shown in Table IV, were highly variable and deviated from the nominal value by greater than an order of magnitude. The results from these measurements are summarized in Table V.

The variability of the 10^7 ratio measurements is thought to be a result of two conditions: 1) The ionizing filaments may have been contaminated with a small amount of iodine; 2) Iodine from the analysis was being deposited on the molybdenum ion lens plates inside the mass spectrometer which would then reevaporate during the next analysis, causing an error in the results. A summary of the results of this study is given in Table VI.

TABLE II
 10^5 RATIO MEASUREMENTS

Filament	I-127 Chart ^a Divisions	Scale Factor	I-127 Equivalent (10^6 Counts)	I-129 ^a Counts	10^5 Ratio
1	26.0	10	0.554	3.9	1.4
	72.4	10	1.54	3.8	4.1
	69.7	10	1.49	3.8	3.9
	66.0	10	1.41	3.4	4.1
	25.2	100	5.37	8.3	6.5
	23.0	100	4.90	7.3	6.7
	21.0	100	4.48	6.8	6.6
	10.2	1000	21.73	30.1	7.2

TABLE II (contd)
10⁵ RATIO MEASUREMENTS

Filament	I-127 Chart ^a Divisions	Scale Factor	I-127 Equivalent (10 ⁶ Counts)	I-129a Counts	10 ⁵ Ratio
2	17.9	1000	38.14	128.8	3.0
	17.7	1000	37.72	116.3	3.2
	16.9	1000	36.01	102.8	3.5
	28.5	1000	60.73	134.4	4.5
	25.8	1000	54.98	135.6	4.1
	23.0	1000	49.01	121.3	4.0
	20.0	1000	42.62	105.0	4.1
	36.4	1000	77.57	197.5	3.9
	33.3	1000	70.96	180.2	3.9
	29.1	1000	62.01	160.8	3.9
3	74.0	1000	157.7	503.7	3.1
	73.7	1000	157.1	471.4	3.3
	73.0	1000	155.6	448.4	3.5
	72.5	1000	154.5	427.6	3.6
	70.4	1000	150.0	436.4	3.4
	68.5	1000	146.0	417.0	3.5
	66.5	1000	141.7	405.3	3.5
	53.7	1000	114.4	333.5	3.4
	52.5	1000	111.9	336.9	3.3
	51.5	1000	109.7	339.3	3.2
	50.5	1000	107.6	335.1	3.2
	49.5	1000	105.5	336.0	3.1
	48.5	1000	103.4	335.2	3.1
	47.5	1000	101.2	337.3	3.0
4	76.5	10000	1,630	3405.9	4.8
	62.7	10000	1,336	3559.8	3.7
	65.8	10000	1402	4229.9	3.3
	61.5	10000	1311	3430.7	3.8

^a All counts and chart readings have been baseline corrected.

TABLE III
10⁵ RATIO SUMMARY

Filament	Mean Ratio	Standard Deviation
1	5.1×10^5	2×10^5
2	3.8×10^5	0.45×10^5
3	3.3×10^5	0.19×10^5
4	3.9×10^5	0.64×10^5
Mean of 4 filaments	=	$(4.0 \pm 0.76) \times 10^5$
Mean after deleting filament 1	=	$(3.7 \pm 0.32) \times 10^5$

TABLE IV
10⁷ RATIO MEASUREMENTS

Filament	I-127 Chart ^a Divisions	Scale Factor	I-127 Equivalent (10 ⁶ Counts)	I-129a Counts	Measured Ratio
1	15.0	10000	319.7	527.7	0.061×10^7
	14.5	10000	309.0	609.1	0.051×10^7
	12.0	10000	255.7	613.4	0.042×10^7
	11.5	10000	245.1	630.4	0.039×10^7
	24.0	1000	51.5	926.6	0.006×10^7
2	5.1	10000	108.7	210.4	0.054×10^7
	41.0	1000	87.4	78.0	0.11×10^7
	24.8	1000	52.9	364.2	0.013×10^7
	19.1	1000	40.7	369.4	0.011×10^7
3	11.6	10000	247.2	1010.9	0.024×10^7
	12.0	10000	255.7	752.9	0.034×10^7
	12.4	10000	264.2	655.3	0.040×10^7
	11.4	10000	242.9	608.6	0.040×10^7
	11.2	10000	238.7	561.9	0.042×10^7
	26.7	10000	569.0	466.6	0.12×10^7
	26.5	10000	564.7	468.0	0.12×10^7
	26.4	10000	562.6	444.8	0.13×10^7
	26.2	10000	558.3	440.7	0.13×10^7
	15.0	100000	3196.0	526.9	0.61×10^7
	13.0	100000	2770	494.1	0.56×10^7
	11.8	100000	2515	473.3	0.53×10^7

^a All counts and chart readings have been baseline corrected.

TABLE V
10⁷ RATIO SUMMARY

<u>Filament</u>	<u>Mean Ratio</u>	<u>Standard Deviation</u>
1	0.400 x 10 ⁷	0.021
2	0.047 x 10 ⁷	0.046
3	0.20 x 10 ⁷	0.23
Mean of 3 filaments		= (0.096 ± 0.090) x 10 ⁷

TABLE VI
SUMMARY OF MEASUREMENTS

Stock Solution	Nominal Value	=	590
	Measured Value	=	590.6 ± 4.5
Blend 1	Nominal Value	=	4 x 10 ⁵
	Measured Value	=	(3.7 ± 0.32) x 10 ⁵
Blend 2	Nominal Value	=	2 x 10 ⁷
	Measured Value	=	(0.096 ± 0.090) x 10 ⁷

The conclusions drawn from the first part of this study were:

- 1) The newly developed ionizers can be used to measure iodine isotopic ratios equal to approximately 10⁵ with a precision and accuracy better than 20%.
- 2) The major problem associated with the measurement of wide isotopic ratios is thought to be due to iodine contamination effects.

After the successful development of a technique to measure isotopic ratios up to 10⁵, a study was performed to measure the minimum amount of iodine that must be delivered to the mass spectrometer to accurately measure a ¹²⁷I/¹²⁹I ratio of 10⁴. To determine this amount, a standard blend with a ratio of 8 x 10³ was loaded in decreasing amounts and the ratio measured as a function of filament loading. The results are shown in Table VII.

TABLE VII

ISOTOPIC RATIO MEASUREMENTS AS FUNCTION OF FILAMENT LOADING

<u>Filament Loading (ng I)</u>	<u>Measured Isotopic Ratio</u>
9000	9.3×10^3
2000	9.1×10^3
800	9.5×10^3
80	1.0×10^4
16	1.2×10^4
10	1.9×10^4
8	1.4×10^4
1	2.6×10^4

From these results a criteria of 80 ng I delivered to the mass spectrometer was used as the objective of the gas chromatography development described in the next section to assure 10^4 ratios with a precision and accuracy better than 25%.

III. GAS CHROMATOGRAPHY DEVELOPMENT

The development of the GC technique to measure organic and elemental iodine was done in two phases. The first phase used solutions containing the different iodine chemical species and determined optimum column types and operating conditions. The second phase was performed using representative gaseous forms of iodine species to measure minimum detection limits and response.

3.1 Chromatography of Iodine Solutions

Castell, et al.⁷, published the gas chromatographic separation and identification data of several alkyl iodides using glass columns filled with tricresyl phosphate on DMCS-treated Chromosorb W. Castello, et al.⁷ also proposed a homologous series of iodoalkanes as a reference for the calculation of the retention indices of ECD-sensitive substances. Corkill and Giese⁸ used fused silica capillary columns coated with either SE52 or SE54 to analyze the iodothyronines. The analysis of I_2 by GC-ECD is more difficult than the analysis of organic iodides because I_2 is less volatile and more reactive than organic iodides.

In this study the analysis of I_2 by GC-ECD was investigated as a function of detector, injector, and column temperatures. The calculated retention indices were compared to the results of Patte, Echeto, and Laffort⁹.

Analysis of iodine compounds were performed with a Varian Model 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector. Two columns were used: a 30 cm x 0.3 cm stainless steel column of 10% OV-101 on Chromosorb W-HP 80/100 mesh obtained from Varian Instrument Group (Palo Alto, CA); and a 300 cm x 0.3 cm nickel column of 5% SE-30 on Chromosorb W-HP, 80/100 mesh obtained from Alltech Associates (Arlington Heights, Ill.). All experiments were performed using a 30 cm³/min flow with N_2 or 90% Ar/10% CH_4 carrier gas. The column was operated isothermally at 100°C for the retention index experiments.

Methyl iodide, ethyl iodide, 1-iodopropane, and 2-iodopropane were obtained from Aldrich Chemical (Milwaukee, WI) and were used without further purification. The toluene, benzene, and cyclohexane were distilled-in-glass grade obtained from Burdick and Jackson (Muskegon, MI) and used without further purification. The elemental iodine used was resublimed grade obtained from Fisher Scientific (Pittsburgh, PA).

Alkyl iodide solutions were prepared by volumetric dilution: the I_2 solutions were prepared by weighing I_2 crystals to better than ± 0.1 mg, dissolving the crystals in toluene or cyclohexane, and preparing subsequent serial dilutions volumetrically.

3.1.1 Retention Index. The retention index of I_2 was determined in the manner of Castello, et al.⁷ and Patte, et al.⁹ at 100°C for both OV-101 and SE-30 by comparing the retention time of the I_2 peak with methyl iodide, ethyl iodide, 2-propyl iodide, 1-propyl iodide, benzene, toluene, and cyclohexane on the OV-101 column; with methyl iodide, 1-propyl iodide and cyclohexane on the SE-30 column. The I_2 peak was identified by comparing the chromatograms of blank solvents with serial additions of a 13

mg/L I₂ standard solution. I₂ was then assigned to the peak that increased in area in proportion to the amount of added I₂.

Plots of reduced retention time vs. retention index for the two column types are shown in Figures 2 and 3. From these plots, a retention index on OV-101 of 172 + 14 for the alkyl iodide homologous series and 510 + 42 for the n-alkane homologous series was calculated. For SE-30, a retention index of 160 + 16 for the alkyl iodide homologous series and 500 + 52 for the n-alkane homologous series was calculated.

3.1.2 Resolution. The height equivalent to a theoretical plate (HETP) was calculated using the equation:

$$\text{HETP} = \frac{L}{5.54 \frac{(t_R')^2}{W_{1/2}}} \quad (1)$$

where: L is the length of the column;

t_R' is the reduced retention time;

W_{1/2} is the full width at half maximum of the I₂ peak.

At 100°C the HETP for I₂ was 1.1 mm for OV-101 and 39 mm for SE-30. This was significantly less resolution than reported by Castello, et al.⁷ who reported resolutions for alkyl iodides 0.4-0.5 mm. The poorer resolution may be caused by the greater reactivity of I₂ compared to the alkyl iodides. However, the I₂ peak was sufficiently resolved from CH₃I and CH₃CH₂I for analysis. Despite poorer resolution, the SE-30 column was the column of choice because it was more resistant to degradation by the iodine solutions.

3.1.3 Sensitivity. A plot of ECD response vs. quantity of I₂ injected is shown in Figure 4 (column-OV-101; temperature 130°C). From this plot, a detection limit of ~26 ng I₂ was calculated. The ECD response was then studied as a function of injector temperature (Figure 5), column temperature (Figure 6) and detector temperature (Figure 7).

From Figure 5 it appears the sensitivity of the GC-ECD technique is independent of injector temperature in the range of 190 to 220°C; there is no increase in sensitivity above 220°C and sensitivity decreases with decreasing temperature below 190°C. This decrease in sensitivity may be caused by peak broadening from slower vaporization of the solvent in the injector. It does not represent condensation of the I₂ within the injector since there is a constant response when the column temperature is varied in the range of 100-130°C (Figure 6).

The mechanism of the ECD response to I₂ was studied by dividing the I₂ response by the response of a reference compound such as 1-iodopropane^{7,10} or chlorobenzene¹¹. The results of simultaneous measurements of the I₂ to 1-iodopropane and I₂ to chlorobenzene ratio are plotted in Figure 7. The I₂ to chlorobenzene ratio first increases (indicating a non-dissociative capture mechanism at high temperatures) and then decreases (indicating a dissociative capture mechanism at low temperatures). Yet, because it is highly unlikely that a dissociative mechanism

Figure 2. Reduced Retention Time vs. Retention Index for the OV-101 Column

Figure 3. Reduced Retention Time vs. Retention Index for the SE-30 Column

Figure 4. Typical Calibration Curve for I_2 on the SE-30 Column

Figure 5. I₂ Response as a Function of Injector Temperature

Figure 6. I₂ Response as a Function of Column Temperature

Figure 7. Response Ratio of I_2 to Chlorobenzene and I_2 to Iodopropane as a Function of Reciprocal Detector Temperature

would be replaced by a non-dissociative mechanism at higher temperatures, there must be another explanation. Corkill and Giese² also observed a peak in the response vs. reciprocal detector temperature plot for the iodothyronines. They attributed the decreasing response that accompanied increasing temperature to decomposition of the iodine compounds on the narrow bore glass inlet and on the stainless steel and ceramic in the electron capture detector before the iodine compounds reach the collector region. This effect was also observed by Miller and Grimsrud¹².

This explanation is supported by the I_2 to 1-iodopropane ratio, which decreases monotonically with increasing temperature. Because the 1-iodopropane would also undergo decomposition; one would not expect a maximum in the I_2 to 1-iodopropane ratio. Because I_2 is more reactive than 1-iodopropane, this decomposition would decrease the I_2 to 1-iodopropane ratio as the detector temperature is increased. For these reasons, it appears likely that a dissociative mechanism is responsible for the ECD response to I_2 .

A tracer experiment then was performed that confirmed that I_2 was not converted to an organic iodide in the injector or on the column and also measured the transmission efficiency of the column and injector. I_2 in toluene and cyclohexane was traced with ^{125}I . The effluent of the column was routed to an iodine species selective adsorbent sampler in the manner of Keller, *et al.*¹³ The amount of ^{125}I injected and collected by each selected adsorbent was measured by direct X-ray spectrometry of the 27 keV Te $K\alpha$ X-ray using a hyperpure germanium low energy photon spectrometer. Collection periods corresponded to the time required to produce a chromatogram. The results of these experiments are shown in Table VIII. From these results, it appears that significant conversion of the I_2 did not occur either in the injector or on the column. In addition, more than 80% of the I_2 injected onto the column eventually reached the detector.

3.1.4 Demonstration. The applicability of the developed GC technique was demonstrated by analyzing an AgI in concentrated NH_4OH mass spectrometric standard. This standard was stored in a stoppered polypropylene test tube. The samples were traced by adding ^{125}I to the samples and allowing the radioiodine to exchange isotopically overnight. Two 1 mL aliquots of the solution were rapidly acidified to pH $\sim$ 2 with HNO_3 . The nitric acid was covered with a 10 mL layer of toluene at all times to prevent I_2 volatilization losses. One mL of saturated $NaNO_2$ was added to oxidize any free I^- to I_2 ; the resulting I_2 was extracted into the toluene. Three microliters of the toluene was injected onto the GC to measure the I_2 formed; while 1 mL of the toluene was counted with a hyperpure germanium low energy photon spectrometer to determine the chemical yield.

Typical gas chromatograms are shown in Figure 8. The results of these analysis are shown in Table IX. The precision of triplicate determinations was 12% at one standard deviation. Although the determinations were within the 95% confidence interval, the analysis were 23% higher than the nominal make up value. The cause of this bias is unknown. However, one possible explanation is the sample was concentrated by permeation of liquid through the polypropylene test tube. Based on these results, it appears the

TABLE VIII
¹²⁵I TRACER EXPERIMENT RESULTS

<u>Solvent</u>	<u>Fraction of Total Iodine That Reached Detector (%)</u>	<u>Fraction of Transmitted Iodine Found as I₂ (%)</u>	<u>Fraction Transmitted Iodine Found as Organic Iodide (%)</u>
Cyclo- hexane	81 $\pm$ 10	99 $\pm$ 2	1 $\pm$ 2
Toluene	88 $\pm$ 10	90 $\pm$ 2	10 $\pm$ 2

TABLE IX
AgI ANALYSIS RESULTS

<u>Makeup Value (μg I/mL)^a</u>	<u>Aliquot 1 (μg I/mL)^a</u>	<u>Aliquot 2 (μg I/mL)^a</u>
118	157 $\pm$ 38	133 $\pm$ 32

^a $\pm$ 2 σ as determined by precision of triplicate analysis

technique has an accuracy and precision of 10-20% at the one standard deviation level.

3.2 Chromatography of Gaseous Iodine Compounds

The objectives of the gas chromatography development of gaseous compounds were two fold:

- 1) Using the determined gas chromatographic conditions, determine detection limits, precision and accuracy of gas phase CH₃I and I₂;
- 2) Demonstrate the ability to prepare separate CH₃I and I₂ fractions for the mass spectrometric specific activity measurement.

The apparatus used to introduce gaseous samples is shown in Figure 9. Helium carrier gas was directed through a sample bomb or over a permeation tube to generate the required iodine gas phase concentrations.

Figure 8. Typical Chromatograms of I₂ Extraction of Mass Spectrometric Standard

The carrier gas was either directed through a capillary splitter or directly to the eight port valve, depending on the objective of the experiment. The iodine gases were frozen out in a 0.25 cm^3 sample loop with liquid N_2 and the He carrier gas exhausted through a vacuum pump. To measure higher levels of CH_3I , syringe samples were injected directly onto the sample loop. After the required sampling time, the eight port valve was used to divert the He stream and introduce the N_2 carrier gas used by the gas chromatograph, to the 0.25 cm^3 sample loop. The liquid N_2 was removed and the sample loop heated with warm water. After 0.5 minutes the GC carrier gas was diverted around the sample loop to continue the chromatogram; the sample loop was then purged with He in preparation of the next sample.

Methyl iodide standards were prepared by volumetric serial dilutions and using permeation tubes. The serial dilutions were prepared by condensing known amounts of CH_3I and CO_2 into a common container. Concentrations were obtained by measuring the partial pressure of each gas within a known volume and assuming ideal gas behavior.

The CH_3I permeation tubes were prepared from 75 mm x 3.2 mm OD Teflon TFE tubing. The tubes were filled with liquid CH_3I and the ends were plugged with 304L stainless steel rods. These tubes had permeation rates on the order of $0.1\text{ }\mu\text{g min}^{-1}\text{ cm}^{-2}$. As shown in Figure 10, these permeation tubes required several days before constant permeation rates were achieved.

The I_2 permeation sources were prepared from 25 mm pieces of 6 x 8 mm Silastic (Dow Corning) silicone rubber tubing. Each end was plugged with borosilicate glass: one plug was 3 mm rod formed into a hook for easy weighing, the other plug had a test tube end to contain the iodine crystals. All seals were covered with Dow-Corning RTV cement.

The calibration curves determined for CH_3I and I_2 are shown in Figures 11 and 12. Departures from linearity were observed below 0.1 ng for CH_3I and 5 μg for I_2 . These may represent the uncertainty associated with significant blank corrections. Typical GC responses to quantities close to the respective detection limits are compared to a typical blank measurement in Figure 13. The higher detection limits than found in the solution measurements for I_2 using the gaseous sample handling system may be related to of the following factors:

- 1) Increased wall and surface losses on the gas sample handling system;
- 2) Peak broadening due to desorption kinetics of the 0.25 cm^3 sample loop.

The precision and accuracy of the technique as demonstrated by these calibration curves were 10-12%. Because the I_2 cannot be reliably measured below 5 μg , it is not likely to be detected in fuel reprocessing plant off-gases. However, CH_3I may still be quantitated by GC-ECD. Therefore, an experiment was performed to measure any I_2 interference to the CH_3I determination (perhaps by conversion to CH_3I during sample handling). A mixture of 0.763 ng CH_3I was measured alone and in the presence of 3.62 ng I_2 . The results are shown in Figure 14.

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Figure 9. Gas Chromatograph Gas Handling System

Figure 10. Permeation Rate as Function of Time After Preparation

Figure 11. Methyl Iodide Calibration Curve

Figure 12. I₂ Calibration Curve

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Figure 13. Gas Chromatographic Response to Quantities Approximating the Detection Limit

Figure 14. Typical Chromatograms Demonstrating Accuracy of CH_3I Measurement in the Presence of I_2

The two results agreed within the 12% precision established by the method. Therefore, it was demonstrated that traces of I_2 will not bias the CH_3I measurement.

In summary, the conclusions drawn from the gas chromatography development were:

- 1) The GC technique has sufficient sensitivity to measure CH_3I at the 80 ng level required for the isotopic ratio measurement;
- 2) The GC technique does not have sufficient sensitivity to measure I_2 at the 80 ng level required for the isotopic ratio measurement; therefore, another technique for collecting the I_2 fraction must be used;
- 3) The presence of I_2 does not bias the CH_3I determination.

IV. SAMPLING METHODOLOGY

The large difference in GC-ECD detection limits between CH_3I and I_2 required separate I_2 and CH_3I samples be collected and prepared for analysis. The sampling apparatus that was designed is shown in Figure 15. A 250 cm^3 impinger containing 1 M NaOH was used to selectively collect the I_2 , allowing the CH_3I to pass through to the permatube dryer. The NaOH also scrubs oxides of nitrogen from the sample stream to prevent any interference with the GC determination of CH_3I .

The I_2 concentration and isotopic ratio were then measured by submitting the solution to isotope dilution mass spectrometry (IDMS). A description of the technique can be found in standard textbooks, such as that by Choppin.¹⁴ In summary the IDMS analysis requires analysis of two aliquots, one before and one after a known amount of ^{129}I is added to the sample. The concentration is calculated from the change in isotopic ratio due to spike addition.

The permatube dryer dried the sample stream to a dew point of -60°C to prevent condensation in the methyl iodide collection vessel. The permatube dryer operates on the principle of diffusion through thin polymeric membranes, thus minimizing the potential for sample losses through surface reactions. These dryers are fabricated by shaping a perfluorosulfonic acid polymeric membrane into thin walled tubes, typically 0.064 cm thick and 60 cm in length, and mounting as many as 200 tubes into common headers. This multiple tube pack is sealed inside a 4 cm diameter stainless steel shell. In principle, the sample enter the sample inlet, wets the inner wall of the polymer tube; the water continuously diffuses through the polymer into a purge stream which exhausts the removed water vapor.

The methyl iodide collection vessel is a 660 cm^3 glass vessel that can be isolated by a series of valves and inserted into the gas sample handling apparatus shown in Figure 9. The demonstration of each component of the apparatus is described in the following sections.

4.1 Sodium Hydroxide Impinger

The objectives of the sodium hydroxide impinger tests were:

- 1) Achieve high collection efficiencies for I_2 ;
- 2) Achieve high transmission efficiencies for CH_3I ;
- 3) Measure any fractionation of the $^{127}\text{I}/^{129}\text{I}$ ratio due to sampling.

The recovery efficiency was measured using $^{125}\text{I}_2$ generated with a permeation tube containing $^{127}\text{I}_2$ crystals traced with ^{125}I . The I_2 concentration was measured before and after a 250 cm^3 impinger containing 0.1 M NaOH; the measurements were conducted by collecting the on a $^{125}\text{I}_2$ TEDA impregnated charcoal bed and counting the 27 keV Te X-ray on a $\text{K}\alpha$ hyperpure germanium low energy photon spectrometer (LEPS). The results are shown in Table X.

Figure 15. Iodine Sampling Apparatus

TABLE X
RESULTS OF I₂ COLLECTION BY NaOH

Sampling Period (min)	Flowrate (cm ³ /min)	Collection Efficiency (%)
20	250	99.4
20	1900	98.1

As shown in Table X, quantitative collection of I₂ with a NaOH impinger is achievable.

The absence of exchange between collected ¹²⁵I and CH₃¹²⁷I was then demonstrated by bubbling 0.3 mg/m³ CH₃I sample stream through 200 cm³ of 1.85 µCi ¹²⁵I/L at 2.6 L/min for 4 hours. A TEDA charcoal bed collected the methyl iodide penetrating the NaOH impinger. The charcoal bed was then counted to measure the ¹²⁵I that had exchanged with the CH₃I and penetrated the impinger. After 4 hours, 9.0 ± 3.2% of the ¹²⁵I was found on the charcoal bed. Although some of the ¹²⁵I may have been carried onto the charcoal by mechanisms other than exchange (spray from impinger solution, oxidation to I₂) the experiment demonstrated that fractionation was less than the 12% precision of the GC technique.

The high transmission efficiency of the NaOH impinger and permatube dryer was demonstrated by introducing a known concentration of CH₃I to the integrated sampler (shown in Figure 15) and comparing the measured concentration (by GC-ECD, Figure 9) to the known concentration. The known concentration of 0.3 mg/m³ was generated as before. The results are shown in Table XI. These results demonstrate a recovery of 95.1 ± 9.3%, sufficient for the designated purposes. Therefore, the NaOH was deemed suitable as a I₂ sampler.

TABLE XI
RESULTS OF CH₃I TRANSMISSION TESTS

Test Number	CH ₃ I Introduced (ng)	CH ₃ I Measured (ng)	Recovery (%)
1	235	202	86.0
2	228	202	88.6
3	228	208	92.3
4	228	228	100.0
5	228	248	108.8
average =			95.1
standard deviation =			9.3

4.2 Permatube Dryer

The objective of the permatube dryer evaluation was to demonstrate that the CH_3I sample could be dried without fractionating the CH_3I . As noted in section 4.1 (see Table XI), high transmission efficiency had already been demonstrated.

The fractionation was measured by determining the transmission efficiency of a mixture of $\text{CH}_3^{127}\text{I}$ and $\text{CH}_3^{125}\text{I}$ by both GC-ECD (for $\text{CH}_3^{127}\text{I}$) and by counting the 27 kev X-ray (for $\text{CH}_3^{125}\text{I}$). The $\text{CH}_3^{127}\text{I}/\text{CH}_3^{125}\text{I}$ mixtures were prepared by exchanging ^{125}I with $\text{CH}_3^{127}\text{I}$ and preparing permeation tubes with the tagged CH_3I .

The $\text{CH}_3^{127}\text{I}$ was measured using the apparatus shown in Figure 15 (without the NaOH impinger) followed by GC measurement with the apparatus shown in Figure 9. The $\text{CH}_3^{125}\text{I}$ was measured by replacing the methyl iodide collection vessel with a TEDA charcoal bed and counting the 27 kev X-ray on a hyperpure germanium LEPS. The sample flowrate was maintained at 1 L/min and the purge flow was maintained 5.1 L/min. The results of these experiments are shown in Table XII.

The transmission efficiencies shown in Table XII are not statistically different. Therefore, it can be inferred that the dryer was introducing only negligible changes in the isotopic ratio. The efficiencies measured at 1 L/min (Table XII) are lower than the efficiencies measured at 2.6 L/min (Table XI). This may be due to the

TABLE XII
RESULTS OF DRYER FRACTIONATION EXPERIMENTS

Test Number	$\text{CH}_3^{127}\text{I}$ Transmission Efficiency (%)	$\text{CH}_3^{125}\text{I}$ Transmission Efficiency (%)
1	76	ND(1)
2	85	ND(1)
3	81	ND(1)
4	ND(1)	110
5	ND(1)	75
6	ND(1)	141
average	81 ± 5	109 ± 33

(1) ND = Not Determined

larger residence time in the dryer at the lower flowrate. If quantitative transmission for $\text{CH}_3^{127}\text{I}$ such as shown in Table XI, can be obtained by operating at 2.6 L/min, then no observable fractionation should occur. From these experiments, it was therefore, concluded that there were no significant fractionation effects and the sampling apparatus should be operated at 2.6 L/min.

V. INTEGRATED SAMPLE DEMONSTRATION

The integrated sampler was tested to demonstrate its ability to measure:

- 1) CH_3I concentration and isotopic ratio in the presence of I_2 ;
- 2) I_2 concentration and isotopic ratio's in the presence of CH_3I .

The apparatus shown in Figure 16 was used in this demonstration. A CH_3I permeation tube (permeation rate = $0.82 \mu\text{g}/\text{min}$; $^{127}\text{I}/^{129}\text{I} = 3.8 \times 10^3$) was connected to an I_2 permeation tube with a different permeation rate ($0.42 \mu\text{g}/\text{min}$) and different $^{127}\text{I}/^{129}\text{I}$ ratio (2.2×10^3). Both isotopic ratios represent calculated values from mixing standard solutions and were not confirmed experimentally. A sample flowrate of $0.33 \text{ L}/\text{min}$ (a worst case lowest flowrate expected for use with the integrated sampler) was maintained over the two permeation tubes. Using this flowrate, CH_3I losses in the perm tube dryer are maximized as is the CH_3I contact time with the collected I^- in the NaOH impinger.

Two aliquots of the NaOH impinger solution were taken. One was then spiked with a known amount of ^{129}I . The isotope ratio of unspiked sample represents the I_2 specific activity; the difference in the ratio between the spiked and unspiked sample is used to calculate the I_2 concentration.¹⁴ The methyl iodide concentration was measured by GC-ECD. The specific activity of the CH_3I was not measured directly but calculated by ^{129}I mass balance. This technique is analogous to measuring the total ^{129}I (by collecting a sample on a charcoal bed and determining the total ^{129}I by photon counting) and using this number to calculate the CH_3I specific activity. The accuracy of this technique was tested because mass balance calculations will be used to confirm the accuracy of in-plant measurements.

The results of this demonstration are shown in Table XIII. The reason the measurement of I_2 concentration was low cannot be attributed to low recovery in the NaOH impinger (as evidenced by Table X). However, the low concentration measurement and the low isotopic ratio ($^{127}\text{I}/^{129}\text{I}$) measurement can be simultaneously explained if the unspiked $^{127}\text{I}/^{129}\text{I}$ measurement of the NaOH solution was low and the spiked isotopic ratio measurement was accurate (or high). The low CH_3I concentration may occur due to losses in the perm tube dryer caused by the low sample flowrate.

From this worst case demonstration it was concluded that concentrations and specific activities of CH_3I and I_2 can be determined with an accuracy better than a factor of two. This accuracy was considered sufficient because:

- 1) The largest uncertainties in specific activity were conservative, indicating less dilution with stable iodine than is actually present;
- 2) The uncertainties in concentration were conservative, indicating lower levels of stable iodine (assuming accurate total ^{129}I release measurements);

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Figure 16. Integrated Sampler Demonstration Apparatus

3) Specific activity measurements may require corrections in dose calculations of up to four orders of magnitude compared to uncertainties on the order of a factor of two.

Therefore, the integrated sampling technique was considered suitable for nuclear fuel reprocessing plant off-gas streams.

TABLE XIII
RESULTS OF INTEGRATED SAMPLER DEMONSTRATION
SPECIFIC ACTIVITY MEASUREMENT

Iodine Compound	Ratio ($^{127}\text{I}/^{129}\text{I}$)		Measured/Actual
	Measured ($\times 10^3$)	Actual ($\times 10^3$)	
CH ₃ I	4.7	3.8	1.24
I ₂	0.9	2.2	0.45

TABLE XIV
RESULTS OF INTEGRATED SAMPLER
DEMONSTRATION - CONCENTRATION MEASUREMENT

Iodine Compound	Concentration		Difference $\left(\frac{\text{Measured}-\text{Actual}}{\text{Actual}} \right) \times 100\%$
	Measured (mg/m ³)	Actual (mg/m ³)	
CH ₃ I	1.46	2.44	-41
I ₂	0.83	1.29	-35

V. CONCLUSIONS

The major conclusions of this work were:

1) Isotopic ratios of $^{127}\text{I}/^{129}\text{I}$ as large as 10^5 can be successfully measured on samples as small as 80 ng I.

2) Less than 1 ng CH_3I can be measured by gas chromatography in the presence of I_2 , but I_2 must be measured by isotope dilution mass spectrometry using a separately collected sample.

3) The developed integrated sampler can collect separate I_2 and CH_3I samples with high recovery efficiencies and without fractionation provided sample flowrates are maintained above 2.6 L/min.

4) Even under worst case sampling conditions, concentrations can be measured within 40% and isotope ratios can be measured within a factor of two.

Based on these results, the sampling and analysis technique was considered suitable for nuclear fuel reprocessing plant off-gas streams.

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