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DIRECT DETERMINATION OF CESIUM IN PILOT PLANT EFFLUENTS
BY ISOTOPE DILUTION MASS SPECTROMETRY

by

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SLIDE 1 DIRECT DETERMINATION OF CESIUM IN PILOT PLANT EFFLUENTS
BY ISOTOPE DILUTION MASS SPECTROMETRY*

P. Chastagner

At the Savannah River Laboratory, we are routinely determining stable cesium at part per billion levels in simulated defense waste supernate by isotope dilution mass spectrometry. This work is in support of our pilot plant studies of waste

SLIDE 2 immobilization processes. Today, I'll review the analytical problem, the isotope dilution technique for cesium, interferences and contamination control, the novel technique I devised to get around the problems, and the results.

Analytical Problem

SLIDE 3 In our process, the waste supernate will be about 5M in sodium ion with the compound distribution shown. It contains about 60 ppm cesium. For the pilot plant studies, a simulated solution spiked with natural cesium is passed through ion exchange

SLIDE 4 columns where the cesium is removed. The goal is to establish a process with a decontamination factor greater than 10^4 . Therefore, we have to be able to routinely determine cesium in the effluent at the one ppb level. Atomic absorption and flame emission spectroscopic techniques are adequate for the feed concentrations. But only thermal ionization mass spectroscopic

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analysis of isotopically diluted samples has the sensitivity and accuracy required for the measurement of cesium at ppb levels in the effluent.

SLIDE 5

As shown by the well-known equation of Langmuir and Kingdon, thermal ionization efficiencies are strong functions of the work function of the ionizing filament and the ionization potential

SLIDE 6

of the element being ionized. Cesium with an ionization potential of 3.89 V is the most easily ionized element. It can be ionized thermally with nearly 100% efficiency from a rhenium filament, in contrast to the few tenths of a percent efficiency routinely achieved with uranium. The high ionization efficiency allows accurate analyses to be made with very small samples of pure cesium. As you know, sample purity is generally important in thermal ionization mass spectrometry. Under normal operating conditions, impurities migrate to the ionizing filament. There they either ionize and add to the mass spectrum, or they poison the filament. In our case, barium ionizes and overlaps the cesium spectrum at masses 135 and 137. Sodium tends to coat the rhenium ionizing filament and lower the effective work function of the surface. As shown in this slide, when a monomolecular layer of sodium forms on the rhenium filament, the ionization efficiency for cesium drops by a factor of 10^{11} . Thus, this problem must be avoided by techniques which will be discussed later.

Isotope Dilution

SLIDE 7 Cesium is monoisotopic in nature (^{133}Cs). Thus, only radioactive isotopes are available for isotope dilution analyses. The ^{135}Cs isotope with a half-life of 2×10^6 years would be preferred, but it is not available as a separated isotope. Therefore, the more-active ^{137}Cs isotope with a half-life of 30.1 years must be used. The most-enriched mixture available was 35% ^{137}Cs material from Oak Ridge, which had a 133/137 mass ratio of 1.43. Two spike solutions were prepared from the Oak Ridge material, one with about 0.3 ppb ^{137}Cs and the other with about 3 ppb ^{137}Cs . The 133/137 mass ratios increased to 11 and 2.6, respectively, because of natural cesium contamination.

SLIDE 8

The high thermal ionization efficiency of cesium allows us to limit the amount of radioactive cesium we use. In our method, 10 mm³ of sample are mixed with 10 mm³ of spike, and about half of the solution is loaded into the mass spectrometer. Thus, the total amount of ^{137}Cs is about 3 or 30 pg per sample, depending on which spike solution is used.

Analytical Precision

SLIDE 9 These spike solutions and pure cesium standards were used to determine the sensitivity, precision, linearity, and bias of this isotope dilution method. Replicate 10 mm³ portions of the 0.28 ng/cm³ spike showed a relative error of 0.68 ratio units at the 95% confidence level. This is equivalent to a random error of 0.2 ng/cm³ (ppb) in the cesium concentration at the 1 ng/cm³

level. Doubling the noise figure gives us a practical detection limit of about 0.4 ng/cm^3 (ppb). Analyses of pure water and pure cesium standards showed that the method was linear within about 3% and that the bias (accuracy) was within about 10%.

SLIDE 11 Contamination Control

Contamination control is essential when working with low-level samples. It is especially important with a ubiquitous element like cesium. Its global concentration is 7 ppm, more than 10,000 times our detection limit. Barium, another ubiquitous contaminant, has a global concentration of 250 ppm and is a contaminant in the simulated waste supernate. Barium is troublesome because the ^{135}Ba and ^{137}Ba isotopes overlap the cesium mass spectrum. Alkalis and aluminum in the sample interfere with the evaporation and thermal ionization of the cesium in the ion source. If transferred from the sample filaments to the ionizing filament, alkalis and aluminum can effectively stop the ionization process. For example, as already pointed out, the ionization efficiency of cesium drops by a factor of about 10^{11} when the ionizing filament becomes coated with sodium. In addition, these bulk impurities deposit on the ion source and interfere with its operation. Very frequent cleaning is required. Organic materials are also present in some of the simulated waste supernate samples. These materials form ions at every mass, and organic ions at mass 137 are sometimes more numerous than the ^{137}Cs ions.

SLIDE 12 Considerable effort is expended to minimize cesium contamination. In the pilot plant, all sample points are piped into a glove box, and samples are taken in pre-rinsed plastic bottles. In the laboratory, downflow clean air zones are provided over all work areas, reagents for diluting spike materials and rinsing sample vials are purified by sub-boiling distillation, new plastic pipet tips and new pre-rinsed plastic bottles are used for spiking operations, and mass spectrometer filaments are degassed at $>1600^{\circ}\text{C}$ before use. These measures also aid in the control of barium contamination.

SLIDE 13 Mass Spectrometers

 We have two mass spectrometers that are used for this work:
SLIDE 14 the large magnetic instrument manufactured by AVCO shown here
 (note the downflow clean air projector over the ion source region)
 and the Extranuclear quadrupole instrument shown here (note down-
SLIDE 15 flow clean air projector over the analyzer). A large clean air
 projector over the face of a radioactive hood provides double the
 air flow required by the hood and converts the hood to a clean
SLIDE 16 facility (LASL style). Two small downflow clean air hoods provide
 a clean environment for filament outgassing and sample loading
 operations.

SLIDE 17 Our contamination control measures proved adequate for sample spiking and filament loading operations as shown here. However, they were not adequate for dilution and were clearly unsatisfactory when more complex operations were applied for sample cleanup. As can be seen, the blank values for separating cesium from the simulated waste supernate ranged from 20 to more than 100 ppb.

Direct Method

SLIDE 18

At that point, I undertook the development of a direct method in which I loaded spiked samples of simulated waste super-

SLIDE 19

nate directly on the sample filaments. The result was a deposit that looked like the filament on the right, in this photograph, as contrasted to the normal invisible deposit obtained with a pure sample of cesium. The normal heating pattern for thermal ionization could not be used in this direct method because it caused sodium to distill and coat the ion source and the ionizing filament. No significant number of cesium ions were produced under such conditions, and the source had to be cleaned after each sample. However, when the sample filaments were heated for 20 minutes at a low temperature (below that needed to evaporate pure cesium), the cesium in the sample apparently diffused thermally and formed an enriched layer on the surface of the sodium deposit. The cesium could then be distilled selectively to the ionizing filament by slightly increasing the sample temperature. The sodium deposits remained intact and were removed with the sample filaments after the analyses. No significant contamination of either the ion source or the ionizing filament was evident in this case. While cesium ion production appeared to be about 10 to 100 times lower than with pure cesium samples, the observed sensitivity was still adequate for analytical purposes. Some barium distilled to the ionizing filament, but its interference could be controlled by running the ionizing filament at very low temperatures. The

SLIDE 20

mass 136 and 138 peaks for barium were monitored, and a correction was made for residual barium interference at mass 137. Organic interference was detected by monitoring the 140 peak as well as the 136 and 138 peaks. When organic material is present, the 140 peak is usually significant, and the 136/138 ratio is nearly 1 rather than the normal 0.11 barium ratio. As shown in this graph, continued heating of the sample filaments at a slightly elevated temperature drove off the organic material and permitted an accurate analysis to be made. When the organic material was gone, the 133/137 ratio reached a maximum, the 136/138 barium ratio dropped to normal, and the 140 peak dropped to normal background levels.

Results

This direct method has been in routine use to evaluate pilot plant ion exchange performance for about 1½ years; more than 1300 analyses have been made. The early work was done with the large magnetic instrument. Now that the thermal ionization quadrupole instrument has become available, it is used exclusively for the cesium analyses. This new instrument is about ten times less sensitive than the magnetic instrument, but it is more highly automated and is faster. The relative precisions and accuracies with the direct method are identical for the two instruments, and there is no reason to continue to use the more sophisticated instrument for this program. Very little sodium is transferred to the ion sources, and more than 500 samples can be analyzed

before cleaning is required. The average value obtained for samples of ion exchange column effluent that should be less than one ppb is about 0.7 ppb with an overall calculated error (95% C.L.) of ± 0.8 ppb. The overall accuracy of higher concentration samples is about $\pm 30\%$. Sample contamination has not proven to

SLIDE 23

be a problem. Samples are taken frequently, and when one becomes contaminated, it is immediately apparent as shown in this graph

SLIDE 24

of a series of samples taken before column breakthrough. The utility of the isotope dilution technique is shown in this slide. Columns 1 and 2 were in series, and only those points after the onset of Column 1 breakthrough are plotted. The point of Column 1 breakthrough is precisely defined as is the continued efficient performance of Column 2.

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① DIRECT DETERMINATION OF CESIUM
IN PILOT PLANT EFFLUENTS BY
ISOTOPE DILUTION MASS SPECTROMETRY

② OUTLINE

Analytical Problem

IDMS Technique

Interferences

Contamination Control

Analytical Techniques

Results

③ TYPICAL WASTE SUPERNATE COMPOSITION

2.2 M	NaNO ₃
1.1 M	NaNO ₂
0.75 M	NaOH
0.5 M	NaAlO ₂
0.3 M	NaSO ₄
0.3 M	NaCO ₃
60 ppm	CsX

④ CESIUM CONCENTRATION IN SIMULATED WASTE SUPERNATE

Feed	$>5 \times 10^{-4}$ M (~60 ppm)
Effluent	$<5 \times 10^{-8}$ M (~6 ppb)

⑤ LANGMUIR - KINGDON EQUATION

$$\frac{n^+}{n^0} \propto \exp \frac{e(W - IP)}{kT}$$

W = Work Function

IP = Ionization Potential

⑥ RELATIVE IONIZATION EFFICIENCIES

<u>Element</u>	<u>IP</u>	<u>W</u>	<u>Relative Number of Ions</u>
Cs	3.89 V	5.0 V*	5.9×10^4
		2.3 V **	1.5×10^{-7}
U	6.11 V	5.0 V *	3.7×10^{-3}

* Re filament: W = 5.0 V.

** Na surface: W = 2.3 V.

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ISOTOPIC DISTRIBUTION IN
OAK RIDGE CESIUM

<u>133</u>	<u>135</u>	<u>137</u>
50%	15%	35%

133/137 Ratio = 1.43

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¹³⁷Cs SPIKE MATERIAL

<u>¹³⁷Cs Concentration</u>	<u>133/137 Ratio</u>
0.28 ng/cm ³	11.0
2.8 ng/cm ³	2.6

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CESIUM ISOTOPE RATIO MEASUREMENTS

<u>Material</u>	<u>133/137 Ratio</u>	<u>Summary</u>
0.28 ng/cm ³ Spike	11.06	
	11.27	
	11.06	$\bar{R} = 11.17$
	11.2	$S = 0.29$
	11.5	$tS = 0.68$ (95% C.L.)
	11.0	$= 6.1\%$
	11.7	$= 0.19$ ng/cm ³
	10.7	
	11.04	

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PURE CESIUM STANDARDS
ISOTOPE DILUTION MEASUREMENTS

<u>Calculated</u>	<u>Measured</u>	<u>Relative Error</u>
0 ppb	0 ppb	0.0%
9,790	9,670	-1.2%
9,790	10,120	+3.3%
97,900	95,000	-3.0%

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CONTAMINANTS

<u>Material</u>	<u>Concentration</u>	<u>Source</u>
Cesium	7 ppm	Global
Barium	250 ppm	Global
Alkalis	0 - 5 M	Sample
Aluminum	0 - 0.5 M	Sample
Organics	Varies	Sample

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Cs CONTAMINATION CONTROL

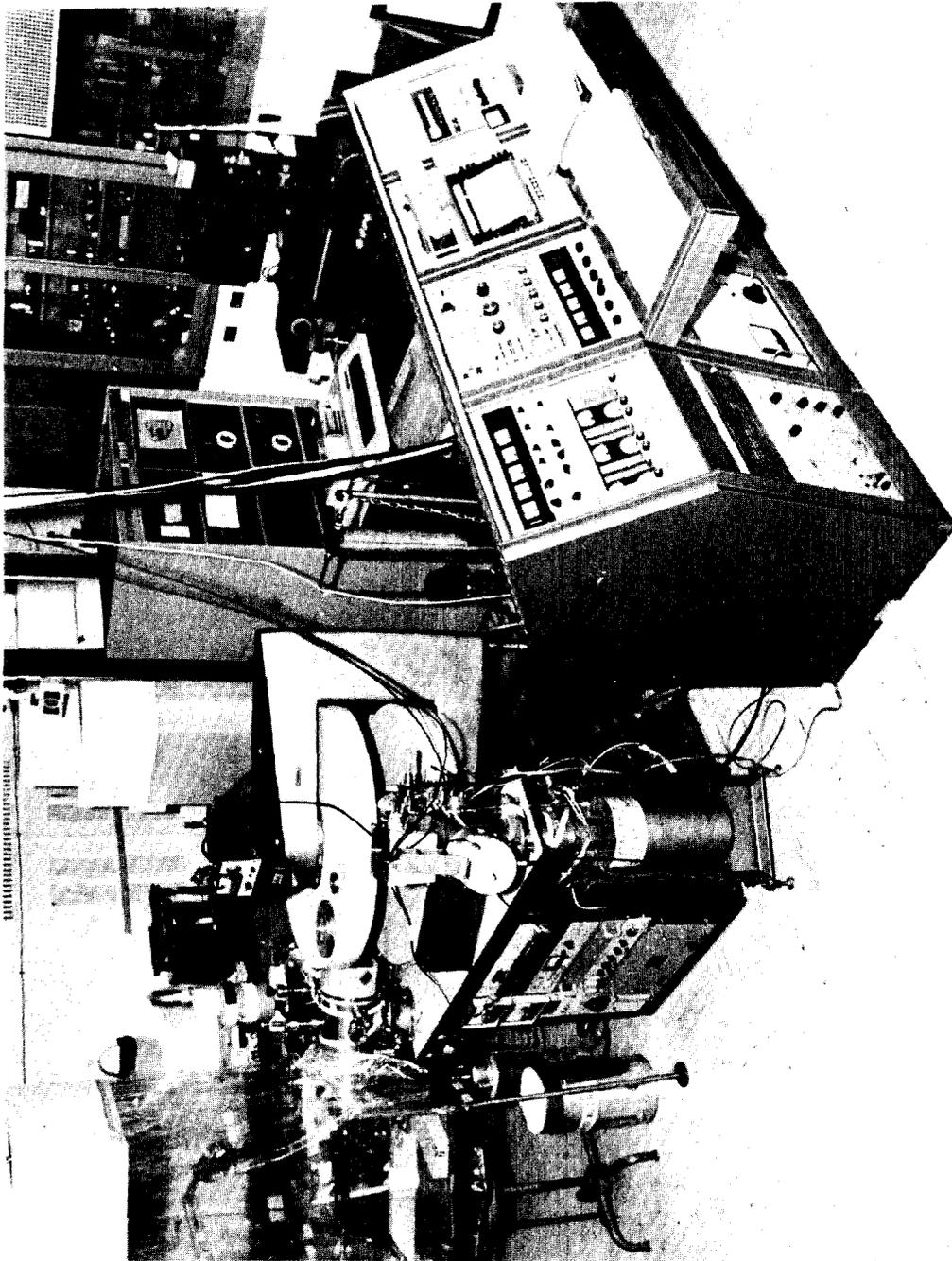
Pilot Plant

Sample points in glove box
Pre-rinsed plastic sample bottles

Laboratory

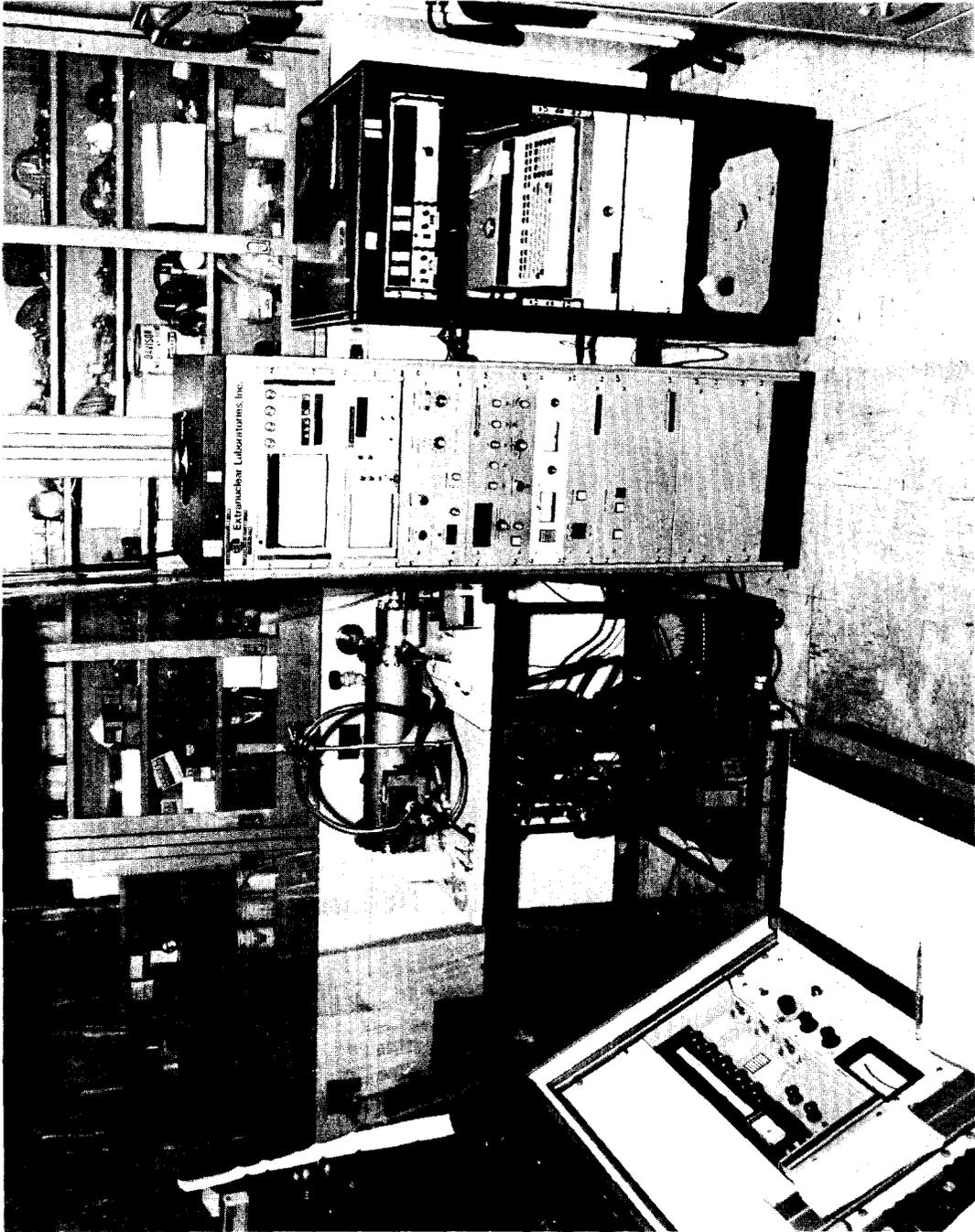
Reagents by sub-boiling distillation
New plastic pipet tips
Pre-rinsed plastic sample vials
Downflow clean air work zones
Degassed filaments

13

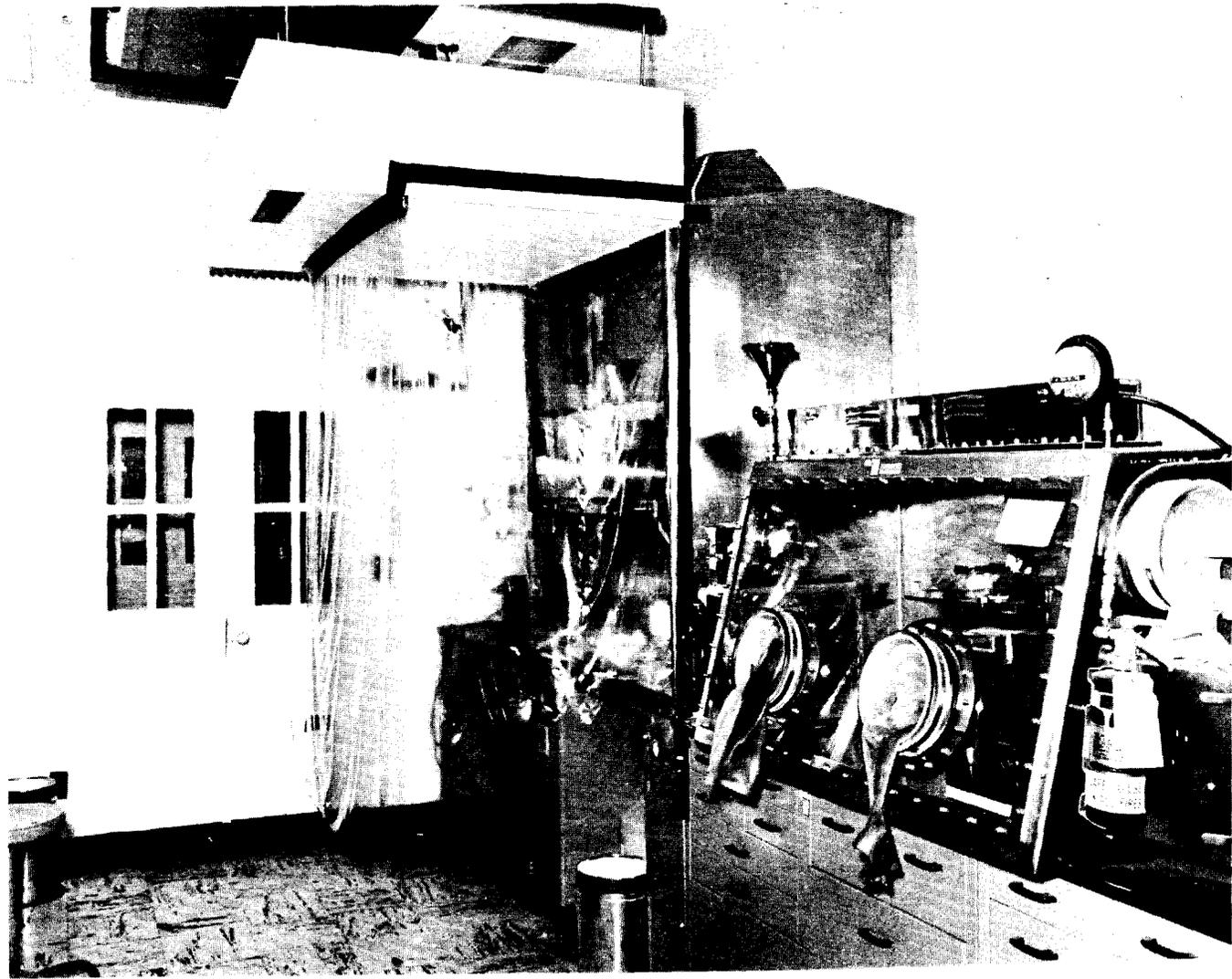


AVCO Mass Spectrometer

14



Extranuclear Quadrupole Mass Spectrometer



Clean Air Module and Radioactive Hood

16



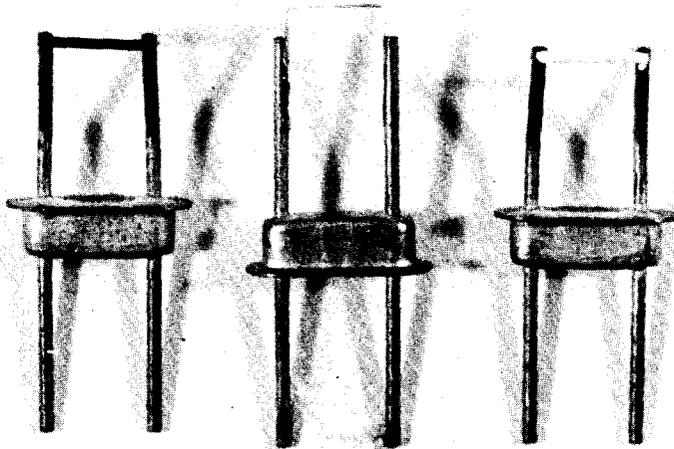
2' x 2' Clean Air Hoods

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CESIUM BLANK

<u>Operation</u>	<u>Cesium Pickup per cm³</u>
Direct Spiking	<0.5 ng
Simple Dilution	3 - 10 ng
Ion Exchange Procedure	20 - >100 ng

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Sample Filaments

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TECHNIQUE FOR DIRECT IDMS DETERMINATION
OF CESIUM IN WASTE SUPERNATE

10 mm³ Sample + 10 mm³ Spike

Use Triple Filament Assembly

Load 5 mm³ on Each Sample Filament

Dry Sample and Load into M.S.

Preheat Sample for 20 Minutes

Distill Cesium Slowly to Ionizing Filament

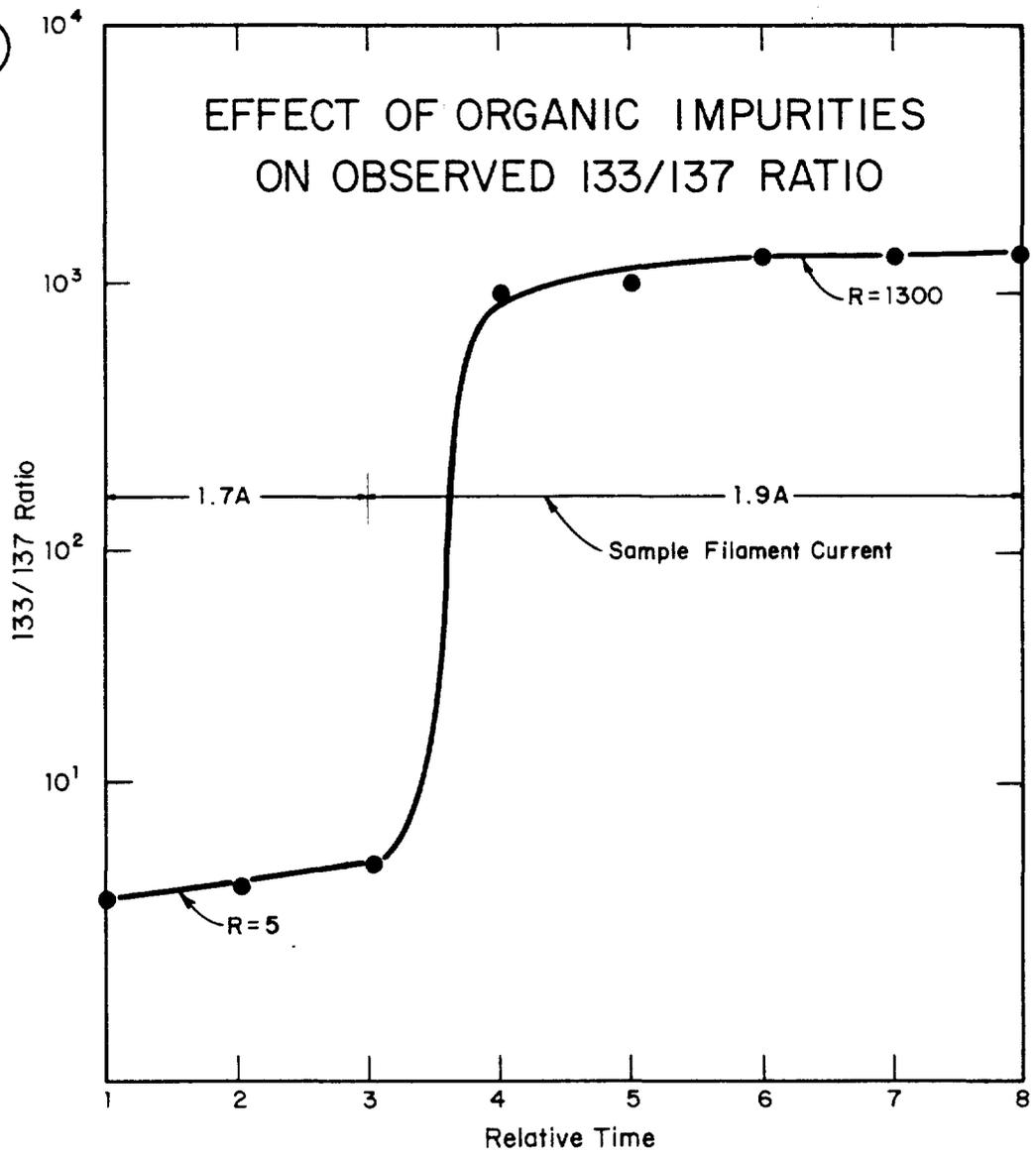
Measure 133/137 Ratio

20

SPECTRAL INTERFERENCES

- Barium
- monitor 136 and 138
 - control filament temperature
 - correct 137, if necessary
- Organics
- monitor mass 140
 - monitor 136/138 ratio
 - monitor 133/137 ratio
 - run until 133/137 maximum value

(21)



(22)

THERMAL IONIZATION MASS SPECTROMETERS

	<u>AVCO</u> <u>35 cm Radius</u>	<u>Extranuclear</u> <u>Quadrupole</u>
Sample Size	2 pg	20 pg
Dynamic Range	$>10^4:1$	$\sim 10^3:1$
Sample Rate	5-6/8 hr	6-10/8 hr
Precision, 95% C.L. (Pure 2.8 ng/cm ³ Cs)	± 0.2 ng/cm ³	± 0.4 ng/cm ³
Output	Ratio Data	Complete Analysis
Samples-to-Date	1200	100

(23)

SUMMARY OF RESULTS

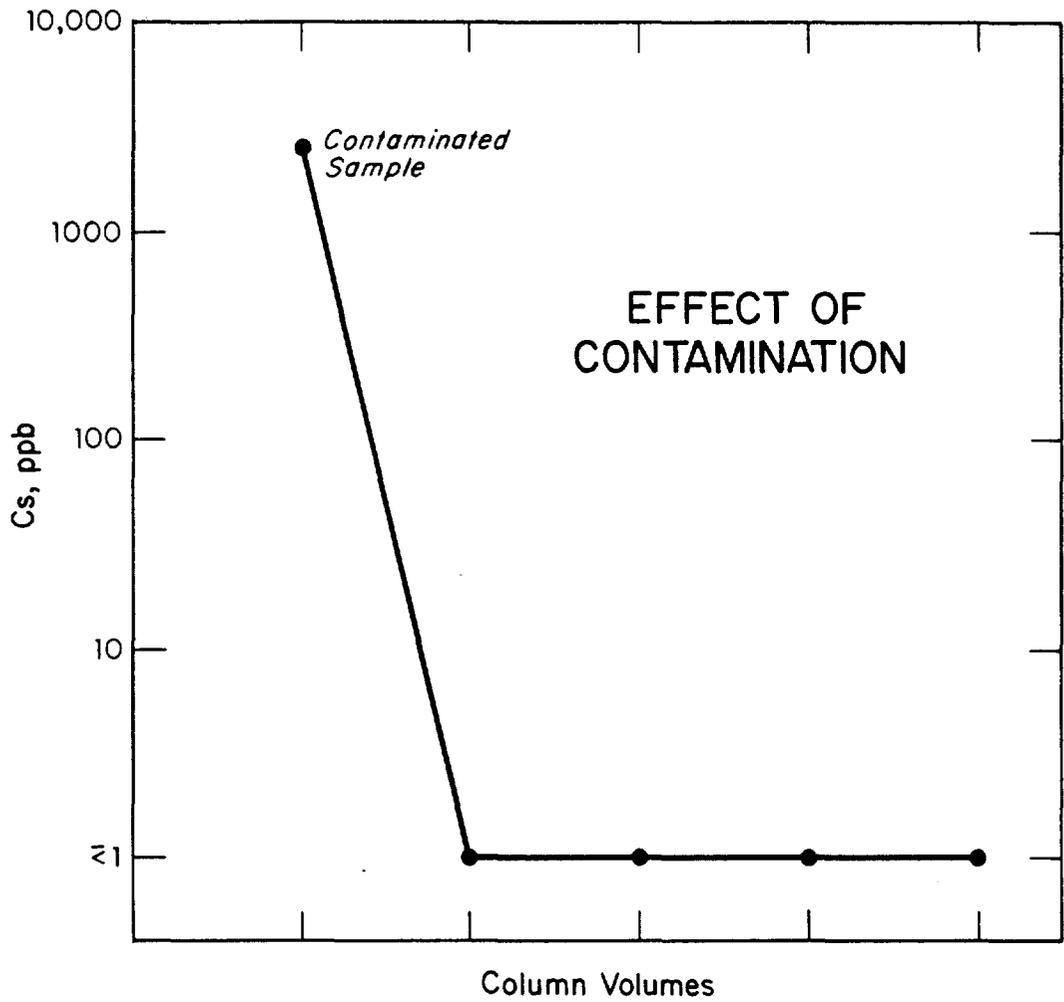
COLUMN 2 EFFLUENT

Expected Cesium Concentration	<1 ng/cm ³
Measured Concentration Average of 22 Samples	0.7 ± 0.8 ppb (95% C.L.)

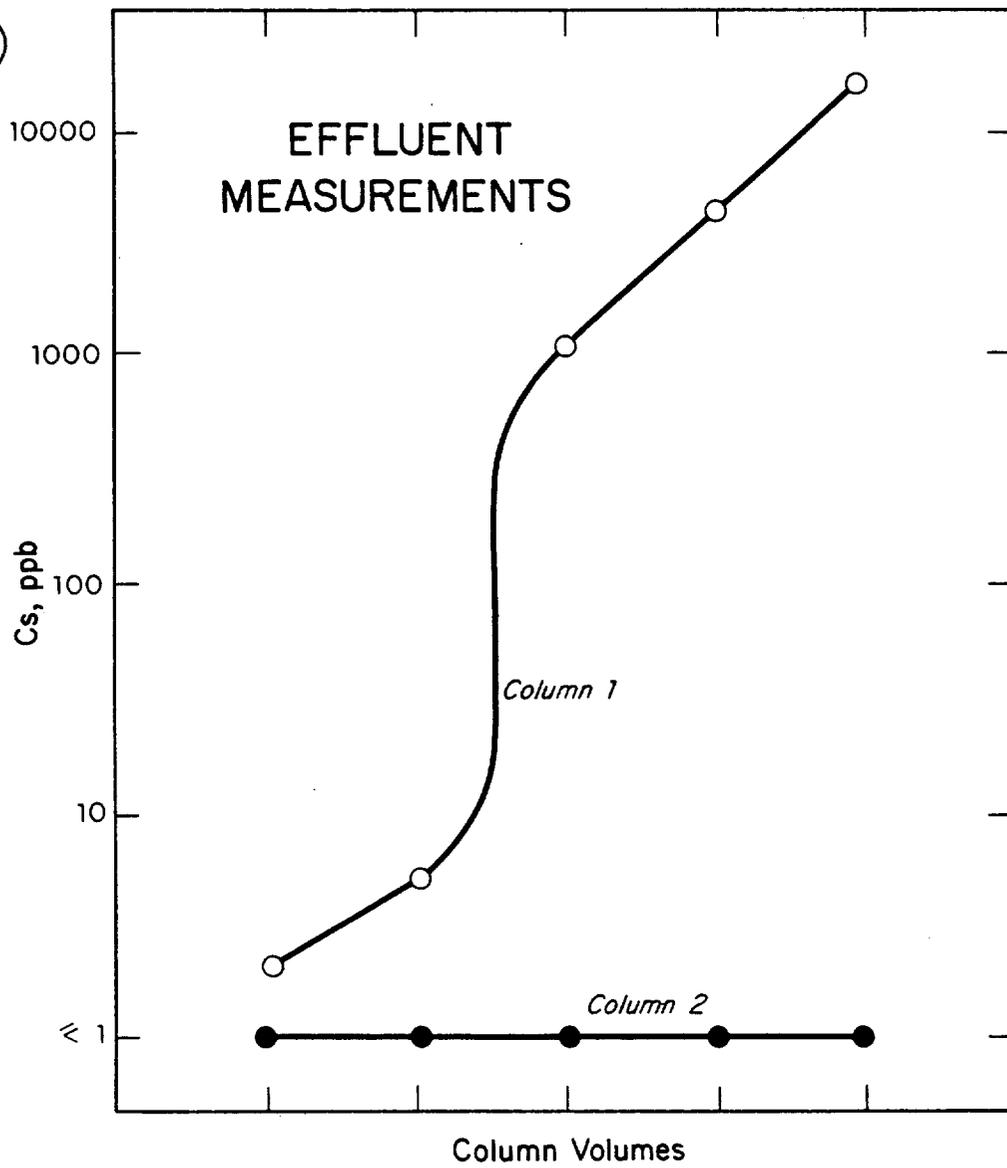
5 DUPLICATE SAMPLES

Cesium Concentration Range	2,000 to 60,000 ng/cm ³
Average Relative Difference	$\pm 30\%$ (95% C.L.)

(24)



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DL1000-0307-92-112
N00-64-08