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A SIMPLIFIED METHOD FOR THE PREPARATION OF MICRO SAMPLES FOR THE SIMULTANEOUS ISOTOPIC ANALYSIS OF URANIUM AND PLUTONIUM

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ABSTRACT

In this simplified technique a basic anion resin is employed to selectively adsorb plutonium and uranium from 8 M HNO_3 solutions containing dissolved spent reactor fuels. After a few beads of the resin are equilibrated with the solution, a single bead is used for establishing the isotopic composition of plutonium and uranium. The resin bead separation essentially removes all possible isobaric interference from such elements as americium and curium and at the same time eliminates most fission products contamination in the mass spectrometer. Small aliquots of dissolver solution that contain 10^{-5} g of U and 10^{-8} g of Pu are adequate for preparing about ten resin beads. By employing a single focusing, tandem magnet type mass spectrometer, equipped with pulse counting for ion detection, simultaneous plutonium and uranium assays are obtained. The quantity of each element per bead may be as low as 10^{-9} to 10^{-10} g. The carburized bead, which forms as the filament is heated, acts as a reducing point source and emits a predominance of metallic ions as compared to oxide ion emission from direct solution loadings. In addition to isotopic abundance, the technique of isotope dilution can be coupled with the ion exchange bead separation and used effectively for measuring the total quantity of U and Pu. The technique possesses many advantages such as: reduced radiation hazards from the infinitely smaller samples, thus less shielding and transport cost for sample handling; greatly simplified chemical preparations that eliminate fission products and actinide isobaric interferences; and the minor isotopes are more precisely established.

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INTRODUCTION

The need to analyze isotopically very small samples of plutonium and uranium in dissolver solutions of spent reactor fuels prompted an investigation into the possibility of using anion resins for the separation of both elements and direct loading of a single resin bead onto a mass spectrometer filament. This approach permits analysis of Pu free from isobaric interferences from americium and curium since these elements do not adsorb on anion resin from 7-8 M HNO_3 solutions. Pu and U have been analyzed in this laboratory for some time from a direct loading of a dissolver solution, but only the 239, 240, and 242 isotopes were clear of interferences in the Pu analysis; isotopic U analysis, however, could be done from such solutions without serious problems. Direct loadings of dissolver solution are troublesome due to the high concentration of salts and fission products loaded with the U and Pu. Frequently using direct loading of solution, the isotopic measurement was made on the PuO_2^+ ions because it was difficult to introduce enough reducing agent (in our system, benzene vapor) to obtain metal ion emission. A discussion of the reduction methods used for improving the metal ion emission is given by Arden and Gale.[1]

Many investigations of anion exchange resin separations of plutonium from various ions have been reported.[2,3] The method chosen for this work involves the use of Dowex 1-X2 anion resin in a solution of 7-8 M HNO_3; under these conditions, Pu and U have distribution coefficients of 10^4 and 10^1, respectively. This favorable Pu distribution coupled with the fact that Pu/U ratio in spent reactor dissolver solutions is about 10^{-2} makes a desirable situation for Pu and U for a simultaneous determination. An equilibration of resin with 7-8 M HNO_3 acid solution of the dissolver solution enhances the Pu concentration in relation to the uranium. This technique possesses many obvious advantages, such as:

1. Small samples may be handled and shipped without heavy shielding, thus reducing shipping costs.
2. Simple chemical treatment reduces separations costs.
3. Metal ion signals are enhanced by orders of magnitude from point source, thus more precise data are obtained.
4. Minor isotopes needed for "fingerprint" safeguards assessment are more precisely established.
5. Contamination is less likely from the minor sample treatment.
6. Contamination of the instrument with fission products is virtually eliminated.
7. The americium and curium do not adsorb, thus eliminating these interferences in the analysis.

EXPERIMENTAL PROCEDURE

Acceptance by many investigators of anion resin for the adsorption of anionic complexes led to the selection of Dowex-1 as the adsorbing medium for this investigation. Analytical reagent grade Dowex-1, 2% cross-linked, 100-200 mesh resin converted to the nitrate form and equilibrated with 8 M HNO_3 provides a resin which has the desired adsorption characteristics for Pu and U. An aliquot of dissolver solution containing appropriate concentrations of uranium and plutonium is pipetted into a small centrifuge cone containing several prepared resin beads. Dissolver solutions not at 8 M HNO_3 are adjusted to this molarity with distilled 16 M HNO_3. The resin beads are allowed to equilibrate in 0.1-0.2 ml of this solution for 24-48 hours, which is enough time for the beads to adsorb both U and Pu in sufficient amounts to allow simultaneous mass spectrometric analysis of each element.

A single bead is taken from solution by employing a small glass loop (Fig. 1) that surrounds the resin bead. This allows one to remove a bead from the solution for transference to a mass spectrometer filament. This procedure is not difficult, especially with the aid of a stereomicroscope. When the bead is removed from the cone, excess solution remaining with the bead is removed by touching the end of the loop to a clean, adsorbing tissue. The bead is then transferred to a rhenium V-type filament (Fig. 2) using a tungsten needle by touching the bead to the filament. The bead loaded onto the filament is shown in Fig. 2 inset. Several techniques have been tried to insure bead retention while handling and inserting the loaded filament into the mass spectrometer. Crimping the filament together has been found to be the most satisfactory method in terms of sample integrity and bead retention; collodion and other glueing agents have been satisfactorily tested.

The ORNL mass spectrometer (Fig. 3) used in this investigation is of the single-focusing tandem magnet type described previously.[4-6] Ions are detected by a secondary electron multiplier behind the receiver slit. The pulses which result from ions hitting the first dynode are amplified and counted. The instrument has 30-cm radius and 90° deflection in each magnet which gives a spectrum that is very clean because of the reduction of scattered ions (abundance sensitivity of 10^6). Only zone-refined rhenium is used for making the single "V" filaments. The sample handling device which permits mounting and installing five or six loaded "V" filaments at once has been described by Christie and Cameron.[7]

First, Pu is isotopically analyzed at the lowest possible filament temperature which will give reliable results. The temperature, usually between 1400°-1500°C, should never exceed 1500°C. Above 1500°C, U^+ emission becomes significant and will add to the observed ^{238}Pu signal. After completing the Pu analysis, the temperature should be gradually raised to 1600°-1700°C to burn off the Pu so that ^{238}Pu interference is eliminated in the subsequent uranium analysis. When ^{238}Pu emission becomes insignificant, the U is analyzed by increasing the filament temperature (1750°-1850°) to the optimum emission range for U$^+$ ions.

EXPERIMENTAL RESULTS AND DISCUSSION

When analyzing spent reactor fuel samples, the amount of Pu loaded per bead for isotopic analysis was unknown; however, good analyses were achieved from aliquots containing 30 ng Pu and equilibrated with six to ten resin beads. Assuming 100% loading efficiency, each bead would contain from 3-5 ng Pu. In order to establish more precisely the amount on each bead and also determine the minimum amount that could be analyzed, controlled experiments were conducted. Graded standard solutions of Pu were used to determine the resin loading efficiency over a concentration range of 10^4. From each experiment, one bead was removed for isotopic analysis and another for measuring by α-counting the Pu adsorption efficiency. The efficiency ranged from 30-60% over the concentration range of 0.1 to 100 ng Pu.

The minimum sample loaded on a bead that will give reliable data on all isotopes is about 0.5 ng; the results of this experiment are tabulated in Table 1. The U-238 contaminant from the filament and/or reagents start affecting the small ^{238}Pu peak. Below 0.05 ng Pu, the signals are too low to obtain worthwhile data on any isotopes except possibly 239 and 240. The extreme sensitivity enhancement of the ion exchange bead-pulse counting mass spectrometry technique is indicated by the isotopic values for ^{239}Pu and ^{240}Pu from the bead containing only 0.003 ng Pu.

The ability to measure sequentially the isotopic composition of Pu and U depends primarily upon the initial U/Pu ratio. The effect of various initial U/Pu ratios was studied to determine the ratios that would give reliable analysis from a single bead loading. Experimental evidence indicates that U/Pu ratios of 100 or larger are satisfactory for the isotopic determination of both elements, but, however, when the U/Pu ratio is 10 or less, only Pu isotopic values are measurable.

In order to evaluate the remote possible mass discrimination effect of the ion exchange resin bead, NBS uranium and plutonium samples were analyzed by the bead technique. The isotopic data for U (SRM U-015) and Pu (SRM-947) are summarized in Tables 2 and 3, respectively. The comparisons for all isotopes fall within the 95% confidence limits of the measurements; thus, there is not any observable mass discrimination contribution in the ion exchange chemical purification. In Table III the Pu values were corrected to 13 October 1971; a $t_{1/2}$ of 14.3Y was used for ^{241}Pu. The precision and accuracy by which the minor isotopes are measured on these reference standards is indicative of the capability of the two-stage ORNL type mass spectrometer.

A correction for ^{238}U contamination in the ^{238}Pu mass position can be made by scanning the ^{235}U position while analyzing Pu and correcting the ^{238}Pu for the appropriate amount of ^{238}U after determining the isotopic 238/235 ratio from the uranium analysis.

$$^{238}Pu_{corrected} = {}^{238}Pu - \left({}^{235}U \cdot \frac{^{238}U}{^{235}U}\right)$$

The effectiveness of this correction was determined by isotopically measuring the 238/239 Pu ratio of a typical dissolver solution after chemically separating the Pu using the thenolytrifluoroacetone (TTA) extraction method.[8] A ratio of 0.01156 compares very well with the resin bead value of 0.01158. To make such a correction, it is necessary that the background of the counting system be exceedingly low; i.e., 1-2 counts/min.

The correction can only be made practical on high burn-up fuel where the Pu-238/239 ratio is >0.01 and the 238/235 ratio is <50. If the desired analysis requires that a reliable ^{238}Pu measurement be made and the ^{238}U correction method is impractical, uranium can be removed from the bead by washing with dilute (up to 3 M) nitric acid.

As a further utility test of the resin bead technique for low levels of Pu, the isotope dilution technique was used to analyze Pu concentrations below 10^{-12} g levels. A highly enriched ^{242}Pu spike was equilibrated with the Pu in the sample prior to the ion exchange bead purification. The results summarized in Table IV are compared to the values obtained by α-spectrometry. The agreement is considered excellent for such low Pu levels. The isotope dilution mass spectrometric technique with the resin bead offers more safeguarding information at lower Pu concentrations than does α-spectrometry.

The simultaneous method for Pu and U has been used on spent reactor fuel samples in this laboratory for over one year. Some typical routine results from dissolver solutions are shown in Table V. Plutonium isotopic analyses were done by the resin bead method, and for comparison purposes after chemical separation using TTA. Uranium isotopic analyses were also made on the same bead loading following the plutonium analyses. The comparison shows an apparent bias between the two methods; in all the results (Table V), the 241 and 242 isotopes are higher by the TTA method than by resin bead. Since on the average 90 percent of the difference between the methods is in the 241 isotope, the source of the bias is apparently due to the poorer decontamination of americium by TTA. With the resin bead technique, on the other hand, tests have shown that ^{241}Am interference on ^{241}Pu is negligible.

Resin beads have been stored as archive samples for a period of one year and still are useful for establishing both the U and Pu isotopic values. Radiation damage to the resin bead has not been observed.

CONCLUSIONS

Results from these experiments indicate that reliable isotopic analysis of plutonium and uranium in spent reactor fuels can be done with minimal chemistry and sample handling on very small samples. An aliquot of a typical dissolver solution containing approximately 10 μg U, 50 ng Pu, and 10 μCi of fission products would be sufficient sample for making the determinations. The precision of an analysis expressed as relative standard deviation is <1% on major isotopes. The assay of ^{238}Pu, if in the range of 0.1 at.%, can be measured by the simplified resin bead technique. Ways of improving the ^{238}Pu assay are demonstrated. The resin bead technique coupled with isotope dilution is very useful for very low-level Pu measurements.

The main advantages of this simplified method are:

1. Decreased analytical laboratory separation costs. For example, field inspectors could adapt the separations technique and mail 3 or 4 beads to the laboratory for mass analysis.

2. Reduction of radiation hazards in handling small samples in an unshielded laboratory.

3. Reduction of sample transportation costs in the Safeguards programs. Decontamination factors for fission products are high; Am, Cm and Cf are completely separated.

4. Provides a second technique for obtaining reliable ^{238}Pu values.

The lessening of radiation hazard in shipping and the resulting saving in transportation costs probably are the most important advantages. This aspect of the method would be very important in Safeguards analyses whether on a national or international basis.

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REFERENCES

[1] Arden, J. W. and Gale, N. H., "Separation of Trace Amounts of Uranium and Thorium and Their Determination by Mass Spectrometric Isotope Dilution," Anal. Chem., Vol. 46, No. 6, May 1974, 687-691.

[2] Buchanan, R. F., Faris, J. P., Orlandini, K. A., and Hughes, J. P., U. S. At. Energy Comm. Rept. TID-7560 (1958).

[3] Kressin, I. K. and Waterbury, G. R., "The Quantitative Separation of Plutonium From Various Ions by Anion Exchange," Anal. Chem. 34 (12), 1598 (1962).

[4] White, F. A. and Collins, T. L., "A Two-Stage Magnetic Analyzer for Isotopic Ratio Determinations of 10^4 to 10^1 or Greater," Appl. Spectry., 8(4), 169 (1954).

[5] Dietz, L. A., Pachucki, C. F., Sheffield, J. C., Hance, A. B., and Hanrohan, L. R., "Further Development of the Two-Stage Mass Spectrometer for Isotopic Analysis of Uranium" Anal. Chem., 32, 1276 (1960).

[6] Cameron, A. E., Christie, W. H., McKown, H. S., Rainey, W. T., Jr., and Smith, D. H., "Analytical Mass Spectrometry at Oak Ridge National Laboratory," ORNL-4643 (1971).

[7] Christie, W. H. and Cameron, A. E., Rev. Sci. Instrum., 37, 336 (1966).

[8] Moore, F. L. and Hudgens, J. E., Jr., "Separation and Determination of Plutonium by Liquid-Liquid Extraction," Anal. Chem., 29, 1767 (1957).

TABLES

TABLE I. PLUTONIUM ISOTOPIC ANALYSIS AT VARIOUS CONCENTRATIONS

Pu, ng/bead	Atom Percent 238	239	240	241	242
0.003	(.023)	94.0	5.64	0.31	0.027
0.05	0.0124	94.150	5.556	0.261	0.0182
0.6	0.0095	94.152	5.563	0.257	0.0173
3.	0.0095	94.149	5.565	0.258	0.0179
10 ng Pu Std.	0.0096	94.136	5.572	0.265	0.0175

TABLE II. ISOTOPIC ANALYSIS OF SRM U-015 STD. BY RESIN BEAD METHOD

	Atom Percent-Date Analyzed (7-8-75)			
	234	235	236	238
1	0.00846	1.537	0.0163	98.438
2	0.00856	1.548	0.0165	98.428
3	0.00851	1.540	0.0165	98.435
4	0.00865	1.526	0.0164	98.449
ORNL Avg.	0.00854	1.538	0.0164	98.437
S. D.	0.00008	0.009	0.0001	0.009
NBS Certified Value	0.00850	1.5323	0.0164	98.443

TABLE III. ISOTOPIC ANALYSIS OF SRM-947 STD. BY RESIN BEAD METHOD

	Atom Percent	Date Analyzed	(7-1-75)		
	238	239	240	241	242
1	0.292	76.303	18.412	3.808	1.185
2	0.294	76.281	18.421	3.823	1.181
3	0.291	76.321	18.440	3.784	1.178
4	0.293	76.264	18.421	3.818	1.187
Avg.	0.292	76.293	18.424	3.808	1.183
S. D.	0.001	0.025	0.012	0.017	0.004
Corr. to 10/13/71 - ORNL Value	0.298	75.717	18.290	4.521	1.174
10/13/71 - NBS Value	0.296	75.696	18.288	4.540	1.180
95% C. L.	±0.006	±0.022	±0.022	±0.006	±0.004

TABLE IV. LOW LEVEL PU ANALYSIS - COMPARISON WITH α SPECTROMETRY

Sample No.	Total Pu* gram	dis/min	
		Mass Spec	α-Spec
MS-1	1.5×10^{-11}	2.43	2.44
MS-2	1.6×10^{-12}	0.258	0.244
MS-3	5.3×10^{-13}	0.087	0.08

*Measured by isotope dilution mass spectrometry after adsorption on bead.

TABLE V. PLUTONIUM ISOTOPIC COMPOSITION COMPARISON - RESIN BEAD vs TTA EXTRACTION

Plutonium Isotopic Analysis, at.%					Separation Method
238	239	240	241	242	
0.628	68.082	21.254	7.893	2.143	RB
0.626	67.824	21.245	8.137	2.168	TTA
0.826	70.799	17.198	9.333	1.844	RB
0.822	70.569	17.328	9.401	1.880	TTA
0.635	68.059	21.257	7.883	2.166	RB
0.637	67.745	21.282	8.162	2.174	TTA
0.815	71.319	17.042	9.067	1.757	RB
0.814	71.179	17.065	9.176	1.766	TTA

RB = DOWEX 1-X2 Anion Resin bead.
TTA = Thenoyltrifluoroacetone extraction.

FIGURES

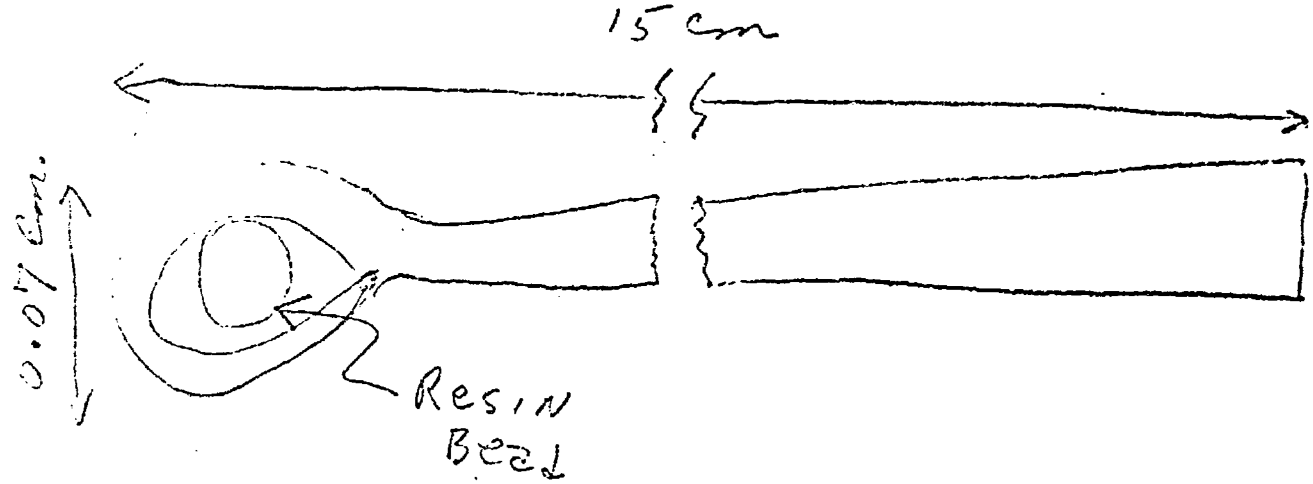

Figure 1. Glass Loop for Retrieving Resin Beads

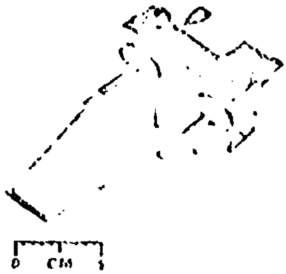

Fig. 2. Mass Spectrometer "V" Shaped Rhenium Filament Loaded With Resin Bead

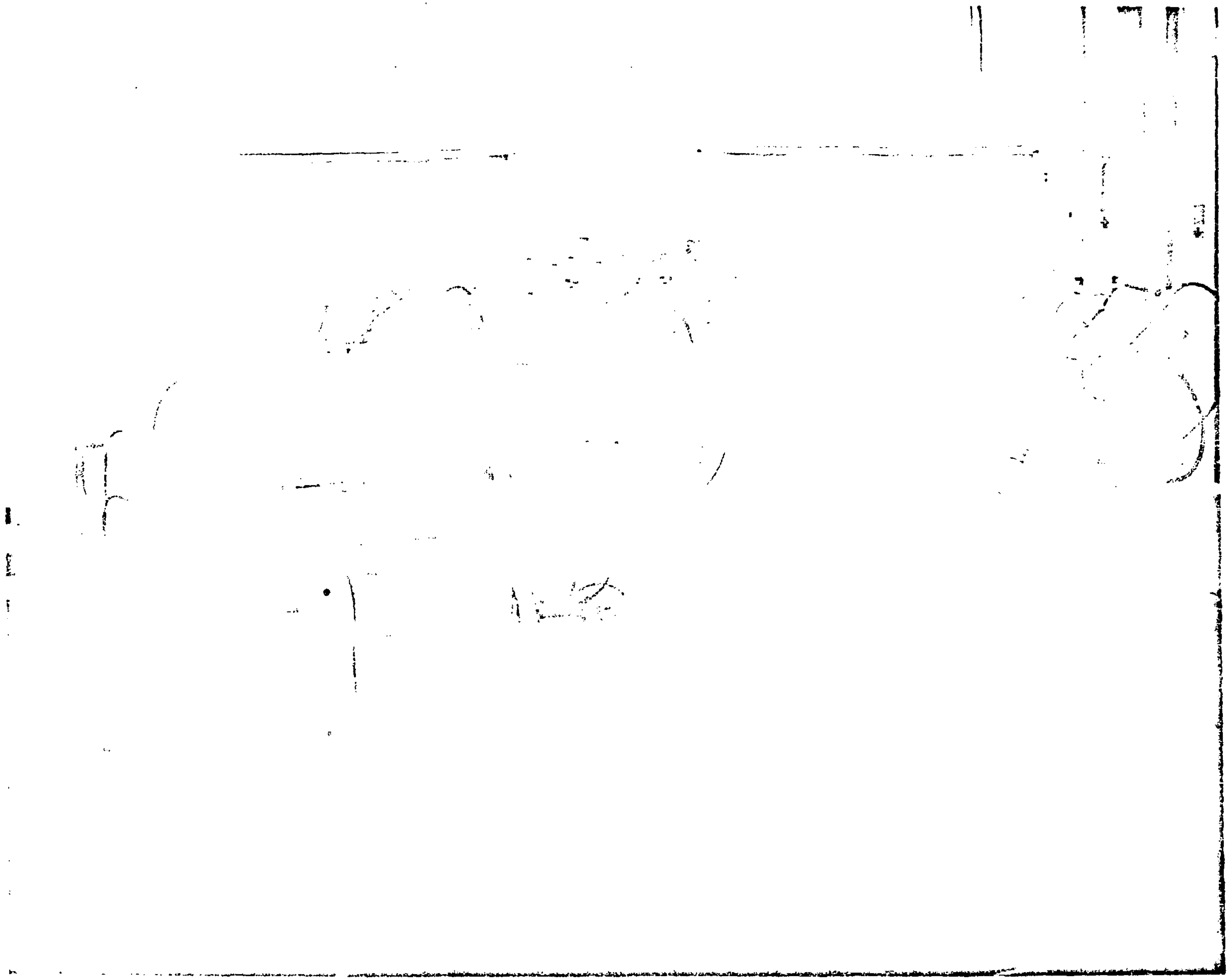

Fig. 3. ORNL Tandem Magnet Mass Spectrometer