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DEVELOPMENT OF RESIN-BEAD ISOTOPE-DILUTION MASS SPECTROMETRIC TECHNIQUES FOR TC-99 ANALYSIS

MASTER

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ABSTRACT

An isotope dilution mass spectrometric method has been developed for the analysis of Tc-99 after isolating it onto anion exchange resin beads. A single resin bead containing Tc-99 and Tc-97 spike is loaded onto a rhenium V-shaped filament for thermal emission mass spectrometry. The application of this technique requires the use of a mass spectrometer of high abundance sensitivity and pulse counting capability for the necessary ion detection sensitivity.

The use of reducing agents to improve metal ion production and increase ionization efficiency of Pu and U samples loaded as solutions onto filaments is an accepted practice in many mass spectrometry laboratories.[1,2] The mechanism for the increased ion emission obtained from a resin bead in comparison to loading samples as solutions probably results from the point source for the ion optics represented by the bead combined with the reducing action supplied by the carbonaceous material of the bead when it is decomposed at about 1000-1200°C during the initial filament heating. This prevents loss of sample as volatile oxides and enhances metal ion emission.

This paper discusses the development of the technique, including the mass spectrometer, choice of filament material, scanning modes, interferences, and present achievable sample sensitivities.

INTRODUCTION

This method is an extension of the resin-bead sample loading technique developed at ORNL primarily for small samples of uranium and plutonium.[3] The resin-bead method was chosen since a very sensitive and specific method is necessary for measuring low specific activity Tc-99 in environmental

samples. The high fission yield (6.3%) of Tc-99 and very long half-life (2.1 x 10^5 y) make this radionuclide potentially hazardous in animal food chain systems.

The usual method of Tc-99 analysis is beta counting, which has a sensitivity limit of about 10 pg (0.2 pCi). Since this is a non-specific method with relatively poor sensitivity, an isotope dilution mass spectrometric method using a spike of Tc-97 has been developed here and at Pacific Northwest Laboratories by Kaye[4] and co-workers. The main difference between the methods is the filament loading technique. In Kaye's method, technetium is loaded on the filament and reduced to the metallic state with H_2, whereas in our technique the technetium is adsorbed onto an anion resin, and a single bead is loaded onto the filament. The ionization efficiency of Tc is approximately 50 times greater loaded on resin beads when compared to loading it as solutions. The limit of detection is 0.1-0.2 picogram and is near the expected limit due to uncertainties caused by hydrocarbon interference and that caused by Mo in the Re filament at the mass 97 position.

Mass Spectrometer

The mass spectrometer used in this work is of the single focusing, tandem magnet type.[5] The design used at ORNL is based on that developed by White and Collins,[6] which utilizes the "C" configuration. The instrument shown in Figure 1, has 30-cm radius and 90° deflection in each magnet, which gives a clean spectrum with high abundance sensitivity. Ions are detected by a secondary electron multiplier behind the receiver slit. The detector used is an RCA type 6810A 14-stage multiplier and has a gain of 10^6 in the pulse-counting mode. Data are stored in a PDP-11 computer for later reduction and processing.

Filaments

Filaments for this work are made from zone-refined rhenium. They are of the V-shaped design and are prebaked in an auxiliary vacuum system for at least 30 minutes at 2000°C to remove impurities and reduce the molybdenum background as much as possible. Measurements have been made to determine the best filament material for use in Tc analyses. We found that of the three metals (Re, W, and Ta) tested, the order of sensitivity for Tc is Re>W>Ta. The sample changer used has been described by Christie and Cameron.[7] It is a "ferris" wheel upon which are mounted six sample filaments. It is driven from outside the vacuum system by a rotary-motion feed-through.

Tc-97 Preparation

Approximately 2 μg of Tc-97 was made by irradiating 25 mg of isotopically enriched ^{96}Ru for 20 days in the High Flux Isotope Reactor at ORNL at a neutron flux of 6 x 10^{14} neutron cm^{-2} sec^{-1}. Half of the target has been chemically processed to recover technetium isotopes and the other half retained for future use. The yield from the processed target was 1.6 μg having the following isotopic composition:

97	98	99
79.642 ± 0.097	20.175 ± 0.100	0.183 ± 0.006

This is sufficient technetium to run several hundred samples using approximately 1 ng per sample. We were surprised to find the high ^{98}Tc and ^{99}Tc content of the product, but the amount of ^{99}Tc in the spike will not affect its usefulness except perhaps in samples containing very low (near 1 picogram) concentrations. Assuming the contribution of the sample to be 20% greater than the ^{99}Tc in the spike, the detection limit would be about 0.2 picogram.

Isotopic Analysis Procedure

Resin beads are loaded onto filaments in a chip of collodion with the aid of two low-powered microscopes: one for removing the bead from the microscope slide on which it is stored, and another for putting the bead in the V-shaped rhenium filament. Loaded filaments are placed in the source region and evacuated to <5 x 10^{-7} torr before analysis.

The resin bead is decomposed in a slow, step-wise manner by applying d.c. current. Usually decomposition is complete at 1000-1200°C and mass scanning is started. The Tc masses at 97 and 99 are scanned, and it is also necessary to scan masses 98 and 100 for correcting the Mo contribution to the ^{97}Tc signal. Mass position 100.5 is scanned to make a correction for electronic noise. Analysis is made at the lowest possible temperature to minimize Mo interference. Data are usually taken at about 1900°C. Peak hopping is used for data accumulation to improve statistics and sensitivity, since this method of data taking eliminates time lost scanning between peaks.

RESULTS AND DISCUSSION

Two significant interferences have been uncovered with mass measurements at 97 and 99 during the course of this work. These are Mo at 97 and hydrocarbons primarily affecting low levels of Tc-99. Ruthenium at mass 99 has been eliminated as a possible interference since it has not been observed in the analysis of blank filaments, chemical blanks, and technetium standards.

The correction for ^{97}Mo can be reliably made if the ^{97}Tc ion signal equals or exceeds the ^{97}Mo ion signal. Normally this ratio is exceeded. Reducing filament length and using initial bake-out before bead loading minimizes the Mo signal. We are now getting average ratios of about 10 for ^{97}Tc/^{97}Mo for 0.5 ng ^{97}Tc standards. For estimating the Mo correction, we use the average obtained from natural ^{96}Mo and ^{100}Mo. A drawing of a Tc spectrum is shown in Figure 2. This shows the spectrum obtained from the combination of the ORNL spike and natural Mo from the rhenium filament.

During the course of this work, hydrocarbon background has been a real problem, especially when trying to achieve the highest sensitivity for ^{99}Tc. It is impossible to correct it by monitoring another mass, since it varies from filament to filament and ratios are not constant. We have looked for the source of the contamination and have not been successful. We find it in blank filaments as well as loaded ones; therefore, we have ruled out the resin bead as the source. Oil diffusion pumps are used for partial evacuation of the source region before turning on the ion pumps, and it was postulated that this could be the source. Liquid nitrogen pumping was added to the source region without any obvious effect. A promising method that we have recently developed is to resolve the hydrocarbon from the metal ion peaks. The hydrocarbon masses are approximately 0.2 amu above the metal ion masses, and with greatly reduced slit widths between the magnets, we can resolve the hydrocarbon and metal peaks as shown in Figure 3. This makes the analyses more difficult for the operator and reduces the signal, but is more than worth the sacrifice of intensity. A comparison of the results obtained on the ORNL-prepared spike using narrow center slits to resolve out hydrocarbons is shown in Table I. A tremendous improvement in precision is noted; also, the lower values for the minor isotopes would be expected since there is no hydrocarbon contribution to them.

Table I

Isotopic Analysis of ORNL Tc-97 Standard

Mass	Atom Percent a	Atom Percent b
97	79.260 ± 0.574	79.642 ± 0.097
98	20.509 ± 0.523	20.175 ± 0.100
99	0.231 ± 0.061	0.183 ± 0.006

a) normal conditions.
b) narrow center slits.

Mixtures of ^{97}Tc and ^{99}Tc have been analyzed to determine the sensitivity and reliability of the method. For this experiment, a graded set of ^{99}Tc standards from 11.6 to 1 x 10^{-4} ng were mixed with a constant amount of ^{97}Tc (∿0.9 ng). The results are shown in Figure 4. Some problems are noted in the low concentrations, but the linearity is quite good down to 10^{-4} ng. This work was done in collaboration with T. J. Anderson at the Savannah River Laboratory. The ^{97}Tc spike used was from his laboratory and does not contain measurable amounts of ^{98}Tc and ^{99}Tc; therefore, the sensitivity is much better than for the ORNL spike discussed earlier.

ACKNOWLEDGMENT

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MODEL DATE

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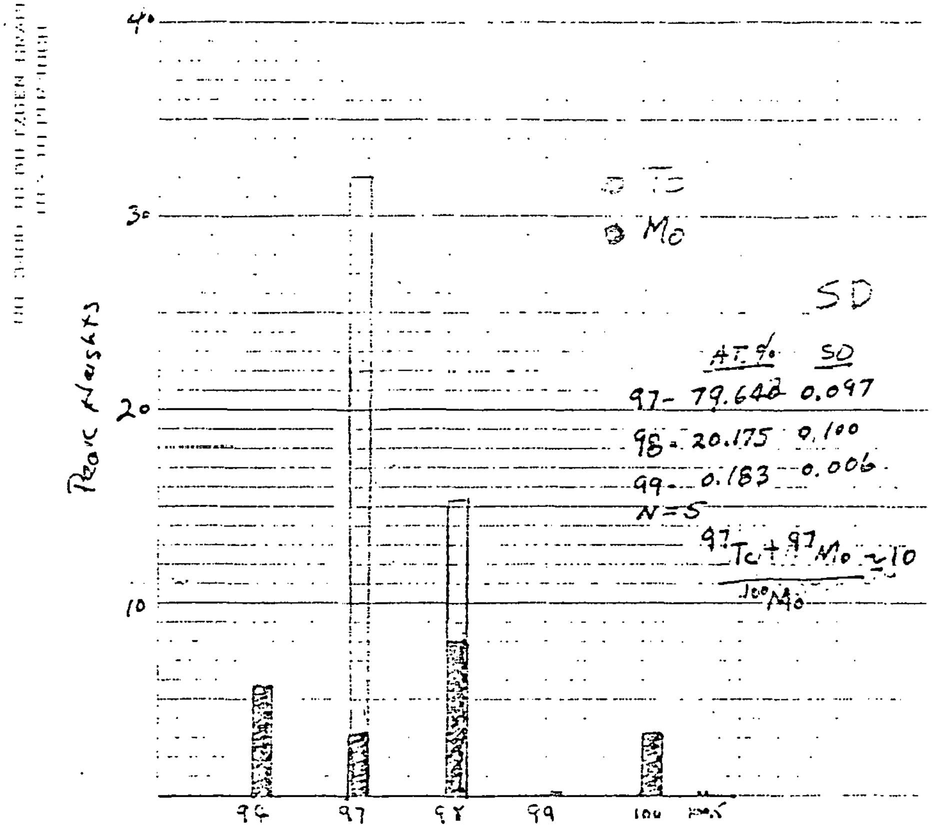


SD

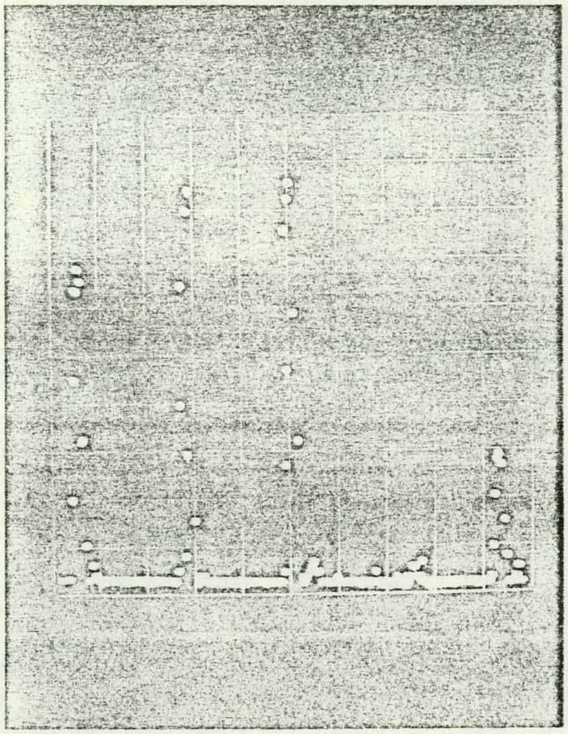
	AT.%	SD
97-	79.642	0.097
98-	20.175	0.100
99-	0.183	0.006

N=5

$\frac{^{97}Tc + ^{97}Mo}{^{100}Mo} \simeq 10$

Tc spectrum

Fig. 2



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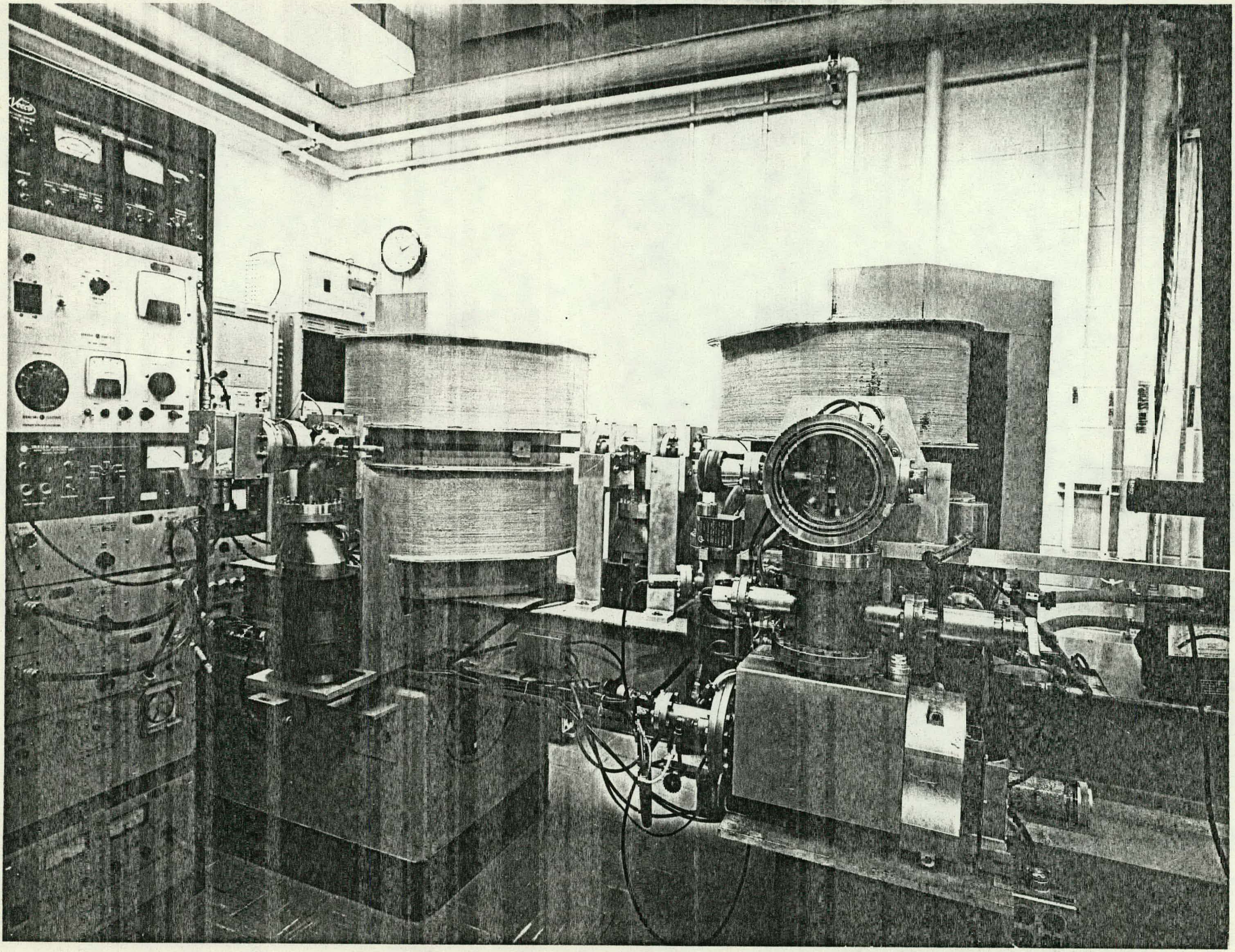
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