ORNL/TM-6563

Single-Stage Mass Spectrometric Analyses of Resin Bead Samples

David H. Smith
R. L. Walker
L. K. Bertram
J. A. Carter

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION · FOR THE DEPARTMENT OF ENERGY

BLANK PAGE

ORNL/TM-6563

Contract No. W-7405-eng-26

PROGRESS REPORT FOR:

Division of Safeguards & Security

Analytical Chemistry Division

SINGLE-STAGE MASS SPECTROMETRIC ANALYSES OF RESIN BEAD SAMPLES

David H. Smith, R. L. Walker, L. K. Bertram,
and J. A. Carter

Date Published: October 1978

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

TABLE OF CONTENTS

SUMMARY

Plutonium and uranium from dissolver solutions loaded on resin beads can be analyzed on single-stage mass spectrometers with little or no degradation of results provided proper care is exercised with regard to sample handling techniques. Additionally, storage of samples on resin beads is feasible for periods at least as long as six months provided the beads are not exposed to residual HNO_3 and air; it is probable that beads will retain their integrity much longer than six months when stored under collodion, but as yet no data to support this contention have been collected.

Conventional or commercial mass spectrometers can readily be adapted to the resin bead technique by installing a pulse-counting detection system. The cost of such conversion will vary depending on whether or not a data acquisition system will be needed. A reasonable estimate is that the cost will be in the neighborhood of $15,000; this figure includes the price of a multi-channel analyzer to serve as a temporary data storage device, but does not include the cost of a computer.

It does not appear that it will be practicable to switch easily back and forth between pulse-counting and current integration modes unless the instrument is provided with a movable Faraday cup. Using the same multiplier in both modes would undoubtedly degrade its performance in each. The requirements of low background counting rates and high gain for pulse counting, and of relatively high signal handling capacity in current integration are mutually incompatible if demanded of the same multiplier.

ABSTRACT

The resin bead sample loading technique has been applied to a conventional single-stage mass spectrometer equipped with pulse counting. Data obtained are comparable to those obtainable from similar instruments using conventional techniques.

INTRODUCTION

Recent restrictions imposed on the shipment of fissile material has caused Safeguards to reassess many of its analytical techniques with a view to minimizing the amount of sample required. Isotopic analysis of uranium and plutonium by mass spectrometry is a key factor in the accountability systems of both the domestic and international safeguards programs. The recently developed resin bead sample loading technique[1,2] has manifold advantages in this context. With this technique, dissolver solutions of Pu, U, and various fission products are adjusted to 8N HNO_3, and a number of Dowex anion resin beads are exposed to them for 1-40 hours. During this time, 0.5 to 1 ng of U and Pu are absorbed by each bead. A single bead constitutes one sample for the mass spectrometer, and Pu and U are analyzed sequentially from it off a single Re filament. Thus, the bead not only serves as a convenient vehicle upon which to introduce samples to the mass spectrometer, but it also serves as its own separating device by isolating Pu and U from all fission and actinide products, except Np, which constitutes neither a health hazard nor an interference in isotopic analyses.

Because of the small amount of material absorbed on the bead, it is necessary that the mass spectrometer be equipped with a pulse counting detection system. Previous work,[1,2] has been confined to this laboratory's multi-stage instruments.[3] The object of this study was to assess the

applicability of the resin bead sample-loading technique to more conventional mass spectrometers by analyzing a number of samples on a single-stage instrument.

EXPERIMENTAL

Instrumental

The mass spectrometer used is of ORNL design,[4] but does not differ in any significant way from several commercially available instruments. It has a 90-degree magnet with a 30-cm central radius of curvature. High vacuum is achieved by ion pumps, with normal operating pressures $<5 \times 10^{-8}$ torr. Figure 1 is a photograph of the instrument, and Fig. 2 is a photograph of its electronic console. A pulse-counting detection system, comprised of an RCA type 6810 electron multiplier as the detector, an ORTEC discriminator, an ORTEC scaler, and an ARL preamplifier, was installed. A sweep control unit similar to one previously developed[5] was also installed. Figure 3 is a block diagram of the system. This system, which operates under the control of Digital Equipment Corporation PDP 11/10 computer, scans the mass range by adjusting the source high voltage. Only peak tops are scanned, and it is possible to sweep each peak top any pre-selectable number of times for each traversal of the entire mass region. Two background positions were swept: one to allow correction for background noise, and the other to allow correction for scatter from the ^{238}U peak. In addition, corrections for contributions to the 238 mass position were made for U (during Pu analyses) and Pu (during U analyses) by monitoring ^{235}U and ^{239}Pu, respectively. Figure 4 is a photograph of the sweep control panel.

The instrument was calibrated by analyzing 15 NBS U-500 isotopic uranium standards. Both dead time and bias correction were calculated from this standard, and the latter was continuously monitored by daily analysis of an NBS U-010 standard. The bias correction was recalculated each day on the basis of the last ten standards analyzed. The dead time was determined to be 30 nsec, and the bias correction ranged 0.26 percent per mass to 0.52 percent per mass. The variation in the latter figure was almost certainly due to aging of the electron multiplier. The average of the $^{235}U/^{238}U$

ORNL-PHOTO 73740

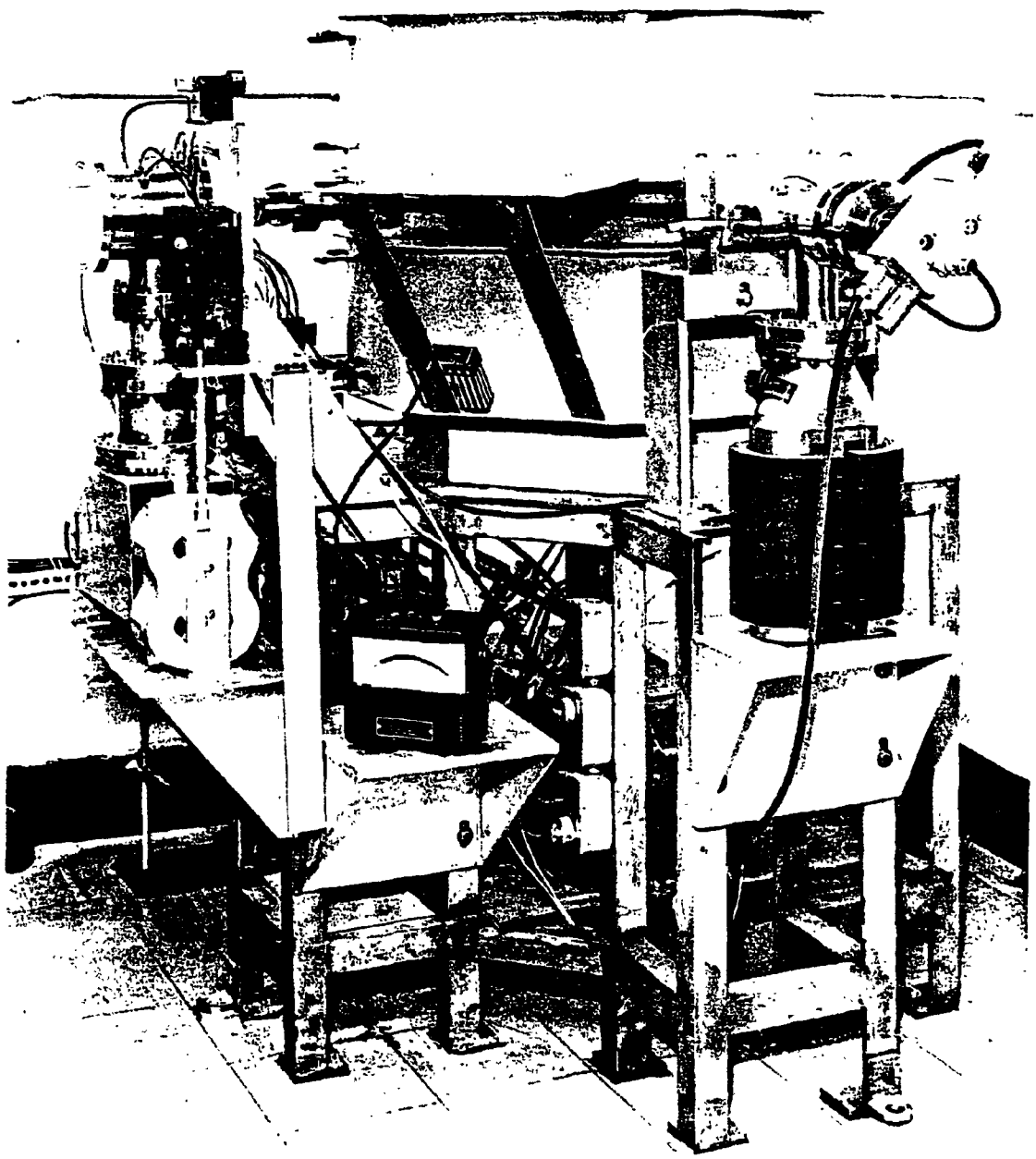

Fig. 1. Photograph of the ORNL Single-Stage Mass Spectrometer

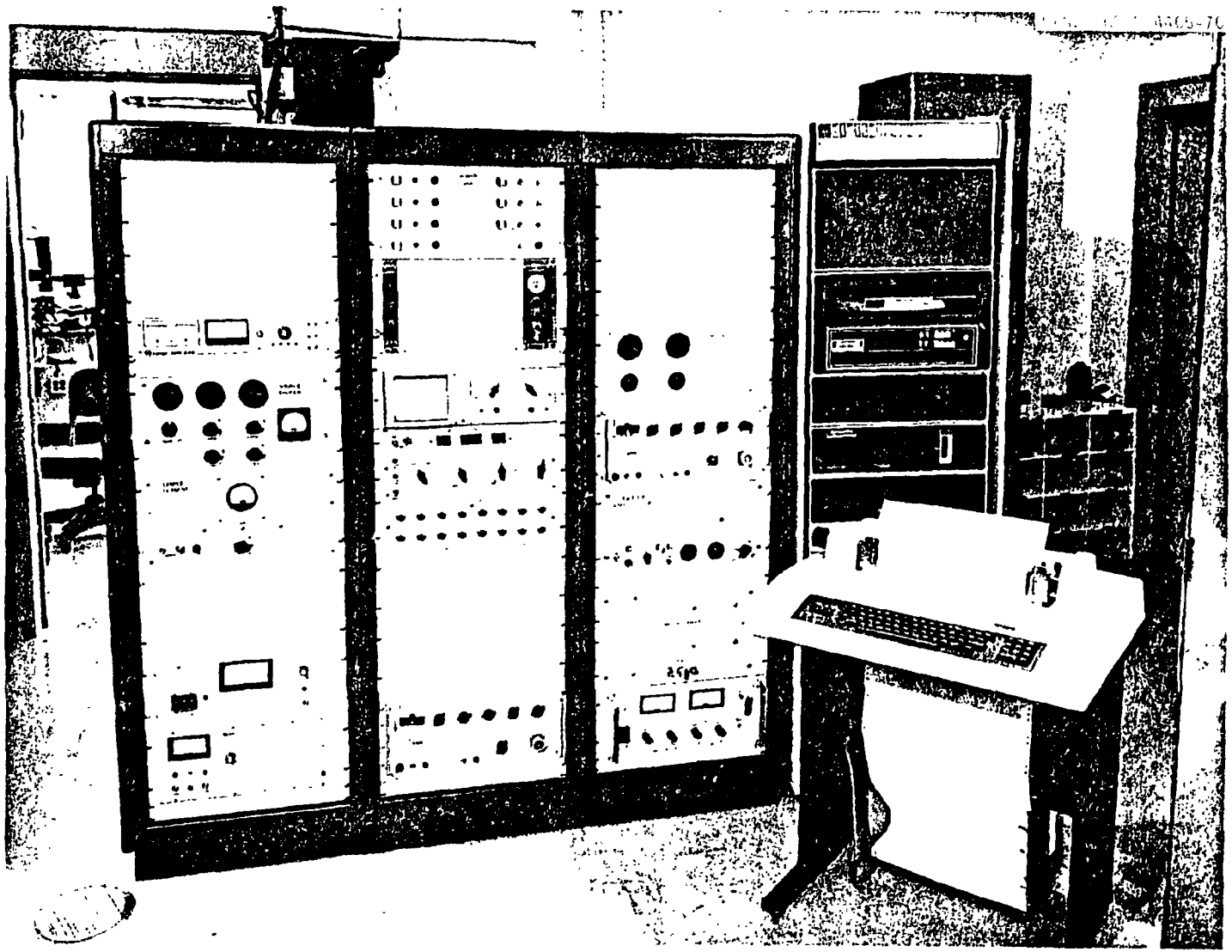

Fig. 2. Photograph of the Electronics Console

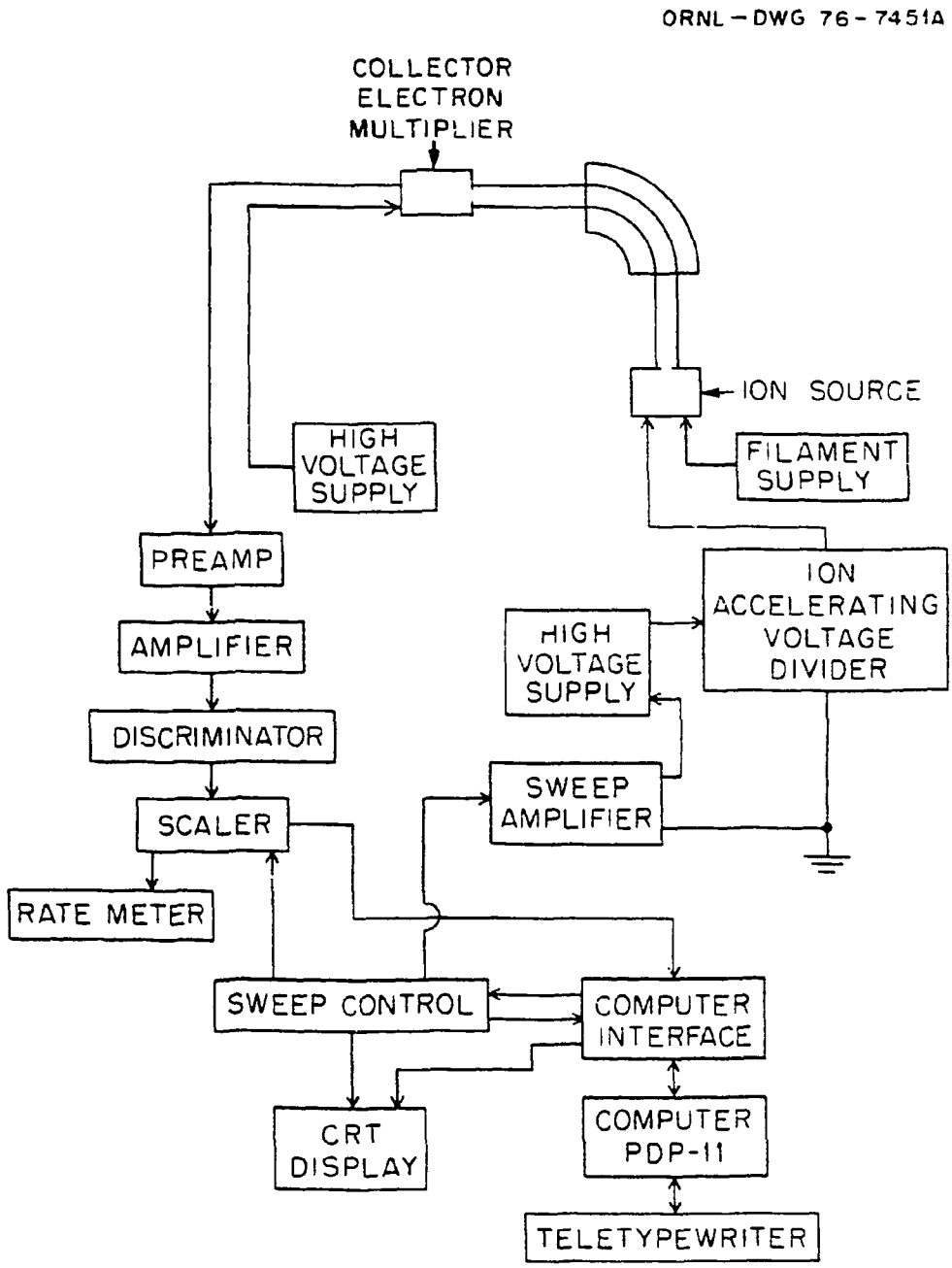

Fig. 3. Schematic Diagram of the Sweep Control/Data System

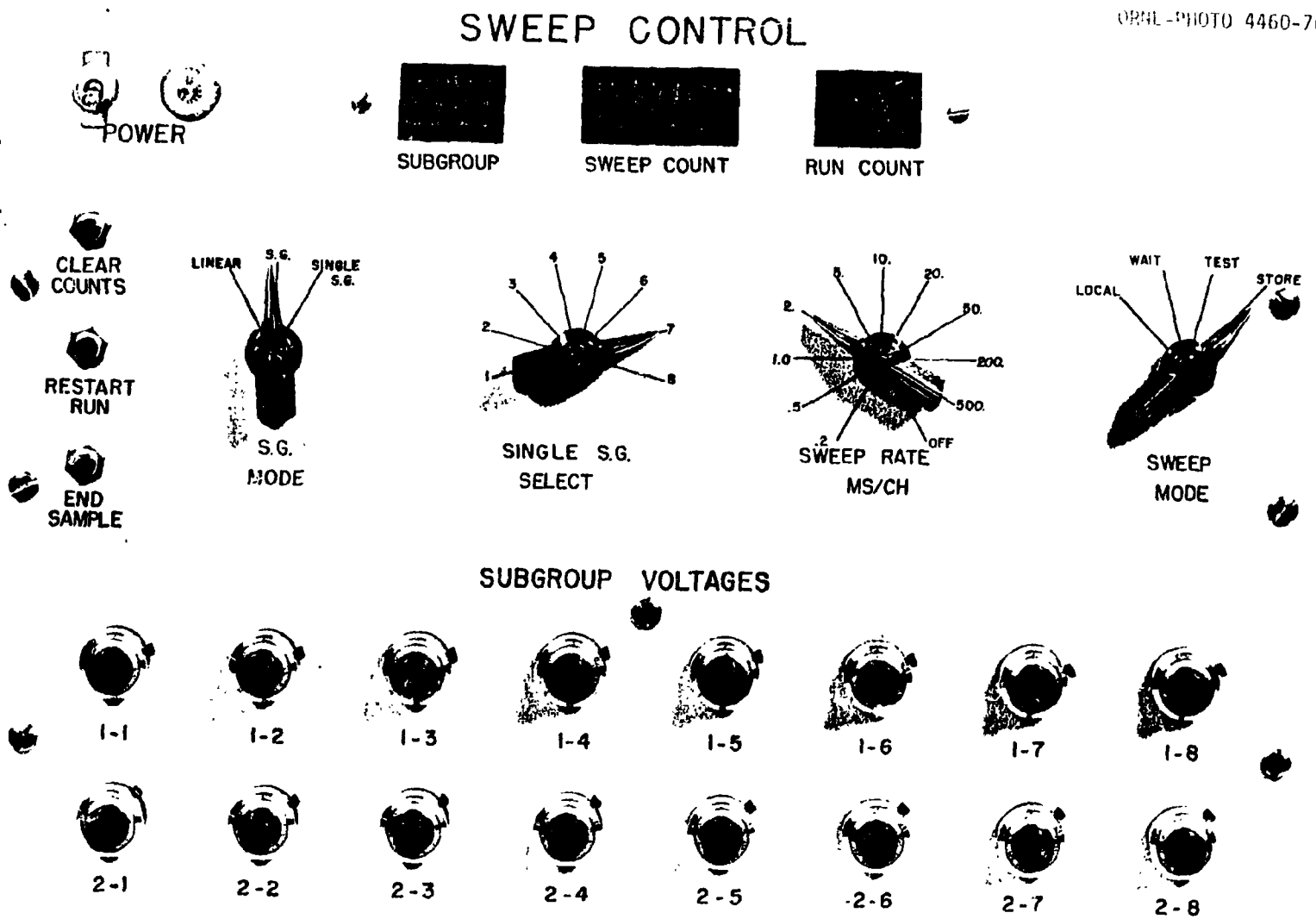

Fig. 4. Photograph of the Sweep Control Panel

ratio for the eight NBS-010 standards analyzed during this period was 0.01013 ± 0.00004.

Samples

The samples chosen for analysis were selected from among those previously analyzed on a multi-stage mass spectrometer so that comparisons of results could be made. These included one (SAU-14) loaded at the International Atomic Energy Agency Safeguards Analytical Laboratory near Vienna, which had previously been used to compare results from ORNL and IAEA two-stage instruments. Exposure time of the beads to the samples ranged from 24 to 40 hours; approximately 1-3 ng of Pu and U were on each bead.

The beads were exposed to the solutions in January, 1978. The data in this report were taken in July/August, 1978, and it was found that the beads had largely disintegrated during the interim. The beads had been exposed to air during this time and had apparently been oxidized by the combination of air and HNO_3. Two beads were found that were essentially intact and which provided good analyses. Two more analyses were obtained by dissolving the sample still on the residue of the remaining beads in 8 $\underline{M}$ HNO_3 and exposing the resulting solution to two beads; both dissolution and absorption were carried out in the polyethylene funnels in which the original beads had been stored.

This same procedure was carried out on NBS-947 and NBS-947/NBS-010 mixtures that had also been prepared by the IAEA.

One sample of mixed NBS-947/NBS-010 was run from a bead loaded at ORNL in November, 1977, and stored on a microscope slide under a drop of collodion. The bead was completely intact.

Results in all of the above cases were indistinguishable from those obtained from freshly made beads. No attempt has been made to isolate these data from those obtained from freshly loaded beads in the presentation in the next section.

RESULTS AND DISCUSSIONS

Results obtained from NBS-010, NBS-500, and NBS-947 are summarized in Table 1. The data-taking system, both hardware and software, was designed

Table 1

Results from Standards

	NBS-010		NBS-500	
	234/235	235/238	234/235	235/238
NBS	0.00538	0.01014	0.01043	0.9998
ORNL	0.00549 ±0.00032	0.01013 ±0.00004	0.01041 ±0.00010	1.0006 ±0.0036
	8 analyses		13 analyses	

	NBS-947			
	238/239	240/239	241/239	242/239
NBS*	0.00370	0.24147	0.04309	0.01559
ORNL	0.00377** ±0.00013	0.24119 ±0.00069	0.04327 ±0.00031	0.01557 ±0.00021
		22 analyses		

*Corrected to August 13, 1978 (see text).
**12 analyses (see text).

on the assumption that it would be used in conjunction with a multi-stage mass spectrometer. Because of its lower abundance sensitivity, the single-stage instrument used in this work did not give a clean enough spectrum to yield usable ^{236}U isotopic measurements with this system. It would not be too difficult to modify the system to allow collection of reliable 236 data, but it was judged not to be worth the effort involved. Hence, no ^{236}U results are reported.

Similarly, when ^{238}U contributed too large a signal to that mass position during analysis, correction of ^{238}Pu for its presence failed. This occurred in just under half the Pu analyses (10 out of 22). The frequency of occurrence of this problem was undoubtedly enhanced by the fact that an inexperienced operator was running the samples. On the other hand, it may be that such a problem is too difficult to avoid in the sequential analysis of Pu and U from a single bead. If such is the case, it would be relatively simple to wash the U off the beads and either reabsorb it on clean beads for analysis or load it as a solution.

It should be pointed out that the NBS values for the isotopic abundances quoted for the NBS-947 standard have been corrected to August 13, 1978. The half-life used for ^{241}Pu was 14.3 years. Precisions in all cases were calculated from the formula:

$$SD = \left[\frac{\Sigma(x-\bar{x})^2}{n-1}\right]^{\frac{1}{2}}$$

where x = individual value and $\bar{x}$ is the average of n analyses.

Table 2 contains data from "real world" samples and lists the results obtained from both ORNL two-stage and the ORNL single-stage instruments. In nearly all cases the limits of error overlap.

With the exceptions noted above, we feel that the results in Tables 1 and 2 are comparable to those obtainable using conventional mass spectrometric techniques and that neither precision nor accuracy need be sacrificed in using resin bead methodology. Naturally, because of the small quantities of material involved, the hazards of contamination are greater, but we found that meticulous attention to detail becomes a habit and have experienced few difficulties in this area. In addition, mastering the techniques required for manipulating the resin beads looks much more formidable than it actually is, and more than makes up for the trouble involved by reducing the amount of chemistry required.

Another advantage gained through use of the resin bead is increased ionization efficiency. Known amounts of U and Pu were loaded on different beads and run to exhaustion, accumulating all counts of the most abundant isotope. Results of duplicate analyses for U gave one ion collected for each 700 atoms loaded; for Pu it was one in 80 (1.2%). This is approximately an order of magnitude higher than typical results obtainable from solution loadings. There are at least two factors contributing to this enhanced sensitivity. One is that a resin bead is very close to a point source and thus conforms more nearly to the ideal ion optical condition; a solution loading is drawn by capillary action to the two ends of the canoe-shaped rhenium filaments and does not approximate a point source well. The second factor is that, since the sample is in intimate contact with the reducing agent (the resin bead), it is thus much more completely reduced than a solution is when it is reduced by heating in a benzene atmosphere.

Table 2

Results from Comparison Samples

SAU-14

U	No. of Analyses	234/235	235/238		
2-stage		0.01030	0.01216		
1-stage	4	0.01015 ±0.00025	0.01220 ±0.00008		
Pu		**238/239**	**240/239**	**241/239**	**242/239**
2-stage		0.0093	0.3116	0.1020	0.03149
1-stage	4	0.0097 ±0.0006	0.3121 ±0.0008	0.0992 ±0.0008	0.03153 ±0.00011

K-1

U	No. of Analyses	234/235	235/238	238/233	
2-stage (unspiked)	2		0.00198 ±0.00001		
1-stage (unspiked)	4		0.00202 ±0.00003		
2-stage (spiked)	2	2.42 ±0.03	0.00236 ±0.00004	2.113 ±0.010	
1-stage (spiked)	4	2.34 ±0.04	0.00244 ±0.00004	2.096 ±0.013	
Pu		**238/239**	**240/239**	**241/239**	**242/239**
2-stage (unspiked)	2	0.00057 ±0.00028	0.05858 ±0.00022	0.00219 ±0.00001	0.00019 ±0.00001
1-stage (unspiked)	4	0.00022 ±0.00006	0.05862 ±0.00014	0.00224 ±0.00001	0.00037 ±0.00001
2-stage (spiked)	2	0.00033 ±0.00007	0.05863 ±0.00006	0.00223 ±0.00001	0.3415 ±0.0002
1-stage (spiked)	4	0.00023 ±0.00003	0.05864 ±0.00024	0.00231 ±0.00001	0.3397 ±0.0017

There are almost certainly other factors at play (surface physics,[6] etc.), but the two discussed appear to be the most important ones.

CONCLUSIONS

We conclude that Pu and U samples loaded on resin beads can be analyzed on single-stage mass spectrometers with little or no degradation of results provided proper care is exercised with regard to sample handling techniques. In addition, storage of samples on resin beads seems feasible for periods at least as long as six months provided the beads are not exposed to residual HNO_3 and air; it is probable that beads will retain their integrity much longer than six months when stored under collodion, but as yet we have no data to support this contention.

Conventional mass spectrometers can readily be adapted to resin bead analysis by installing a pulse-counting detection system. The cost of such conversion will vary depending on whether or not a data acquisition system will be needed. We estimate that the cost will be in the neighborhood of $15,000; this figure includes the price of a multi-channel analyzer to serve as a temporary data storage device, but does not include the cost of a computer.

Unfortunately, it does not appear to us that it will be possible to switch easily back and forth between pulse-counting and current integration unless the instrument is provided with a movable Faraday cup. Using the same multiplier in both modes would undoubtedly degrade its performance in each. The requirements of low background counting rates and high gain for pulse counting, and of relatively high signal handling capacity in current integration are mutually incompatible if demanded of the same multiplier.

References

1. R. L. Walker, R. E. Eby, C. A. Pritchard, and J. A. Carter, Anal. Lett. 7, 563 (1974).

2. J. A. Carter, R. L. Walker, R. E. Eby, and C. A. Pritchard, International Symposium on the Safeguarding of Nuclear Materials, Vienna, Austria, IAEA-SM-201/9.

3. D. H . Smith, W. H. Christie, H. S. McKown, R. L. Walker, and G. R. Hertel, Int. J. Mass Spectrom. Ion Phys. 10, 343 (1972).

4. D. H. Smith, ed., USDOE Report ORNL/TM-6485, in press.

5. D. H. Smith, H. S. McKown, W. H. Christie, R. L. Walker, and J. A. Carter, USDOE Report ORNL/TM-5485, June, 1976.

6. D. H. Smith, J. Chem. Phys. 55, 4152 (1971).