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Resin Beads as a Sample Acquisition and Loading Medium for Mass Spectrometric Analysis

R. L. Walker
D. H. Smith
H. S. McKown
H. C. Smith
J. A. Carter

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Analytical Chemistry Division

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Abstract

This volume is a revised version of a previous edition of this work, "Practical Aspects of the Resin Bead Technique for Mass Spectrometric Sample Loading."[1] It has been updated to include current practice and expanded to cover more topics. Appendices are included to provide step-by-step instructions for many of the required operations. Among the new material covered is the bulk preparation procedure and hot cell operations.

1. INTRODUCTION

An earlier version of this work described some of the practical aspects of loading uranium and plutonium samples collected on resin beads onto mass spectrometer filaments.[1] There has been widespread interest in this technique, and we have taught staff members from several different laboratories the mechanics of sample loading.

Since use of the technique seems to be spreading and since we have modified it both to make its application easier and to meet the demands of other laboratories, it seems desirable to produce a description of our current practices. Although a series of publications[2-9] covers most of the material presented here, this paper will serve as a convenient reference and have a decidedly practical emphasis by including much step-by-step detail of the various operations involved. Among the developments reported herein are procedures for acquisition of samples in a hot cell, for loading one thousand beads with uranium and plutonium to reduce the chance of significant contamination, and for loading virtually any amount of sample from 1 ng to 1 μg on each bead. Step-by-step descriptions are contained in the appendices.

Using resin beads leads to many important advantages over conventional solution loads. The combination of its sample collecting ability and its convenient use as a sample transfer medium constitutes a powerful argument in its favor. The principal advantages are these:

1. Simplicity and ease of sample acquisiton, even in a hot cell.

2. The quantities of uranium and plutonium on each bead can be made small enough (1-3 ng) so that shipping is no problem.

3. Clean separation of uranium and plutonium from fission products and other actinides.

4. Each bead serves as a convenient vehicle for loading samples onto mass spectrometer filaments.

5. Sample collection efficiency in the mass spectrometer is improved.

II. EQUIPMENT

1. First and foremost, a mass spectrometer with sufficient sensitivity to analyze uranium samples is required. A pulse-counting instrument is no longer needed since quantities in excess of 1 μg can now be loaded on each bead. This is sufficient sample for analysis on commercial instruments such as the Vacuum Generators 354E and Finnigan MAT 261. A photograph of an ORNL instrument is shown in Fig. 1.

2. A laboratory hood or other clean area in which to mount microscopes and do the resin bead handling. This helps significantly in keeping the sample apparatus clean, which is crucial for this operation. Too high an air flow causes problems by blowing beads away from the work area.

3. A good (medium power) microscope. ORNL uses a Wild M5-Pol binocular microscope. Most of the resin bead handling is done with the help of this microscope.

4. A lower power microscope to use when putting resin beads on filaments. ORNL uses a Bausch and Lomb Model YB6145 stereo-microscope; a three-dimensional imager is helpful in this operation. Both microscopes and hood are shown in Fig. 2.

5. An assortment of needles, preferably, but not necessarily, of tungsten or stainless steel, mounted in handles.

6. All glassware should be soaked in the same medium the samples will be in, i.e., 6-8 M HNO_3. When an item is to be used, it should be rinsed with triple distilled water and left in an oven until it is needed.

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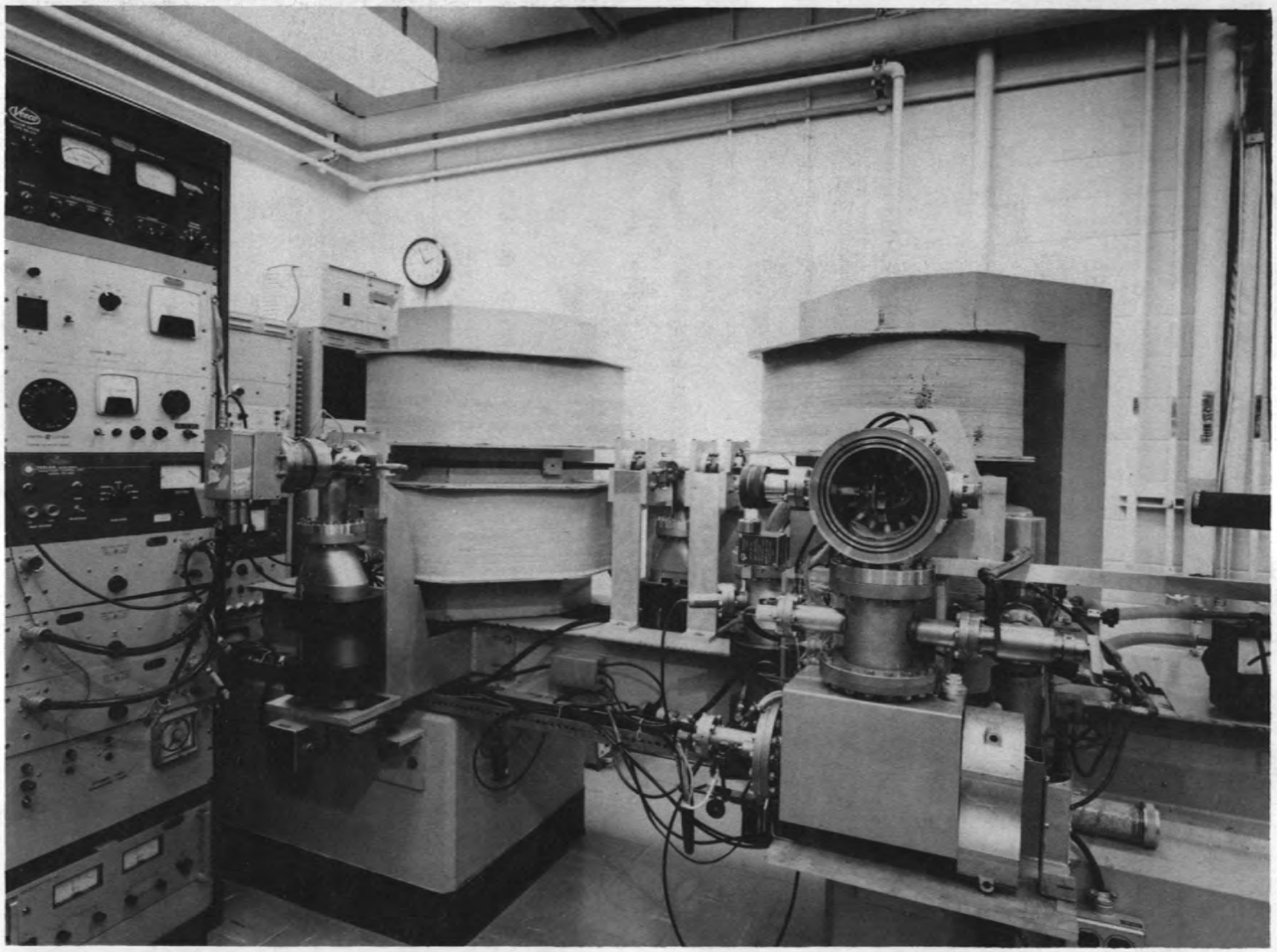

Figure 1. ORNL high abundance sensitivity mass spectrometer.

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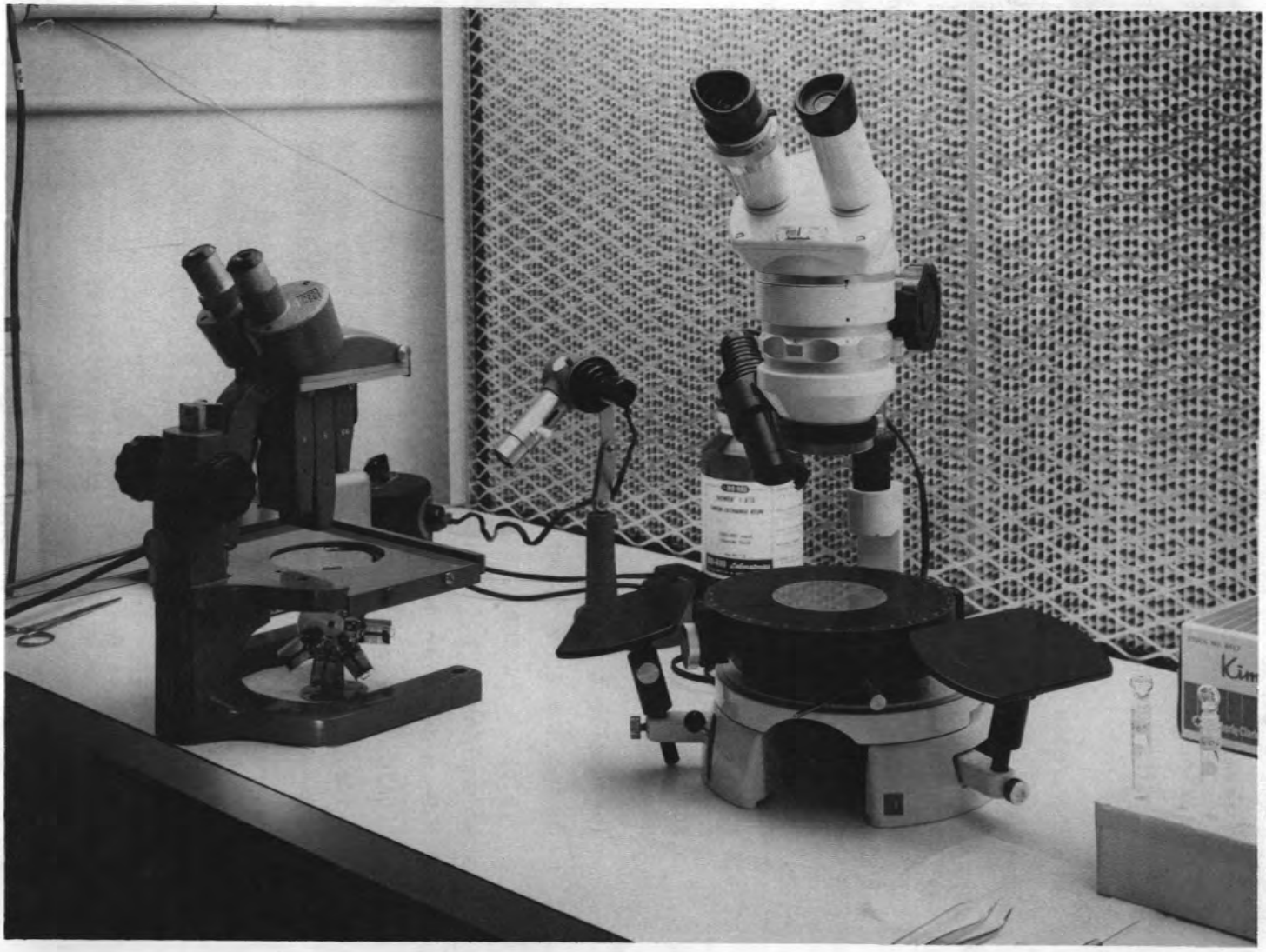


Figure 2. Sample loading area showing microscopes.

7. Resin beads should be conditioned by soaking in 8 M HNO_3 for 10-30 minutes. Do not discard an old batch of beads before the new one has been verified to be suitable for use. It should be pointed out that resin beads deteriorate as they age, whether soaking in acid or in the original bottle. We do not recommend keeping beads longer than 2-3 years in the original container.

8. The resin bead-8 M HNO_3 mixture should be kept in a plastic (polypropylene) container. HNO_3 leaches uranium out of glass and thus introduces contamination. We have found, however, that beads degrade rapidly when left in contact with HNO_3 and no longer store them thus for long periods (6-12 months maximum). To generate a large supply of beads in the nitrate form, expose the beads to acid for 10-30 minutes by agitating on a vortex mixer. Wash them until the waste water is neutral and store in triple distilled water. We keep such beads no longer than 18 months.

   The smallest beads (which are not usually used) can be separated during the above step by withdrawing the supernatant liquid with a pipet. Further segregation of small numbers of beads can be accomplished by breaking off the tip of a 20 μl pipet so 500-μm-diameter beads will fit into it. Withdraw 10-20 μl of liquid from a slurry of beads and deposit it on a microscope slide. Absorb excess water with a tissue and put in a drying oven at 100°C for about 15 seconds. Individual beads of the desired size can be selected while viewing through a microscope.

   It is obviously not practical to select beads individually when large numbers of them are wanted. An effective method of obtaining large quantities of beads of approximately the same size is to pass them through two consecutive filters made of mesh. We use 40 mesh followed by 60 mesh; this will isolate beads with diameters of 250-420 μm between the two sieves; such beads weigh about 3 μg each. Appendix 1 is a description of how to isolate a thousand resin beads.

9. Polyethylene or polypropylene microfunnels with fritted discs. These are tips of disposable chromatographic columns. (Kontes Glass Co., P.O. Box 729, Vineland, NJ 08360). Shown in Fig. 7.

10. Caps and plugs for microfunnels. (Y-12 Dwg. T2B-29681). Shown in Fig. 7.

11. Polypropylene Econo-columns, (Bio-Rad or equivalent, Cat. No. 731-1110). Shown in Fig. 8.

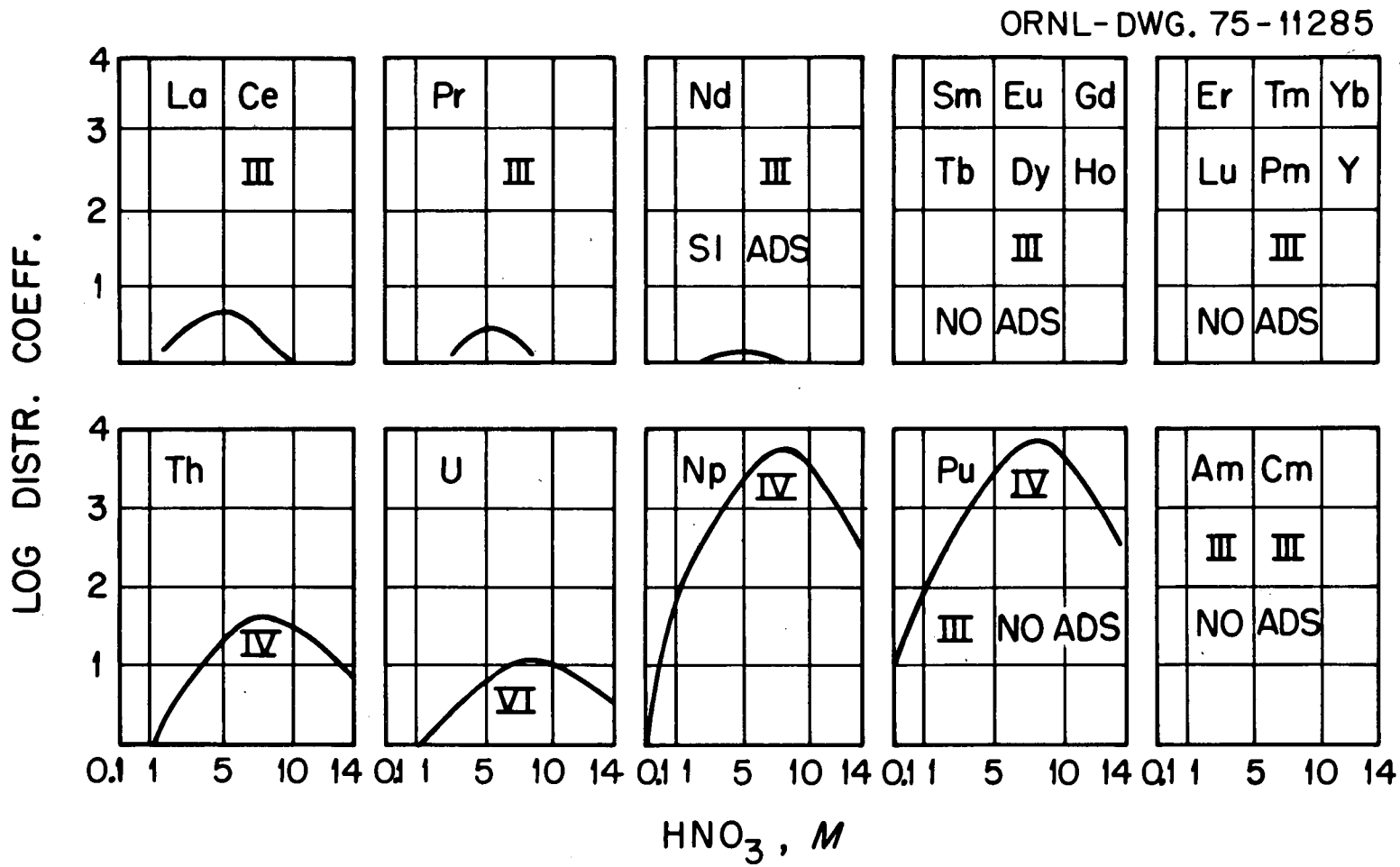
III. SAMPLE COLLECTION

Figure 3 shows the distribution coefficients of various elements in 8 M HNO_3.[10] As can be observed, near-complete separation of uranium and plutonium from fission products and most other actinides is achieved by extracting from such a medium. Thorium and neptunium are the only elements to adsorb appreciably in addition to uranium and plutonium. Neither causes isobaric interference in mass spectrometric analysis and thus does not degrade the results. Indeed, if and when a thorium-based fuel cycle is put into operation, it will be desirable to extract thorium along with uranium and plutonium. We have already developed the mass spectrometric techniques to analyze sequentially Pu, U, and Th from the same resin bead. Figure 4 is an outline of our procedure for collecting samples from power reactor spent fuels.

Samples are collected by adjusting the target solution to 8 M in HNO_3. The concentration in uranium is adjusted to yield the desired amount on each bead. Table 1 lists results of adsorbing uranium from 0.5 ml solutions. One thousand beads were exposed, and the initial uranium concentration varied; as the table shows, we were able to get from 7 to 75 ng per 250 μm-diameter bead by adjusting only the one parameter.

Table 1. Uptake of Uranium by Resin Beads from 0.5 ml Solutions

Total U in sol. μg	U/bead in sol. μg	U/bead on beads x 10^{-6} ng/μm^3	U/bead, assuming 250 μm diameter, ng
100	0.1	0.87	7.1
500	0.5	2.90	23.7
1000	1.0	6.00	49
1500	1.5	9.19	75



IONIC METAL ADSORPTION BY STRONGLY BASIC ANION EXCHANGE RESIN (Dowex 1-X2)

Figure 3. Distribution coefficients of various elements in 8M HNO_3.

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OUTLINE OF THE RESIN BEAD METHOD OF SAMPLE PREPARATION

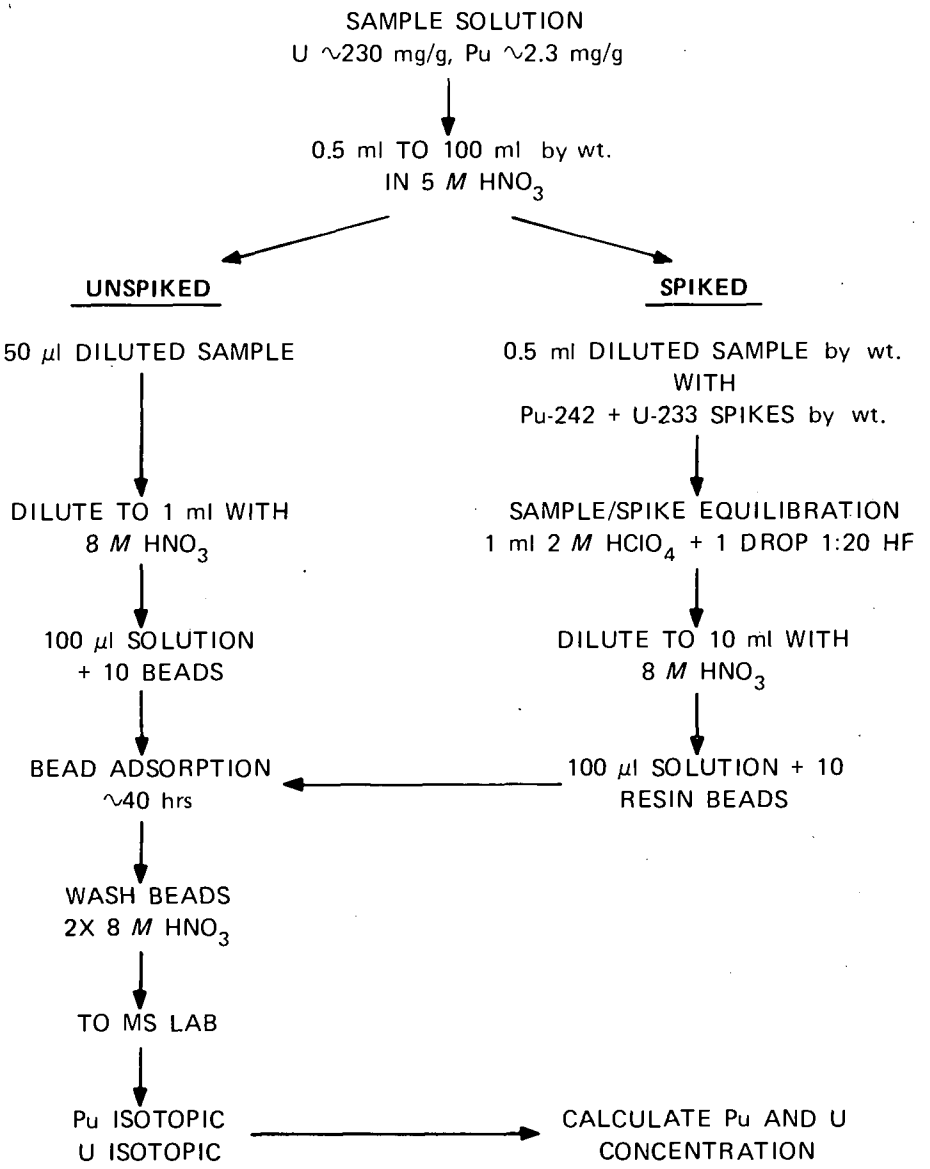


Figure 4. Outline of resin bead procedure.

Figure 5 plots the amount of uranium loaded per bead at three different sample volumes versus initial uranium concentration; the maximum we have loaded is about 40 x 10^{-6} ng U/μm^3 of bead. We aim for one μg of uranium per bead exposed to give 1-3 ng of uranium loaded on each bead.

To load beads more heavily, we reduced the volume sampled to 0.2 ml and exposed 100 beads to it. The results are given in Table 2.

Table 2. Uptake of Uranium on Resin Beads from 0.2 ml Solutions

Total U in solution μg	U/bead in solution μg	U on beads $(ng/\mu m^3)x10^{-6}$	Bead diameter, μm	U/bead, ng
2030	20.3	43.8	229	275
2030	20.3	43.4	284	520
2030	20.3	42.2	348	930

In this way we were able to adsorb up to 1 μg uranium per bead.

Synthetic mixtures of uranium and plutonium were made to verify adsorption of both elements. A solution containing 6 mg of uranium and 20 μg of plutonium (a 300/1 ratio) gave results summarized in Table 3. It has been our experience that, if uranium adsorption is correct, plutonium adsorption will also be correct. Thus, by adjusting uranium concentration, sampling volume, bead size, and washing conditions, we can reproducibly load anywhere from 0.1 ng to over 1 μg per bead.

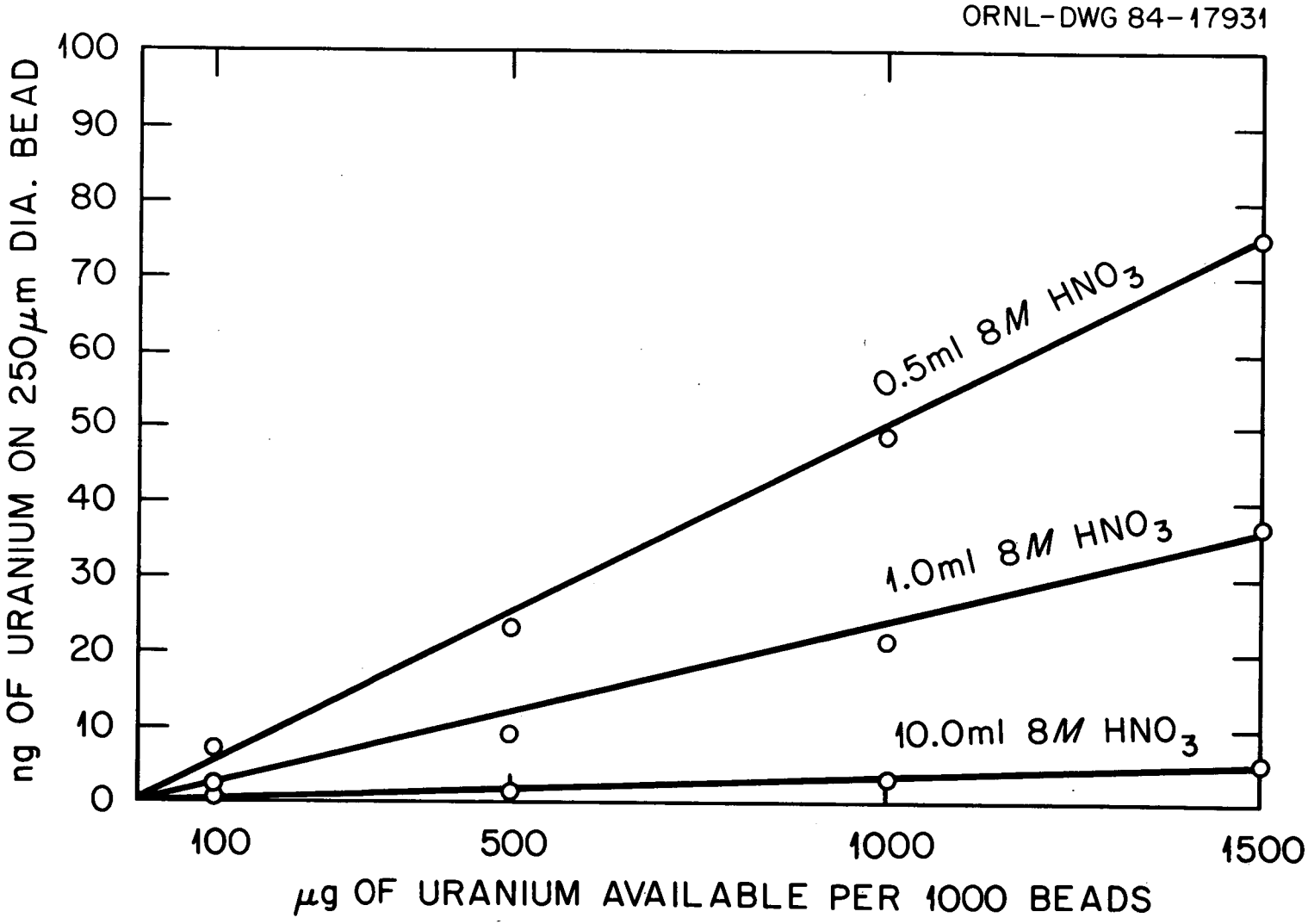


Figure 5. Uptake of uranium is initial uranium concentration.

Table. 3. Uptake from a Solution with a 300/1 U/Pu Ratio

Bead Diameter μm	Bead Volume $x10^{-6}$ μm^3	U on bead ng	Pu on bead ng	U conc. on Bead $ng/\mu m^3 x10^{-6}$	Pu conc. on Bead $ng/\mu m^3 x10^{-6}$
367	25.73	1190	146	46.3	5.67
348	22.06	995	120	45.1	5.44

Early experiments were performed to establish the range of U/Pu ratios over which the technique could be applied.[2] Ratios much below 10 led to near-saturation of the bead with plutonium and made uranium analysis extremely difficult. Ratios much greater than 1000 led to similar problems in plutonium analysis. It is unlikely that uranium-fueled reactors (e.g., LWR) will be operated in such a way as to produce a U/Pu ratio below 10. However, breeder reactors do produce ratios significantly below 10; we have successfully modified our technique to accommodate ratios down to about 3. Modifications include reduction of the volume used to wash the beads and a different approach to burning off plutonium before starting to take uranium data. Reducing our wash volume from two column volumes to one reduces the amount of uranium washed from the beads. The amounts of plutonium and uranium from breeder reactor fuels typically adsorbed on beads has not yet been determined; however, our observations that plutonium runs at a lower temperature and is much more difficult to burn off indicates that more is present than in other spent fuels. One result of this fact is that plutonium analyses are quite precise; this is especially important for ^{238}Pu, where precise measurements can be obtained, even for low abundances (0.01%). This has allowed us to relax our criterion that $^{239}Pu/^{238}U$ be 0.1 or less before starting to accumulate uranium data; correction to the 238 mass position can now be applied with a high degree of precision, which in turn leads to a precise uranium analysis. We have successfully measured uranium ratios when the $^{239}Pu/^{238}U$ was 10 or less.

IV. LOADING SAMPLES ON BEADS IN AN OPEN LABORATORY

Extract a number of conditioned resin beads from the acid or water storage medium with a clean transfer pipet and deposit them on a clean microscope slide. It will take about 30 minutes for the beads to reach optimum dampness—they should be wet, but with no water standing on the slide. Beads that are too wet cling to each other and are virtually impossible to work with individually. Beads that are too dry become electrostatically charged and are also virtually impossible to control.

While waiting for the beads to reach suitable wetness, carefully clean the microscope stage with a lint-free wiper and triple-distilled water. Kimwipes are suitable for this purpose. It is extremely important to keep the stage clean. When the beads are ready, use a fine glass or stainless steel rod to segregate some of those of roughly equal size, viewing the operation through the microscope. Separate these into bundles containing the number of beads you want to put into each sample (usually 3-10). Pick up each bundle of beads (5 beads can be picked up simultaneously) with the glass rod and put them into the sample solution by gently touching the tip against the glass below the liquid level. Verify the position of the beads through the microscope.

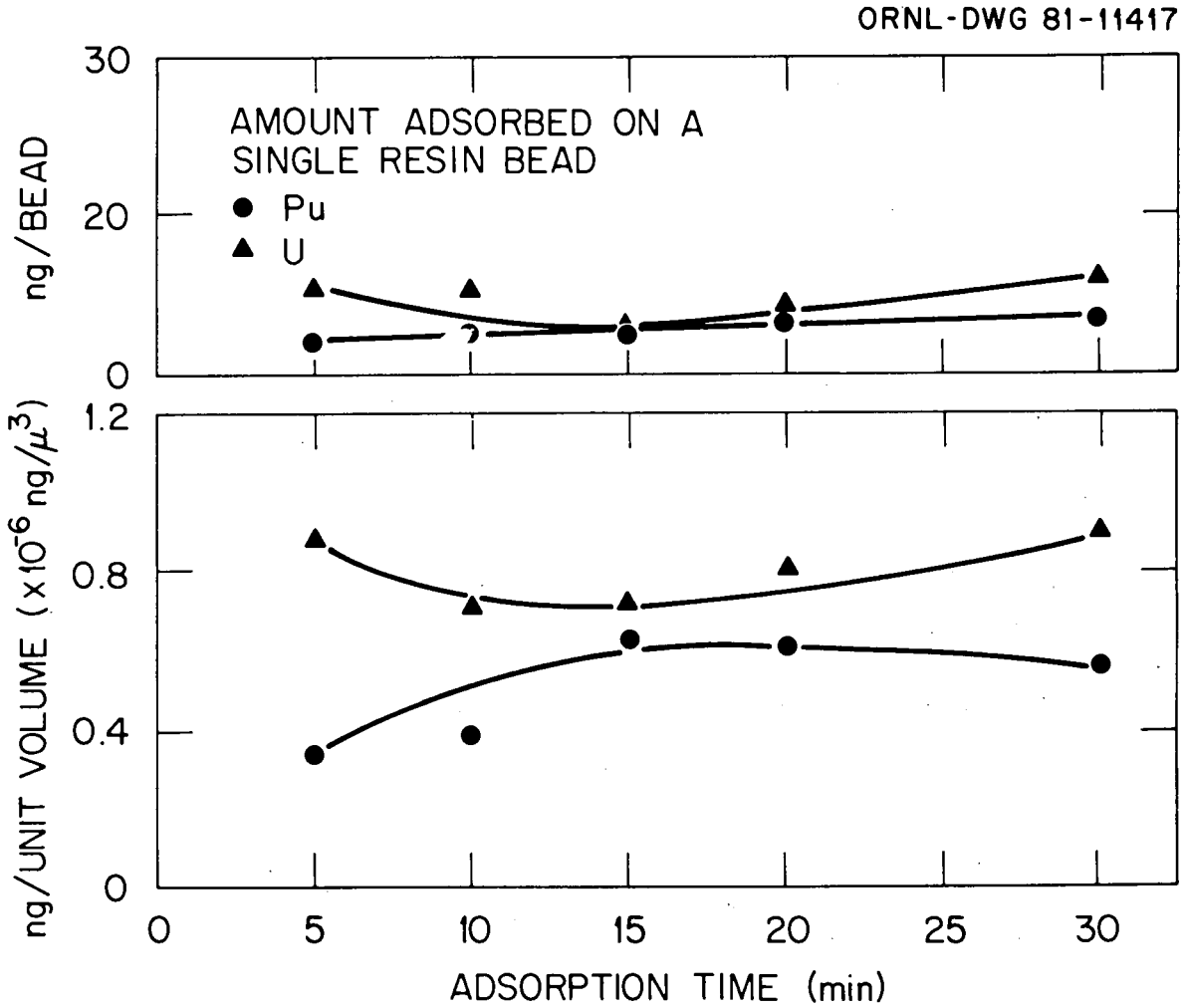
Our experience with personnel of the Power Reactor and Nuclear Fuel Development Corporation (PNC) of Tokai, Japan led us to develop procedures for loading 1000 beads to reduce the effect of contamination[8] and for loading them in a hot cell.[9] A step-by-step description of the hot cell procedure is given in Appendix 6, and one for selecting approximately 1000 beads in Appendix 1.

To reduce sample acquisition time, agitating the solution in contact with the beads is strongly recommended. Under static conditions, overnight (16-24 hour) exposure is necessary for satisfactory loading of the beads; if 1000 beads are to be loaded, static exposure is often unsatisfactory because those beads buried beneath others do not adsorb as much uranium and plutonium as do those on top. Agitation reduces sample

acquisition time to 10-15 minutes and also loads the beads quite uniformly. Figure 6 is a plot versus time of the uptake of uranium and plutonium on resin beads from static solutions; note that uptake is quite rapid initially. For laboratory preparation, the sample should be held in 0.1-0.2 ml of solution placed in a 2 or 3 ml centrifuge cone. Too much liquid makes manipulation of the beads difficult. Thus, the concentrations of uranium and plutonium should be adjusted to give about 10^{-6} g of U and 10^{-8} g of Pu per bead in a 0.1-0.2 ml aliquot. Acid concentration should be 7-8 M HNO_3. These conditions give 1-3 ng uranium and plutonium per bead. Different quantities of sample can be loaded by adjusting conditions according to Table 1 or Figure 5. If total uranium or plutonium is desired, the sample should be spiked and equilibrated prior to its transfer to the centrifuge cone.

Spiking uranium samples is straight-forward and requires only thorough mixing of spike and sample. Plutonium, due to its multiplicity of oxidation states and its tendency to polymerize, is much more difficult to deal with. It is essential in any isotope dilution procedure to achieve isotopic equilibrium between spike and sample; this problem is not unique to resin bead sampling, but applies equally to any isotope dilution procedure applied to any element. Once equilibrium has been achieved, it is unnecessary to obtain quantitative extraction since the information concerning elemental concentration is carried in the spike-to-sample isotopic ratio. Marsh, et al. have made a thorough comparative study of various equilibration procedures for plutonium.[11] The most consistent results were obtained by reduction with Fe(II) and sulfamic acid followed by oxidation with $NaNO_2$. We have adopted this technique and have had excellent results with it. Details are given in Appendix 4.

We use cellulose acetate sample vials with 5-ml volume and about 250 μl of solution. The maximum solution volume that should be used with vials of 5 ml capacity is 400 μl; volumes larger than this too often result in sample leaking out of the vessel. Before mounting on the vortex mixer, the cap should be affixed to the vial with masking tape; a second piece of tape around the bottom serves as a fender to prevent abrasion of the container. Agitation on a vortex mixer for 10-30 minutes is



U And Pu Adsorption on Anion Resin Beads – Batch Method

Figure 6. Adsorption of uranium and plutonium vs. time.

sufficient to load the beads with sample. This should be followed by centrifuging for 30 seconds to ensure that the beads are collected below the surface of the liquid so they will be picked up in the next step.

To load the beads into our micro-adsorption column tip assembly (Figure 7), the sample solution, with the exposed beads still in it, is withdrawn from the cellulose acetate vial in increments of 50-100 μl in a Pasteur pipet and run through the pipet tip (with the filter in place, of course). The beads collect on the filter and are subsequently washed with 200 μl of 8 M HNO_3. Too much washing tends to leach uranium out of the beads, so some care must be exercised. The wash solution can be pulled through the column tip by use of house vacuum or can be pushed through by forcing air, argon, or other suitable gas down through the assembly. For more details, see description in the next section on shipping samples.

If speed is of the essence, the foregoing procedure for collecting the beads in the column tip can be omitted and the beads instead may be distributed on a glass microscope slide. They will be too wet to handle with a single needle, but with care (and practice) can be picked up between two needles.

If the sample is known to contain only trace amounts of the target element, care must be taken to limit the number of beads to which the sample is exposed; using too many beads dilutes the sample by reducing the amount on a single bead. The sample should be preconcentrated if necessary to bring the final sampling volume to 200-250 μl, which is then exposed to three beads. Subsequent steps are identical to those described above.

If the samples to be analyzed are spent fuel dissolver solutions, preparation of beads must be done in a hot cell. We have developed a procedure (Appx. 6) using the adsorption apparatus shown in Fig. 8 which enables us to prepare beads in a high radiation field.

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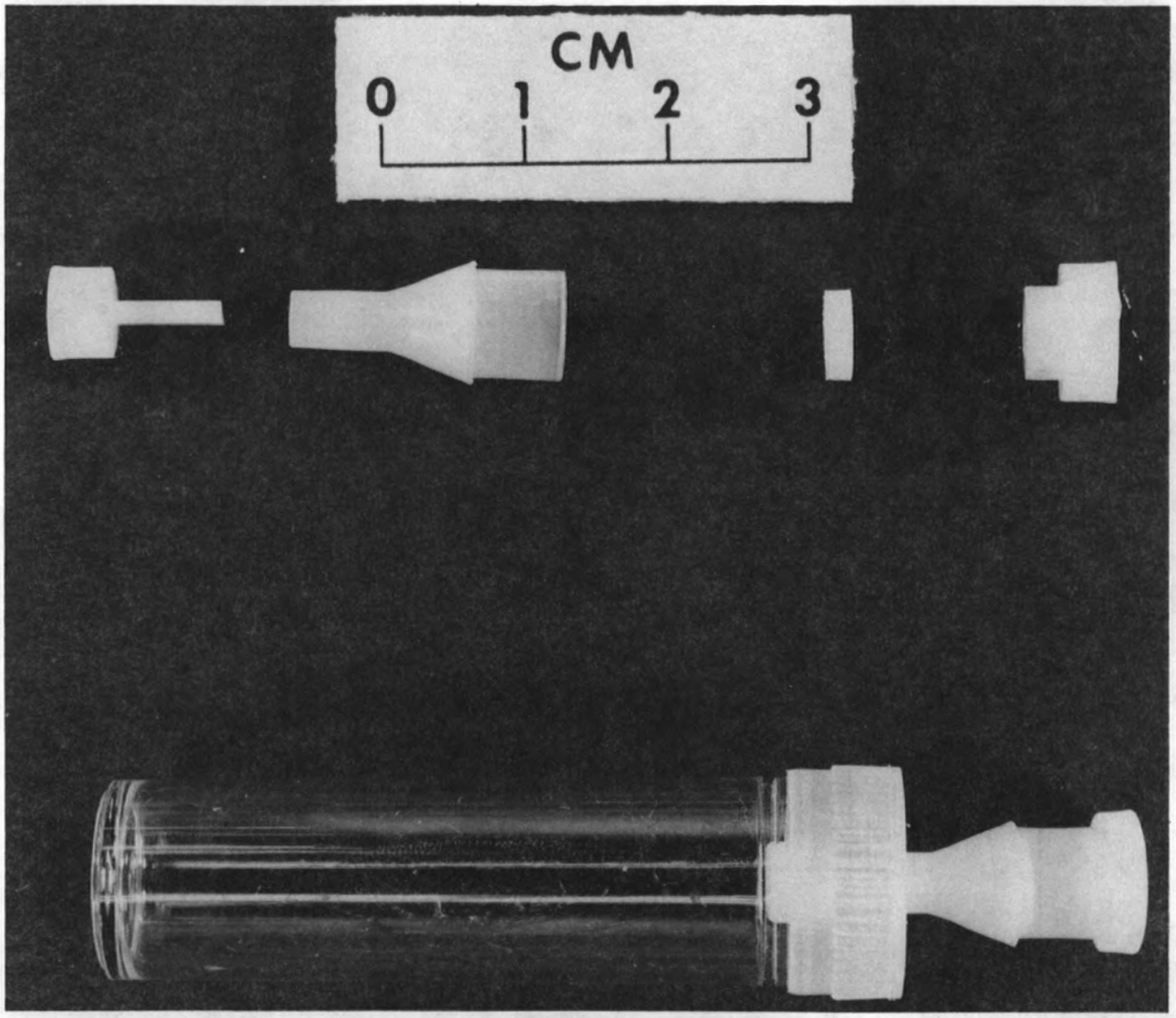

Figure 7. Micro-adsorption column tip assembly.

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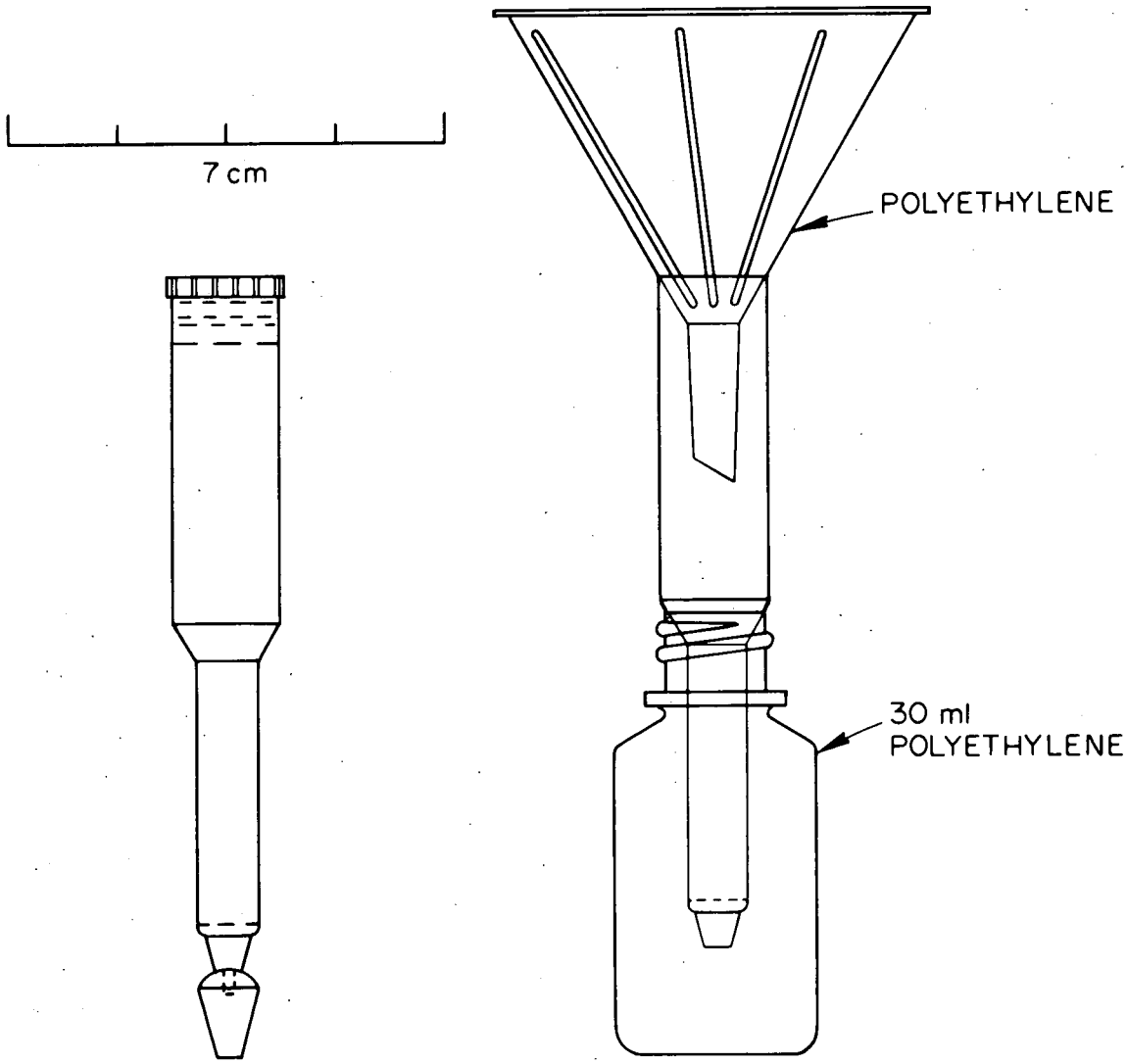

Figure 8. Bulk resin bead adsorption apparatus.

V. LOADING BEADS ON FILAMENTS

Transferring beads to filaments is a simple operation that looks more formidable than it really is. A little practice will allow almost anyone to load a filament in a minute or two. Position a filament under one of the low powered microscopes—only operations involving filaments are done here. The other microscope can't be used for this because it must have a stage, which makes positioning a filament under it virtually impossible.

To isolate the beads from contact with the solution, flick your finger gently against the bottom of the cone to splatter the liquid up on the glass. Some beads should stick to the side of the cone above the level of the liquid. It is a great advantage to have a clean cone to prevent water from remaining beaded on the glass surface, thus obscuring the beads.

Beads to be extracted from direct contact with a solution require the use of a glass or stainless steel loop; the manufacture of the latter is described in Appendix 2. Select a loop of appropriate size (one with a diameter about four times that of the beads) and, using the microscope, drop it around one of the beads on the wall of the cone. The surface tension of the liquid surrounding the bead will cause it to adhere to the loop, and it can be withdrawn from the cone. Still under the microscope, touch a lint-free absorbent paper to the loop, bringing the paper up from beneath the loop. If the geometry of the loop permits, it is a good idea to have it bending down a little. The bead, with decent luck, will move onto the paper as the liquid is adsorbed. If the loop is too small, however, the bead will often remain behind and not transfer. Pick the bead up from the paper with a clean needle and transfer it to the waiting filament.

If the loop you used is a good one, rinse it with 8 M HNO_3, triple-distilled water, and acetone and use it on the next sample. A loop with good geometry is valuable and should be zealously cared for to prolong its life, which should be several months or more.

To reduce problems in shipping, we have developed a funnel that simplifies both bead preparation and sample transport. It is shown in the photograph of Figure 7. It consists of a commercially available chromatographic column tip (the funnel-shaped object), a porous filter, a plug, and a cap. With the cap and plug in place, the assembly is sealed from the environment and prevents contamination from getting in and the sample from leaking out. Such assemblies have been extensively used for international shipment of samples on resin beads. Paraffin has been found to seal the base of the funnel if no plugs are available.

A needle is used for extraction of beads from the column tip. Proper degree of dampness is crucial to this operation. Beads that are too wet cling together and to the sides of the vessel and are virtually impossible to extract one at a time. This condition can be corrected by applying house vacuum through a plastic tube to the bottom of the tip or by forcing a gas through from the top. Nitrogen or argon from a gas cylinder will dry the beads in a few seconds. Air forced through the apparatus from a syringe or micropipet holder is slower but more readily controlled.

Beads that are too dry pick up an electrostatic charge the same (unfortunately) as that of the needle; they are vigorously repelled when the needle is brought into close proximity. This condition can be corrected by adding one μl of 8 M HNO_3 on top of the beads.

There are occasions when the beads will be just a little too dry: some will stick to the needle while others fly away from it. This condition can be counteracted by dipping the tip of the needle into 8 M HNO_3 and then touching the bead. An alternative is to use a small aquarium pump to hold the bead in position at the tip of a capillary smaller in diameter than the bead. This technique has been successfully used at Saclay.[12]

Once the bead is on the needle, it is transferred to a sample filament. In our laboratory, we have found it a great convenience to have

the filament positioned under a different microscope than the one used for bead selection. Both types of needles have inherent characteristics for which allowance must be made. Wire needles are very flexible, and it is easy to catch the tip on the filament or a support leg; upon release, the bead soars into the outer darkness at high velocity. Larger needles made from rod tend to have hooks on the end that make it easy to pick up a bead but not so easy to put it down. With practice, however, these idiosyncracies can be accommodated by the individual's technique and do not constitute a serious problem. A bead on a needle is shown in the photomicrograph of the upper inset of Figure 8.

In the main portion of Figure 9, a photograph of an ORNL filament assembly is shown. The lower inset shows schematically a bead mounted on a filament. The bead is shown larger with respect to the filament than is usual with us. We hold it in place by crimping the filament with clean tweezers; five crimps is about right. If, through the use of large beads or shallow filaments (as on the Finnigan MAT 261), it is not possible to crimp the filament, the bead may be affixed by adding one microliter of 10% solution of collodion in ethanol. A workable technique to add collodion to the filament is to get the drop of solution on the tip of the micropipet and touch the drop to one end of the canoe-shaped filament; capillary action draws the solution the length of the canoe. A too-vigorous flow can dislodge the bead from its optimum position, which is as near the center as possible and at the bottom of the canoe.

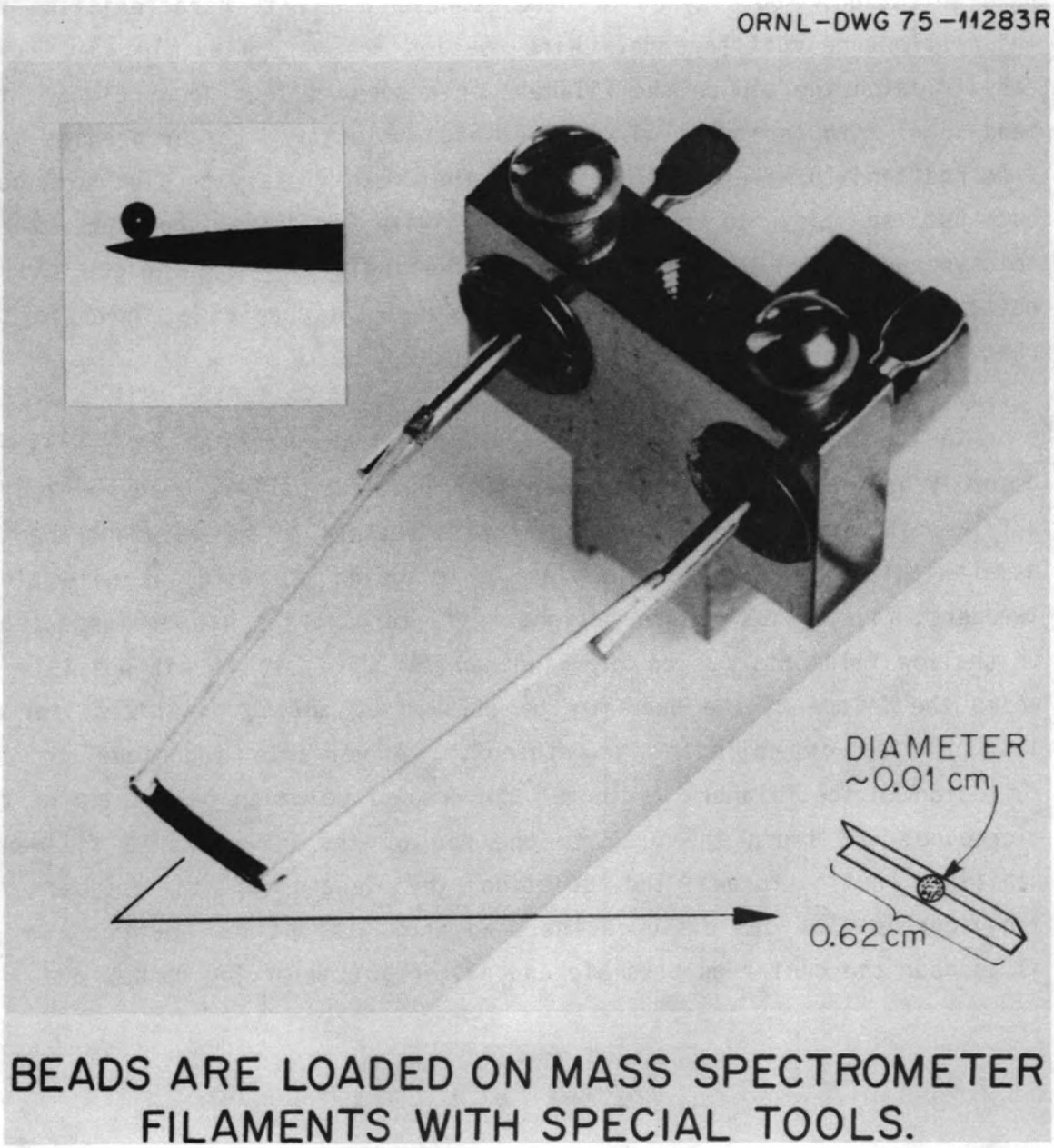

Figure 9. ORNL filament and holder.

VI. LONG TERM SAMPLE STORAGE

If beads with sample on them are to be stored over a long period of time (months or years), it is necessary to seal them from atmosphere to prevent oxidative destruction of the bead. A good way of achieving this is to keep them under collodion on a glass microscope slide. Arrange the beads individually in an array of convenient dimensions on a clean slide and cover each with a small drop of collodion. Ten beads can easily be mounted on a slide with little chance of confusion.

To remove a bead, cut around it through the collodion with a sharp knife or needle—the collodion drop is in general too large to be loaded in its entirety onto a filament. Gently pry the circumscribed area out with a needle—use great care, because it is easy to flick the bead off into space—and mount it directly on the filament.

VII. MASS SPECTROMETRIC ANALYSIS

Unlike those for resin-bead handling, the techniques used once the samples are in the mass spectrometer have not been changed much since they were first described.[2] Details are given in Appendix 7. However, various investigations have led to increased understanding of how the resin bead works and why it yields superior performance in the mass spectrometer.

In all cases, the only point at which unusual care is required is during temperature elevation before decomposition of the bead. Raising the temperature too fast causes an unacceptably high fraction of the beads to leave the filament, probably due to a too-vigorous explosion of the bead in question. The onset of bead decomposition is signalled by a rise in pressure. A pause of a few seconds before raising the temperature again should allow the pumping system to recover. The temperature should be raised slowly and incrementally through the decomposition region with frequent pauses to prevent violent pressure swings. For a base pressure of 10^{-8} torr, the pressure should at no time exceed 10^{-6} torr during these excursions. Once an increase in temperature does not lead to a corresponding increase in pressure, much less care is needed. If a single element is being analyzed, the temperature may be raised in the usual manner to find the ion signal; treatment during data-taking is identical to that for conventional samples.

If plutonium-uranium mixtures are to be analyzed, care must be taken to avoid getting the filament too hot. In single-filament analyses, plutonium is ionized first; too high a temperature leads to an unacceptably large uranium signal that seriously compromises the data at mass 238 and makes reliable extraction of the ^{238}Pu contribution problematic. We usually run plutonium at about 1450°C and 100,000 counts per second on the most abundant isotope. These comments do not apply to isotope dilution analyses of plutonium where it is unnecessary to monitor mass 238.

Once the sufficient plutonium data have been collected, the remainder of that element is burned off. Care must be taken not to exceed 1700°C

during this operation to avoid burning off too much uranium along with the plutonium. The $^{239}Pu^{+}$ signal should be monitored intermittently (due to very high counting rates, there is serious risk of detector damage if it is monitored constantly) during this process. When the $^{238}U^{+}/^{239}Pu^{+}$ ratio exceeds 2, data-taking for uranium may commence. There are occasional samples where data-taking can or must be begun sooner; ^{238}U results may be degraded in these cases.

If thorium is also to be measured, it can be monitored along with uranium, although counting rates will probably be low. Thorium is a difficult element to analyze, ionizing with poor efficiency at high temperature. However, the absence of isobaric interferents simplifies data-taking. When enough uranium data have been taken, the temperature is raised and thorium data are collected; no delay is necessary to burn off uranium.

After data collection is complete, they are processed by a host computer, and a report sheet is generated. The computer programs that perform these operations have been described[13,14] and are logically complex to meet the demands placed upon them. Automatic correction is made to the 238 mass position for plutonium-uranium pairs run from the same bead. Data processing is in all cases automatic and does not require operator intervention beyond initiating execution.

Secondary ion mass spectrometry was used to investigate the details of the resin bead-uranium-rhenium system and has been described in detail elsewhere.[15] Our study revealed that the carbon of the bead gradually dissolved in the rhenium filament: carbon and rhenium do not form a stoichiometric compound but are mutually soluble. Essentially all the uranium was retained in the carbon matrix left after decomposition of the bead; this residue thus acts as a reservoir of sample, feeding it to the ionization region in a controlled manner. Since the work function of a carbon-rhenium mixture is higher (5.84 eV) than that of the pure metal (5.43 eV)[16], most ionization occurs at the bead-filament interface. Figure 10 is a scanning electron micrograph of resin beads in the pure virgin state and after having been heated in vacuo for 30 minutes at 1700°C; the dissolution of the beads in the filament can be clearly inferred from the latter two micrographs.

ORNL-Photo 2241-82

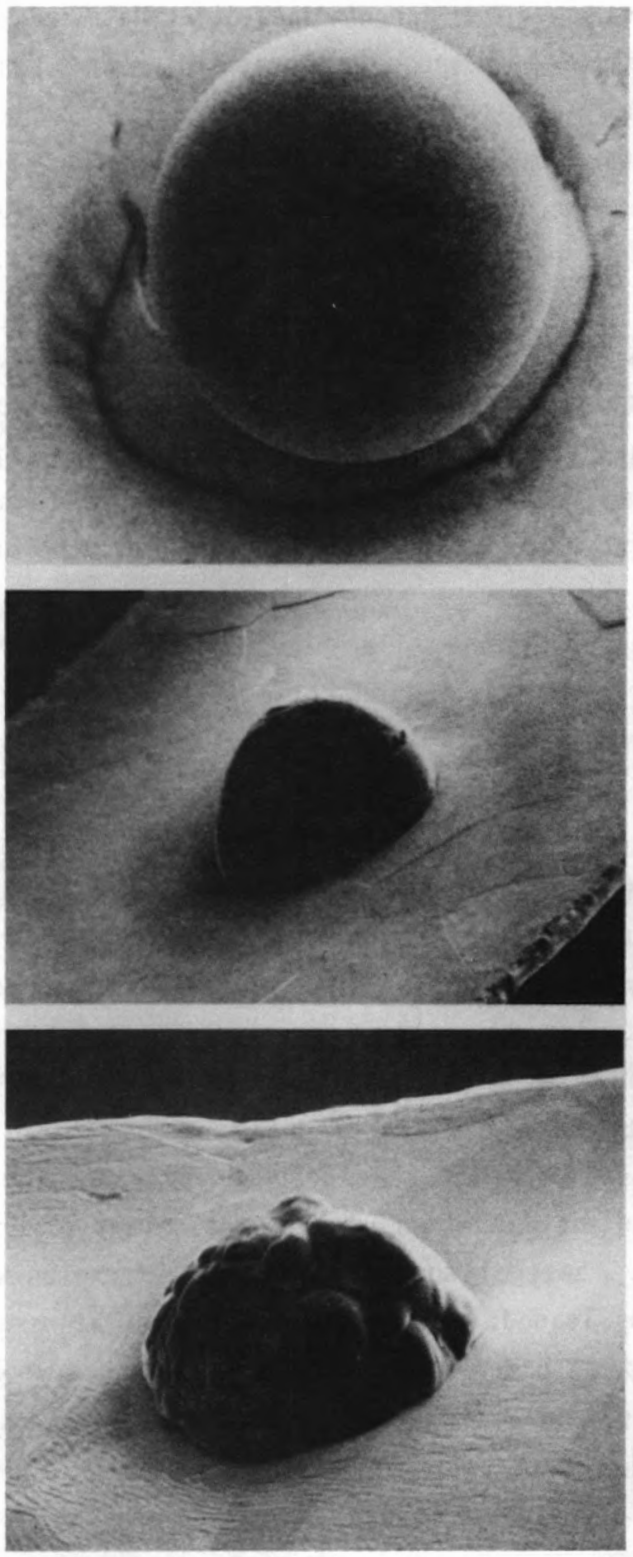

Figure 10. Scanning electron micrographs showing a virgin resin bead (uppermost) and two beads heated for 30 minutes at 1700°C.

During mass spectrometric analysis, several advantages accrue through use of resin beads. The carbon skeleton that remains after the bead decomposes constitutes a reducing environment and significantly reduces loss of sample as oxide (UO^+, UO_2^+, etc.) and other undesired species. It approximates a point source of ions and thus serves to optimize focus of the ion-optical lens elements of the source. Due to its acting as a sample reservoir, evaporation can be controlled to a very fine degree.

Since emission from a bead approximates a point source, we developed an ion source with circular symmetry to take advantage of this fact;[17] older sources had rectangular symmetry. Improved extraction efficiency was obtained which resulted in somewhat improved statistics.

We have measured ion collection efficiencies of both uranium and plutonium from resin beads. (Ion collection efficiency is defined as the number of ions collected divided by atoms of sample loaded and thus measures the efficiency of the entire mass spectrometer: ionization efficiency from the filament, transmission through the ion source and mass analyzer, and conversion efficiency of the detector.) We measured the amount of uranium on several individual beads by fluorimetry. Plutonium was measured by destroying a few beads individually and spiking the redissolved plutonium to perform an isotope dilution analysis. This yielded in each case a concentration in ng per μm^3 of bead for the element in question. To an excellent approximation, this value can be applied to any bead from the same preparation. Knowledge of the diameter of the bead being analyzed then yielded the amount of uranium or plutonium on the filament. Several such analyses gave one ion collected for each 700 uranium atoms loaded; the figure for plutonium was one in 80. These figures are about an order of magnitude better than we obtain for typical solution loadings. In addition, they were much more consistent and didn't exhibit the wide scatter often observed with solution loadings. Ion emission can be much enhanced by adding a slurry of rhenium powder in a solution with a source of carbon, such as sucrose or starch, in a layer over the bead.[18,19]

VIII. CONCLUSIONS

The resin bead constitutes a significant advance as a technique for loading samples for mass spectrometric analysis. Modifications to the original procedure have been made to reduce sample acquisition time, to reduce contamination, and to allow loading virtually any desired quantity of sample on a single bead. These modifications allow application of the technique in almost any environment, from hot cells to clean laboratories to mobile facilities.[20] Nearly any isotopic ratio mass spectrometer can be used, from multi-sector pulse counting instruments to quadrupoles.[20] The technique has been evaluated in a round robin study conducted by the National Bureau of Standards;[21] a number of laboratories were involved and results were at least as good as other round robins using conventional techniques.[22]

The resin bead is a versatile technique and can be used to collect samples other than uranium and plutonium by suitable alterations to the sampling medium and the form of the bead. We have applied it to neodymium, technetium,[23] and quaternary ammonium salts.[24] Partial separation of neodymium from samarium is achieved by extracting from a medium of 10% 1-1 HNO_3 and 90% methanol. Neodymium adsorbs more strongly than samarium under these conditions. Separation from samarium is not quantitative, but the amount of samarium left is small enough to allow it to be burned off the filament prior to analysis of neodymium.

We do not claim that the procedures described in this report are the only ones that will work, or even that they are the best ones. They have been evolved over about ten years' experience and work smoothly in our laboratory. It is to be expected that each technician will develop individual techniques best suited to his or her needs, but this document should serve to describe a good way to start.

We feel the resin bead's rapid sample acquisition, ease of handling, and excellent mass spectrometric behavior make it the sampling method of choice whenever it can be applied.

REFERENCES

1. R. L. Walker, C. A. Pritchard, J. A. Carter, and D. H. Smith, USDOE Report ORNL/TM-5505, July 1976.

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

3. J. A. Carter, R. L. Walker, R. E. Eby, and C. A. Pritchard, "Safeguarding Nuclear Materials," IAEA-SM-201/9, Vienna, 1976, Vol. 2, p. 461.

4. D. H. Smith, R. L. Walker, L. K. Bertram, J. A. Carter, and J. A. Goleb, Anal. Lett. 12(A7), 831 (1979).

5. D. H. Smith, R. L. Walker, and J. A. Carter, J. Inst. Nucl. Materials Management 8(4), 66 (1980).

6. J. A. Carter, R. L. Walker, D. H. Smith, and W. H. Christie, Int. J. Environ. Anal. Chem. 8, 241 (1980).

7. R. L. Walker, D. H. Smith, J. A. Carter, D. L. Donohue, S. Deron, Y. Asakura, K. Kagami, S. Irinouchi, and J. Masui, J. Inst. Nucl. Materials Management 10(3), 43 (1981).

8. R. L. Walker, J. A. Carter, and D. H. Smith, Anal. Lett. 14(A19), 1603 (1982).

9. D. H. Smith, R. L. Walker, and J. A. Carter, Anal. Chem. 54, 827A (1982).

10. J. P. Faris and R. F. Buchanan, Anal. Chem. 36, 1158 (1964).

11. S. F. Marsh, R. M. Abernathey, and J. E. Rein, Anal. Lett. 13(A17), 1487 (1980).

12. M. Dubois, private communication.

13. D. H. Smith, ORNL/TM-7002, Sept. 1979; ORNL/TM-8356, August, 1982.

14. D. H. Smith, Chem. Biomed, and Environ. Instrum. 10, 27 (1980).

15. D. H. Smith, W. H., Christie, and R. E. Eby, Int. J. Mass Spectrom. Ion Phys. 36, 301 (1980).

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

17. P. J. Todd, H. S. McKown, and D. H. Smith, Int. J. Mass Spectrom. Ion Phys. 42, 183 (1982).

18. D. H. Smith and J. A. Carter, Int. J. Mass Spectrom. Ion Phys. 40, 211 (1981).

19. L. W. Green, N. L. Elliot, and T. H. Longhurst, Anal. Chem. 55, 2394 (1983).

20. D. H. Smith, J. R. Walton, H. S. McKown, R. L. Walker, and J. A. Carter, Anal. Chim. Acta 142, 355 (1982).

21. J. D. Fassett and W. R. Kelly, Anal. Chem. 56, 550 (1984).

22. W. Beyrich and P. de Bievre, IAEA International Symposium on Recent Advances in Nuclear Safeguards, IAEA/SM-260/33, Nov. 1982.

23. T. J. Anderson and R. L. Walker, Anal. Chem. 52, 709 (1980).

24. G. L. Glish and D. H. Smith, Int. J. Mass Spectrom. Ion Phys. 51, 39 (1983).

APPENDIX 1

A TECHNIQUE DESIGNED TO DELIVER APPROXIMATELY 1000 RESIN BEADS

A. Preparation of resin bead stock mixture

1. Using a 10-ml graduated, glass-stoppered centrifuge cone, add anion resin beads in the NO_3^- form to a volume of 4 ml.

2. Add triple distilled H_2O to cone to a total volume of 7 ml.

B. Bead delivery to sample container

1. By hand, shake stoppered cone until beads are uniformly mixed and suspended in the water.

2. Without delay, remove stopper and withdraw a few drops of mixture into a medicine dropper (one that will deliver $\sim$20 drops per ml).

3. Quickly deliver one (1) drop of the resin bead-H_2O mixture into a 15-ml polyethylene sample bottle.

4. Set aside for later addition of prepared sample solution for bead adsorption step using vortex mixer.

APPENDIX 2

PREPARATION OF STAINLESS STEEL LOOPS FOR USE IN LOADING RESIN BEADS

1. Cut a 12-13 cm length of 0.5 cm diameter stainless steel wire.

2. Immerse about 1 inch of one end into HCl at 80°C until 1 cm of the end has a diameter of 200 μm or less.

3. Clamp about 1 mm of pointed end with hemostat and bend to about a 60° angle.

4. Clamp about 1.5 mm and make another 60° bend.

5. Bend the 1 mm (Step 3) until end is at or near (do not overlap) side of wire, forming an oblong loop with a size about 400 x 800 μm.

6. Electropolish the loop in a 1:3 mixture of glycerin and H_3PO_4 until the wire of the loop has a diameter of about 100 μm.

7. Boil loop in 1:1 HNO_3.

8. Rinse with a 3X distilled H_2O and acetone.

9. Dry with lint-free absorbent paper.

10. Insert into a Corning 25-microliter disposable pipet to give ease of manipulation.

APPENDIX 3

PREPARATION OF POLYETHYLENE FUNNELS FOR RESIN BEAD ADSORPTION

Because of the small quantities of sample required (ca. 1 ng), extreme care must be taken to avoid contamination of the beads either from the environment or from other samples.

A. Preparation of resin beads (anion or cation)
   1. Put ∿2 ml of resin beads in a 10 ml centrifuge cone.
   2. Add ∿3 ml of 3 x D (three times distilled) 8 M HNO_3.
   3. Mix on vortex mixer ca. 10 min.
   4. Centrifuge, withdraw, and discard aqueous.
   5. Add ∿3 ml of 3 x D H_2O.
   6. Mix on vortex mixer 1-2 min.
   7. Centrifuge, withdraw, and discard aqueous.
   8. Repeat steps E, F, and G to neutral (ca. 7x).
   9. Add 3 x D H_2O and let stand for use.

B. Preparation of polyethylene funnels for resin beads.
   1. Count the funnels, filters and stoppers (top and bottom) needed.
   2. Insert filter into funnel.
   3. Leach all parts in ca. 4 M HNO_3 for about 30 min.
   4. Drain off HNO_3.
   5. Rinse 3 or 4 times with distilled H_2O.
   6. Rinse 2 times with acetone and air-dry in laminar hood or an area known to be clean.

C. Loading anion resin beads in polyethylene funnel for element adsorption.
   1. With the aid of a 10 cc syringe and a new HNO_3-leached Pasteur pipet, withdraw 1 cm (ca. 500 beads) of the preparation from A.

2. Extrude slurry of resin beads onto a new HNO_3-leached microscope slide.
3. Pull H_2O from resin beads by absorption with Kimwipe or equivalent.
4. Put 2 μl of 8 M 3 x D HNO_3 on funnel filter below white spot on side of funnel.
5. Using HNO_3-leached stainless steel needle, pick up one or more resin beads.
6. Put end of needle into the 2 μl of 8 M HNO_3 in polyethylene funnel and beads will be released from the needle.
7. Repeat steps E and F until desired number of beads are in the funnel.

D. Loading cation resin beads in polyethylene funnel for element adsorption.

Same as C except step 4 should be 2 μl of 3 x D H_2O.

APPENDIX 4

EQUILIBRATION OF PLUTONIUM

The exhaustive study of Marsh, et al.[11] should lay to rest the controversy surrounding isotopic equilibration of plutonium for isotope dilution analyses. The problems created by the multiplicity of valence states in which plutonium can simultaneously be present and the tendency of many complexes of that element to polymerize have led to a number of solutions that were more or less successful. Marsh and his colleagues compared ten procedures and found only one that consistently yielded complete equilibration between spike and sample. The preferred procedure involves first reducing with ferrous sulfamate (0.04 mmol Fe (II) and 0.15 mmol sulfamic acid in 5 M HNO_3 for 75 μg of ^{239}Pu). This is followed by oxidation with sodium nitrite (0.9 mmol $NaNO_2$). This procedure gave a value of 0.999 ± 0.003 for the ratio of $^{239}Pu/^{242}Pu$ adsorbed relative to the initial value of this ratio.

A second method is used when analyzing aged dissolver solutions or other sample types containing molecular species. Destruction of polymers and complexes is achieved by evaporating the spiked aliquants to near dryness with $HClO_4$ and HF; the reduction and oxidation steps described above are then executed.

APPENDIX 5

Pu-U RESIN BEAD STANDARDS AND SAMPLES
1000 BEAD PREPARATION

I. SCOPE

This procedure makes possible uniform loading of a point source of ions for mass spectrometer calibration or for quality-assurance purposes. The reduction of radiation by this process makes safer working conditions for the employees as well as simplifying preparation for sample shipment.

II. SUMMARY OF PROCEDURE

One thousand micrograms of uranium and 10 μg of plutonium are equilibrated in 10 ml of 8 M HNO_3 in a 16-ml polyethylene bottle. One thousand anion resin beads are added to the solution (See Appendix 1), mixed 10 minutes on vortex mixer and separated from the solution by filtering through the small polyethylene funnel.

III. SUPPLIES FOR PROCEDURE

A. Reagents

1. Triple distilled 8 M HNO_3 (3 X 8 M HNO_3). Prepared by diluting 51.3 ml of 15.6 N triple distilled HNO_3 to 100 ml with triple distilled H_2O.
2. Anion-exchange resin. Use Dowex 1-X2, 40-60 mesh, and convert to nitrate form with 8 M 3X HNO_3 wash. Wash to pH7 with 3X H_2O and store in 3X H_2O.
3. Triple distilled H_2O (3X H_2O). Double distillation of house distilled H_2O from a quartz still.

B. Apparatus

1. New one-half ounce polyethylene bottle. Leach bottle in 4 M reagent grade HNO_3 one hour or more, rinse well with house distilled and 3X H_2O. Dry with acetone.
2. Pasteur disposable pipets. Clean as in step 1.
3. Small polyethylene sample funnel for use with porous polyethylene disc and top and bottom stoppers. Cleaned as in step 1.
4. Pipet control. Use 10 cc medical syringe.
5. Vortex test tube mixer. Use four position mixer by Scientific Industries, Inc., Springfield, MA.

IV. PROCEDURE

A. Pipet 1000 μg uranium standard and 10 μg plutonium standard into a one-half oz. polyethylene bottle and adjust to a volume of 10 ml and 8 M HNO_3.*
B. Mix for isotopic equilibration.
C. Using a Pasteur pipet, pull 2 cm of resin bead slurry into pipet and extrude into bottle.
D. Put cap on bottle and secure with 1-inch masking tape wrapped around cap and bottle shoulder. (If not secured, cap will screw off due to mixing action.)
E. Secure in position on vortex mixer and mix 8-10 minutes.
F. Position small polyethylene sample funnel on vacuum flask with low vacuum pull.
G. Using Pasteur pipet and control, transfer contents of the one-half ounce polyethylene bottle into the small polyethylene sample funnel.
H. Rinse resin beads in small funnel with 1 ml of 8 M 3X HNO_3.
I. Place top and bottom stoppers in funnel and store in properly documented 5 cc plastic vial to be used as needed.

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*Uranium or plutonium may be omitted for a single element preparation, and the time limit in E may be extended.

APPENDIX 6

PREPARATION OF SAMPLES IN A HOT CELL FOR RESIN BEAD LOADING

1. REAGENTS

   1.1 Nitric acid, conc. ACS reagent grade, triple distilled.

      1.1.1 Nitric acid, ca. 8 M. Dilute conc. acid with equal amount of dist. H_2O.

      1.1.2 Nitric acid, ca 5 M. Dilute 1 part conc. acid with 2 parts dist. H_2O.

   1.2 Anion resin, Dowex 1 x 2, 50-100 mesh, nitrate form.

   1.3 Mixed spike solutions; these must be well calibrated, and the aliquots for analysis should contain ca 0.8 mg ^{233}U and ~0.005 mg ^{242}Pu on weight basis.

   1.4 0.25 M Fe(II) - 1 M NH_2SO_3H (sulfamic acid) mixture; in a 100 ml volumetric flask, dissolve 7 g of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in about 50 ml of distilled water containing 1 ml of conc. H_2SO_4, and to the same flask add 9.7 g sulfamic acid. Dilute to volume with distilled water.

   1.5 3 M $NaNO_2$ - dissolve 2.07 g in 10 ml distilled water; make fresh daily before using.

2. SPIKED SAMPLE PREPARATION PROCEDURE

   2.1 Operations performed outside the analytical hot cell.

      2.1.1 Label two (2) 15-ml polyethylene bottles for each sample. One is used first to obtain the weights of the mixed spike and then the weight of the sample aliquant; the second bottle is used for subsequent containment of the equilibrated sample solution and resin beads.

      2.1.2 Obtain a tare weight on the bottle intended to contain sample plus spike; include the cap in the weighing.

      2.1.3 Add mixed ^{233}U and ^{242}Pu spikes. Reweigh and record spike weight to nearest 0.1 mg.

2.1.4 Label another bottle Fe(II) - NH_3SO_3; add about 1 ml of this solution.

2.1.5 Label another bottle $NaNO_2$; add about 1 ml of this solution.

2.1.6 Add approximately 1000 beads to the second bottle intended to contain the equilibrated spike-sample mixture plus beads (Step 2.1.1). Appendix 1 outlines a procedure for delivery approximately 1000 beads to the bottle.

2.1.7 One funnel for each sample, to be used to transfer the sample to the bottle containing the resin beads.

2.1.8 One plastic pipet for each sample, to be used to add the sample aliquant to the bottle containing the mixed spike.

2.1.9 One bottle containing approximately 10 ml of 8 M HNO_3 per sample.

2.1.10 For each sample preparation, spiked and unspiked, take a polypropylene Econo-Column and break off the tip. Place the column in one of two 30-ml plastic bottles needed for this operation. Very gently insert a #7 cork stopper into the top of the column. This permits its later removal with the manipulator in the cell (Step 2.2.11). Two bottles are needed—one to hold the column and catch the filtered waste and the second to hold the column after preparation (Steps 2.2.15 - 2.2.18).

2.1.11 All the above items are introduced into the analytical hot cell.

2.2 Operations performed in the analytical hot cell with manipulators.

2.2.1 Prepare a 150-200 fold dilution of the input solution. Obtain a tare weight for a 100 ml polyethylene bottle. Add by pipet or medicine dropper ca. 0.5 ml of input solution to the bottle and reweigh. Dilute to 100 ml with 5 M HNO_3 and reweigh to determine weight of diluted sample. Record weights of the input solution and the diluted sample to ±0.1 mg. Mix well by shaking.

2.2.2 Reweigh the bottle containing the spikes to ±0.1 mg. This will be the tare weight for the sample aliquant and should be the same as the recorded weight after spike addition (Step 2.1.3).

2.2.3 Add an aliquant of the diluted sample containing 1 mg of U using a plastic pipet, cap and weigh to ±0.1 mg. Net weight equals the weight of sample aliquant added.

2.2.4 Dilute the spike and sample mixture to about 3 ml with distilled H_2O.

2.2.5 Add three (3) drops of Fe(II)-sulfamic solution and heat at 60°C for 20 minutes using a heat lamp.

2.2.6 Add six (6) drops of 3 M $NaNO_2$ and shake by hand with a manipulator for about 2 minutes.

2.2.7 Add enough concentrated HNO_3 and distilled H_2O to bring the sample to approximately 8 M HNO_3 in a volume about 10 ml. (About 2 ml distilled H_2O + about 4.5 ml concentrated HNO_3).

2.2.8 With the aid of a plastic funnel, pour the equilibrated sample into the bottle containing approximately 1000 anion beads and cap tightly.

2.2.9 Place on the vortex mixer and agitate for 10 minutes at low setting. The beads are now ready to be separated from the solution.

2.2.10 Remove the cap from the bottle containing the beads and the 8 M HNO_3.

2.2.11 With one of the manipulators, gently remove the cork stopper and hold until ready to replace it.

2.2.12 With the other manipulator, put a clean funnel into the top of the filter column. Pour the solution and beads while swirling into the column.

2.2.13 After the solution has drained, wash the beads with 1 ml of 8 M HNO_3.

2.2.14 Carefully remove the column and replace the cork stopper. Press stopper in firmly.

2.2.15 Pick up the column by grasping the cork stopper and transfer it to the clean 30-ml bottle.

2.2.16 Remove and discard the cork stopper.

2.2.17 Transfer the bottle containing the column with beads out of the cell.

2.2.18 Without handling the bottle, remove the column with plastic gloves.

2.2.19 Touch the tip of the column with a clean tissue to remove any remaining liquid; discard the tissue into radioactive waste container.

2.2.20 Put the original cap on the column and check for radiation and contamination on the outside; if any is found, decontaminate.

2.2.21 Put the column inside two plastic bags for shipment to the mass spectrometry laboratory.

NOTE: The total activity of all beads loaded can on occasion be too high (more than 10 mR/hr) to allow removal to the mass spectrometry laboratory. In this case, it is necessary to isolate a few of the beads to reduce activity to an acceptable level. Several beads may be removed by adding a small amount of 1:1 HNO_3 to the beads with a pipet and slurrying; a few beads can then be removed by suction to a small preparation funnel. These operations can be performed in a laboratory hood outside the hot cell.

3. UNSPIKED SAMPLE PREPARATION

3.1 Operations performed in the analytical hot cell with manipulators.

3.1.1 Add 9 ml of 8 M HNO_3 to a clean, 15-ml polyethylene bottle containing 1000 anion resin beads previously prepared outside the hot cell as for spike sample (Step 2.1.6).

3.1.2 Deliver an aliquant of the diluted sample containing 1-2 mg U using a pipet or medicine dropper to above.

3.1.3 Follow the procedure given for spiked sample preparation by repeating Steps 2.2.9 through 2.2.21.

APPENDIX 7

OPERATING PROCEDURES FOR ANALYZING SAMPLES ON ORNL MASS SPECTROMETERS

INTRODUCTION

The amount of bias correction per mass required for any sample is a function of the region of the fractionation curve that data are taken. It thus becomes important to treat all samples as nearly identically as possible. This places stringent requirements on sample treatment prior to data taking. Among the variables affected by these considerations are: quantity of sample loaded, duration and temperature of heating the filament for focusing purposes, instrument calibration, and data collection technique.

INSTRUMENT CALIBRATION

Calibration of the instrument is divided into two measurements which have different requirements for optimum results. Determination of the bias correction should be done using standard loadings that approximate those expected during routine operation. This means that the NBS-U500s should either be loaded on beads or, when loaded as solutions, only a quantity roughly equal to that loaded for routine samples should be used. Our experiments indicate that 10 ng of a solution loading of U closely approximates the behavior of U from a resin bead. This means that 20 ng of NBS-500 would be required because the abundance of the major isotope is about 50%. This will tend to give the same counting rate of $^{238}U^{+}$ at a given temperature that a 10 ng solution loading of NBS-010 would give. NBS-500s should be analyzed at the same counting rate as routine samples (300-350K counts/sec). Dead time determination requires a higher counting rate (500-650 K counts/sec) to improve statistics on ^{234}U. Fifty-ng loadings should be ample for this determination.

SAMPLE PRETREATMENT AND FOCUSING

A. Solution Loadings

1. Solution loadings should deliver about 10 ng U or 1-2 ng Pu to the filament. Reduction with benzene should be effected at ca. 1300°C for ca. 30 sec.

2. To focus, increase the temperature gradually (1-2 min) to obtain enough signal for focusing; this will usually be about 1600°C for U (Oak Ridge pyrometer reading). Optimize focus conditions.
3. Slowly increase the temperature until the count rate is 300-350K counts/sec on the most abundant isotope. This should take about 5 min.
4. Recheck focus conditions, keeping the count rate between 300K/sec and 350K/sec. Check the stability of the beam by observing the count rate over successive one-minute intervals. Do not begin data acquisition until the signal stops growing. If there is any increase in signal intensity during a given minute, repeat the one-minute observation. Slight decay (∿2%/min) is permissible.
5. Start taking data, monitoring the count rate by observing the height of the most abundant peak on the oscilloscope at the end of each run. Recheck focus conditions if excessive decay is observed.
6. In any case, halt data accumulation after 3 runs. Optimize focus conditions and restore the desired count rate by increasing temperature.
7. Again monitor total counts/run, halting data accumulation if the signal intensity increases.
8. Continue as above until the end of the analysis (usually 10 runs).

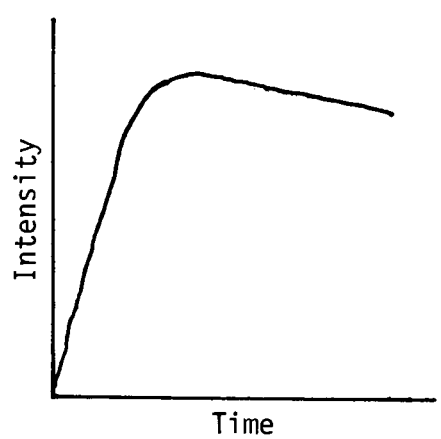
B. Resin Bead Loadings

1. To run Pu and U sequentially from a single resin bead, bring the temperature up very slowly until a pressure burst indicates destruction of the bead.
2. Slowly increase the temperature until Pu^+ ions are observed; optimize focus conditions.
3. Increase the temperature slowly until the intensity of the most abundant Pu isotope (usually 239) reaches 100K counts/sec. Recheck focus conditions.

4. Proceed as described in 5-8 above, being careful not to exceed 1500°C (Oak Ridge pyrometer reading).
5. At the end of Pu analysis, slowly increase the temperature to burn off excess Pu. Monitor the 238/239 ratio; 239 should not be allowed to fall continuously on the collector until its intensity reaches reasonable levels (∿500K counts/sec).
6. When 238/239 >2, increase the temperature until the count rate on the most abundant U isotope is 300-350K/sec. Do not burn Pu off for more than 15 min if you can possibly avoid it.
7. Accumulate U data as described in 5-8 above.

NOTES:

1. There are significant variations between readings of the same filament by different pyrometers. The temperatures quoted are those observed at Oak Ridge.
2. The intensity curve of a typical sample has the following approximate shape:



The goal of these instructions is to insure that data from solution loadings are taken after the maximum in the curve. The reason Pu from resin beads requires 0.3%/mass more bias correction than from solution loadings is that data are being taken on the steeply ascending portion of the curve; thus the lighter isotopes are in higher abundance and higher discrimination corrections are necessary to compensate for the bias.

APPENDIX 8

PREPARATION OF ENVIRONMENTAL WATER SAMPLES FOR URANIUM ANALYSIS

INTRODUCTION

One of the functions of our mobile laboratory equipped with a quadrupole mass spectrometer[20] was to analyze environmental water samples for uranium. Because of limited time and space, it was necessary to devise a simplified, faster sample preparation scheme. The procedure we developed is described in this appendix.

I. Scope

This procedure is designed for expeditious preparation of water samples for mass spectrometric analysis where the time involved is to be minimized.

II. Summary of Procedure

Collect sample in a new 250 ml polyethylene bottle, add 1 ml HNO_3 and mix vigorously (sample is 0.06 N HNO_3). Pipet 1 ml of sample and 1 ml ^{233}U spike (65.6 ng/ml) into a 50 ml beaker, mix by swirling, and evaporate to complete dryness over low flame under heat lamp. Take up in 20 μl loading solution (0.10 N HNO_3), load 1 μl in rhenium canoe filament with resin bead and dry under heat lamp. Add 1 μl (10 μg) sucrose solution and dry under heat lamp if improved sample reduction is desired. Crimp filament to retain resin bead and load filament in mass spectrometer.

III. Supplies for Procedure

A. Reagents

1. Triple distilled HNO_3 (3 x D HNO_3). Prepared from reagent grade HNO_3 by distilling from a quartz flask three times.
2. Triple distilled H_2O (3 x D H_2O). Prepared by double distilling house distilled H_2O.

3. Loading solution (0.10 N HNO_3). Prepared by mixing 0.65 ml 3 x D HNO_3 with 99.35 ml 3 x D H_2O.
4. Sucrose solution (10 mg/ml). Prepared by dissolving 100 mg sucrose in 10 ml 3 x D H_2O.
5. Anion resin beads (Dowex 1 - X2). Prepared by scrubbing 1 ml of resin beads with 4 ml of 8 M 3 x D HNO_3 for 10 minutes, withdrawing HNO_3 and scrubbing beads with 4 ml volumes of 3 x D H_2O; use successive 1-minute scrubs until neutral. Store in 3 x D H_2O.

B. Apparatus

1. Beakers (50 ml). Clean new beakers by boiling in 4 M reagent grade HNO_3, rinse with house distilled H_2O, 3 x D H_2O and acetone. Dry and seal in polyethylene bag.
2. Eppendorf pipet controls and tips.
3. Disposable pipets (1 and 25 μl) by Fisher.
4. Microscopes (2).
5. Microscope slides (new). Cleaned by boiling in 4 M reagent grade HNO_3, rinsed with house distilled H_2O, 3 x D H_2O and acetone.
6. Stainless steel needles (5" long). Cleaned as in Step 5.
7. Curved tip tweezers. Cleaned by dipping in hot 1 M reagent grade HNO_3, rinsing with house distilled H_2O, 3 x D H_2O and acetone.
8. Hemostat. Cleaned as in Step 5.
9. Rhenium filaments. Cleaned by boiling in citric acid, 2 x in house distilled H_2O, rinsed with house distilled H_2O and dried in oven @ 110°C. Filaments are baked @ 1900°C @ 5 x 10^{-7} torr for 1 hour.
10. New polyethylene bottles (250 ml) packaged by vendor: 12 bottles/bag and 12 bags/case.

    Vendor: Preiser Scientific, Inc.
    P. O. Box 551
    900 McCorkle Ave., SW
    Charleston, W. Va. 25322

IV. Procedure

A. Sampling, Treatment and Documentation

1. At sample point, rinse a 250 ml polyethylene bottle with water to be sampled.
2. Fill bottle to shoulder with sample.
3. Mark sample with identification of sample point.
4. Add 1 ml of concentrated 3 x D HNO_3 and mix vigorously.
5. Enter in sample log and assign a Laboratory number.

B. Equilibration of Isotopic Dilution

1. Pipet 1 ml of sample into a 50 ml beaker.
2. Pipet 1 ml of ^{233}U spike solution into beaker with sample.
3. Swirl to mix sample and spike.
4. Place on wire gauge over low flame and evaporate to dryness.
5. Turn on heat lamp over beaker to insure complete dryness.

C. Set-up for Loading Sample

1. Place microscope slide containing anion resin beads on stage of No. 1 microscope.
2. Place hemostat holding filament on stage of No. 2 microscope.
3. Using stainless steel needle, pick up a resin bead at No. 1 and transfer to center of canoe shaped filament at No. 2 microscope.
4. Using curved tipped tweezers, squeeze sides of boat against bead to insure center location during loading of sample.

D. Loading Sample for Mass Spectrometer

1. Take up in 20 μl of loading solution by warming under heat lamp.
2. Load 1 μl of solution in the filament containing one anion resin bead.
3. Dry under heat lamp.
4. Pipet 1 μl (10 μg) sucrose solution into filament.
5. Dry under heat lamp.
6. Crimp with tweezers to retain resin bead.
7. Submit for mass spectrometric analysis.

APPENDIX 9

SOURCES OF EQUIPMENT

Catalog Number	Description and Source
K420160-9004	Columm, tip only, Kontes Scientific Glassware/Instruments, Vineland, NJ 08360
K420162-0000	Disc, polyethylene (filter), as above.
063369-0101	Column plug and cap; specially made according to Y-12 Drawing No. T2B-29681
731-1110	Polypropylene Econo-Column, Bio Rad Laboratories, 32nd and Griffin Ave., Richmond, CA 94804
Model K-500-4	Vortex test tube mixer, 4 position, Scientific Industries, Inc., Springfield, MA
M5-47797	Wild Microscope, Heerbrugg, Switzerland
YB6145	Bausch & Lomb microscope, Chicago Apparatus Co., Chicago, IL
09-745-7250	Hypodermic syringe for pipet control, Company Stores
15-014-9600	Polyethylene bottle, 1/2 oz., Company Stores
15-017-5266	Polystyrene vial w/polyethylene cap, 5 ml, Company Stores
15-093-2265	Forceps (tweezers), curved points, Company Stores
15-169-5350	Pipette, Pasteur, disposable, Company Stores
Chemicals	Ultrex nitric acid - J. T. Baker Chemical Co., 1037 Lower Brownsville Rd., Jackson, TN 38301

Resin, anion, Dowex 1-X2, 50-100 mesh, or equivalent.

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