

Analysis of Plutonium and Uranium by the Resin
Bead-Mass Spectrometric Method*

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ABSTRACT

The development of the resin bead method and the techniques employed in its application to isotopic analysis of Pu and U in highly radioactive solutions of spent reactor fuel will be described. The method, developed primarily for safeguards analyses, may also be applied to isotopic measurements for assessing nuclear fuel cycle technology. Satisfactory analyses of both elements can be obtained from a single resin bead when the initial dissolver solution has a U/Pu ratio in the range of 50 to 300. Optimum bead loadings are 1-3 ng Pu and U; these loadings are obtained if the concentration of the solution is adjusted to about 1 μ g U per bead before the beads are introduced. Isotopic composition measurements of NBS standards using this technique indicate a precision of $\pm 0.5\%$ for minor isotopes in the 1% concentration range and $\pm 0.1\%$ for major isotopes in the 50% range. Analyses of a synthetic dissolver solution give an accuracy for the isotope dilution measurement of Pu and U of $\leq 0.5\%$ with an internal precision of 0.9% and 0.6% for Pu and U, respectively.

KEYWORDS: Resin bead, mass spectrometry, plutonium, uranium, isotope dilution, safeguards

INTRODUCTION

Limitations on the amounts of radionuclides that can be readily shipped make it desirable to perform the analytical measurements required by safeguards on as small samples as possible. This is particularly true for Pu, an element of major safeguards concern.

The use of anion exchange resins to achieve chemical separations is well known.^{1,2} We have extended this idea to use individual resin beads as vehicles for introducing samples into mass spectrometers. The sequential isotopic analysis of Pu and U in spent fuels by the anion resin bead method was first demonstrated at ORNL in 1974.³ Some years earlier, a similar approach had been investigated for isotopic uranium analysis utilizing fully-loaded cation resin beads.⁴ Our procedure involves adsorbing U and Pu from solutions of suitable concentration onto enough resin beads to supply a sufficient number for analyses; one resin bead serves as one sample for the mass spectrometer and contains 1-3 ng each of U and Pu.

The method shows great promise for analyzing Pu and U from highly radioactive spent fuel solutions for process control and for safeguards accountability. The beads can be packaged and shipped or mailed without requiring shielding or other precautionary measures to protect people handling them from radioactivity. Mass spectrometric analysis, which requires instruments equipped with pulse counting detection systems, yields results comparable to those obtainable using conventional chemical separation and mass spectrometry.

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364

RESIN BEAD METHODOLOGY

The method is outlined in Fig. 1 and involves the use of anion resin in a dilute solution of the sample adjusted to $\sim 8 \text{ M HNO}_3$ to selectively adsorb nanogram quantities of Pu and U. The original work done here with the method was designed for an in-house problem with the hope of reducing time, complexity, and cost of the chemical separation and reducing the alpha radioactivity in the mass spectrometry laboratory and in the source region of the mass spectrometer. Under the conditions specified, Pu and U have distribution coefficients of 10^4 and 10^2 , respectively. This favors the adsorption of Pu over U, which results in a Pu/U ratio on the beads of about 1:1 for dissolver solutions whose original Pu/U ratio is 10^{-2} . For the chemical isolation step, an aliquot of diluted dissolver sample is taken so that there will be 1-2 μg of U per resin bead in the adsorption apparatus. The amount of Pu may be predicted from burn-up and reactor characteristics, but usually the quantity accompanying uranium is adequate.

Aliquots for spiking are taken which contain $\sim 1 \text{ mg U}$ and $\sim 10 \mu\text{g Pu}$, where possible. Highly enriched spikes of ^{233}U and ^{242}Pu are added and isotopic equilibration is carried out. We are using HClO_4 and HF to achieve Pu valence adjustment. We have had good results with this technique but are looking at other techniques to eliminate the use of HClO_4 .

Actinide elements that adsorb in 8 M HNO_3 are Th, U, Pu, and Np; rare earths, Am and Cm do not adsorb. Np is not an interferent in the mass analysis since there are no Np isotopes with long enough half lives to interfere at Pu or U mass positions. Although Np gives no significant mass interference, its presence must be considered in terms of the over-all radioactivity that is on a bead since ^{237}Np ($T_{1/2} = 2.1 \times 10^6 \text{ a}$) will be present in spent fuel dissolver samples. Decontamination factors from Am have been measured at $>10^3$. Although some ^{241}Am will be present on the bead from the original solution, most that is there will grow in from the β decay of ^{241}Pu . This small amount can be eliminated after loading into the mass spectrometer before taking Pu data. A discussion of this will be given in a later section on the procedure for analysis of resin beads.

The optimum concentration of HNO_3 is near 8 M , but a range of $\pm 5\text{-}10\%$ around this value is all right for the adsorption. Usually 10 resin beads are used for each adsorption; only two are needed for duplicate analyses, but if beads are lost or if rechecks are needed, a reserve supply is convenient to have for this purpose.

MASS SPECTROMETRY

The mass spectrometers in our laboratory have been previously described.^{5,6} Development of the resin bead technique was done primarily on multi-stage instruments, but a single-stage mass spectrometer has also been successfully used.⁷ The instruments have 90° sector magnets with 30 cm radii of curvature and are equipped with pulse counting detection systems to allow isotopic analysis of U and Pu samples of less than 1 ng.

Scanning the mass spectrum is accomplished by a locally designed sweep control unit interfaced to a DEC PDP-11/34 computer. Any peak in the spectrum can be scanned any pre-determined number of times for each single traversal of the entire mass range. This allows us to optimize our scanning scheme for the requirements of the sample in question. Multiple scans of minor isotopes yield better precision on measurements of their abundances.

We use a "ferris wheel" sample changer,⁸ which allows us to mount six samples in the mass spectrometer simultaneously. Each filament is rotated in turn into position for analysis, which takes 20-30 minutes per element.

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We analyze Pu and U sequentially from a single resin bead. Pu, because of its lower ionization potential, ionizes at temperatures below those required for U and is thus analyzed first. After evacuating the system to 5×10^{-8} torr or less, the temperature of the filament is slowly increased. A pressure burst is observed upon disintegration of the resin bead. The Pu^+ signal is found and brought into optimum focus. If ^{241}Am is present, it will be apparent as a shifting 241/242 ratio. The operator observes this ratio until it stabilizes before proceeding further. The temperature is increased to adjust the count rate on the most abundant Pu isotope (usually 239) to 100,000 counts per second; on no account is 1500°C exceeded because $^{238}\text{U}^+$ becomes too large at temperatures greater than this to be reliably corrected for. Pu data are collected, which takes about 20 minutes. Peak shapes and count rates are monitored continuously during the analysis to make sure it is proceeding smoothly.

After Pu analysis is complete, the temperature is again raised to burn off excess Pu. The ratio of $^{238}\text{U}/^{239}\text{Pu}$ is monitored; when it is greater than 1, the temperature is raised to give a count rate on the most abundant U isotope of 300-350,000 counts per second. The temperature will usually be $1700-1800^\circ\text{C}$ for U analysis, which now proceeds in a manner similar to Pu. It is undesirable to spend too much time burning off excess Pu; U is, of course, evaporating at the same time, and if too long is spent in this step, fractionation of U becomes a problem. We try not to spend more than 10-15 minutes burning off Pu.

We have been analyzing resin bead samples in our laboratory for more than 4 years and have come to prefer this method to loading solutions directly on the filaments. The resin bead serves as a good approximation to a point source for the ion optics, and spectra obtained from resin bead samples are generally cleaner than those obtained from solutions. The result is approximately an order of magnitude improvement in our ion collection efficiency.

QUANTITATIVE ANALYSIS

Mass spectrometric determination of quantities of U and Pu is accomplished through the technique of isotope dilution. In this technique, a known amount of an isotopically enriched spike of known composition is added to the sample solution. The sample and spike are equilibrated, after which it is not necessary to obtain complete recovery of the sample since isotopic ratios are unaffected. Knowledge of the isotopic compositions of spike, sample, and mixture of spike and sample is obtained by mass spectrometric analysis. These data, along with knowledge of sample and spike weights and the dilution factor allow calculation of the concentration of the element in question in the original sample.

ADSORPTION APPARATUS

Figure 2 is a photograph showing an apparatus we have designed to facilitate collecting and shipping samples on resin beads. It consists of a commercially available funnel-shaped liquid chromatographic column tip, a porous filter, a plug, and a cap; the individual pieces are made of polyethylene. The plug and cap are made to our design and may be ordered from Kontes of Illinois, P. O. Box 30, Evanston, IL 60204, by specifying UCND-Y-12 Dwg. T2B-29681; the tip and filter may be purchased from Kontes Glass Co., Vineland, NJ 08360. The entire assembly costs about \$2.00.

In use, an inspector will assemble the funnel, filter, and plug, and introduce a small volume of the solution to be sampled into the unit. The only chemical treatment required is adjusting the solution in pH and U concentration unless it is spiked, where isotopic equilibration of Pu requires adjustment of its oxidation state. Sufficient resin beads are added to provide the required number of replicate analyses; the usual number is ten.

After standing for the appropriate length of time, the plug is removed with the help of an especially designed vial with an insert to grip it and a holder to grip the funnel. The solution drains out, the beads are washed, and the plug and cap inserted. The apparatus, with the sample on the resin beads, is now ready for shipment.

The amount of radioactivity on samples prepared in this way is an order of magnitude below the daily exposure allowed to office workers. Since the bulk of the activity is due to

a emission, the shielding provided by the funnel and its packaging reduces this low level even further. We feel that samples prepared in this way can be shipped through the mail with complete safety.

RESULTS AND DISCUSSION

Early experiments using the resin bead method were designed to elucidate the method's reliability and precision, and to compare resin bead results with results from the conventional, solution-loading technique in normal use.

Time studies were conducted to determine the amount of Pu and U that would adsorb on anion beads from a solution under static conditions. The time required to achieve near maximum adsorption is between 20-30 hrs. Very similar adsorption vs. time curves are obtained from a solution having a Pu/U ratio of 10^{-2} and in which ~ 10 ng of Pu and 1 μ g U per bead are present. One to three ng of each element will adsorb under these conditions. We are now recommending a 24-hr. adsorption time.

Other tests have been made to determine precision of isotopic analysis at various Pu loadings. A set of graded ^{239}Pu standard solutions in 8 M HNO_3 were prepared which contained 10-0.01 ng per resin bead. After 40 hrs., we removed a bead from each concentration. Alpha counting was used to estimate the quantity on each bead. Isotopic analyses of duplicate beads were made to determine the minimum amount required for precise results, and to compare with results obtained from conventional filament loadings. Table I contains the results of these measurements. The minimum amount of Pu required on a bead to give sufficient signals is shown to be ~ 0.5 ng; below this the ^{238}U contamination and background adversely affect the minor isotopes due to poor signal-to-noise ratio.

Table I. Plutonium Isotopic Analysis at Various Concentrations

Pu, ng/bead	Atom Percent				
	238	239	240	241	242
0.003	(0.023)	94.0	5.64	(0.31)	(0.027)
0.05	0.0124	94.135	5.572	0.262	0.0184
0.6	0.0095	94.136	5.579	0.259	0.0175
3.0	0.0095	94.132	5.581	0.260	0.0181
10 ng Pu Solution Load	0.0096	94.136	5.572	0.265	0.0175

One of the steps in the data processing program corrects each element for the isobaric contribution of the other to the mass 238 position. This is accomplished by monitoring ^{235}U during Pu analysis and ^{239}Pu during U analysis. This correction is quite small for U, but can be fairly substantial for Pu. The effectiveness of this correction for Pu was tested by measuring Pu-238/239 ratios of a typical dissolver solution after chemically separating the Pu using the thenyltrifluoroacetone (TTA) method. A ratio of 0.01156 compares quite well with the resin bead value of 0.01158. Results of these tests are given in Table II.

The correction and the determination can only be made accurately on high burn-up fuel where the Pu-238/239 ratio is ~ 0.01 and the U-238/235 is ≤ 100 . Thus, if the best possible mass spectrometric result for ^{238}Pu is required, U is stripped off the bead with 1-3 M HNO_3 and the two elements are analyzed separately.

Table II. Pu-238 Analysis from Single
Bead-Corrected for U-238

Sample	Uncorrected for ^{238}U		Corrected for ^{238}U	
	238/239 Pu		238/239 Pu	
1	0.01302		0.01146	
2	0.02157		0.01167	
3	0.01523		0.01170	
4	0.01163		0.01158	
5	0.01176		0.01160	
6	0.01215		0.01146	

Avg. = 0.01158 = 0.9%

Pu-238/239 value after TTA extraction, 0.01156
Single element solution filament loading.

Additional tests were made by analyzing NBS plutonium and uranium standards. The isotopic data for U (SRM-015) and Pu (SRM-947) are summarized in Tables III and IV, respectively. No mass discrimination for either element is observed, and results obtained are comparable in precision to our measurements made from solution filament loading.

Table III. Isotopic Analysis of SRM-015
Std. by Resin Bead Method

Sample	234	Atom Percent		
		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
Resin Bead Avg.	0.00854	1.538	0.0164	98.437
Std. Dev.	0.00008	0.009	0.0001	0.009
NBS Value	0.00850	1.532	0.0164	98.443

Table IV. Isotopic Analysis of SRM-947
Std. by Resin Bead Method

Sample	238	239	Atom Percent		
			240	241	242
1	0.291	76.235	18.451	3.828	1.195
2	0.293	76.213	18.460	3.843	1.191
3	0.290	76.243	18.477	3.803	1.187
4	0.292	76.209	18.464	3.838	1.197
Avg.	0.292	76.225	18.463	3.828	1.192
Std. Dev.	0.001	0.017	0.011	0.018	0.004
Corr. to 10/13/71	0.297	75.647	18.328	4.544	1.184

Table IV - Continued

	Atom Percent				
	238	239	240	241	242
NBS Certified Value					
10/13/71	0.296	75.696	18.288	4.540	1.180
95% C.L.	0.006	0.022	0.022	0.006	0.004

Table V presents data we obtained from mixed Pu and U NBS standards by the technique over a two-month period; all data presented were obtained from sequential analyses from single resin beads. Agreement between our results and NBS certified values is excellent.

Table V. Mixed Pu and U Standards
on Resin Beads

	NBS-947 Pu			
	238/239	240/239	241/239	242/239
NBS	0.00370	0.24147	0.04309	0.01559
ORNL	0.00371	0.24156	0.04281	0.01559
S.D.	±0.00002	±0.00057	±0.00025	±0.00008

	NBS-500 U		
	234/235	235/238	236/235
NBS	0.01042	0.99971	0.001519
ORNL	0.01034	0.99851	0.001522
S.D.	±0.00005	±0.00209	±0.000005

N = 9 analyses run over a two-month period.

Another, and probably more significant, series of measurements defined the precision and accuracy of the method. Table VI shows the results obtained on synthetic dissolver solutions in which all operations, i.e., weighing, aliquoting, spiking, and isotopic equilibration, were carried out using procedures identical to those for actual radioactive samples. These results indicate an accuracy well within 0.5% from the standard value, with internal precisions of 0.9% and 0.6% for Pu and U, respectively.

Table VI. Results of Synthetic Spent
Fuel Dissolver Solution

Element	Std. Value mg/g	Measured mg/g	Percent Bias
Pu	2.356	2.361 ± 0.021	+0.21
U	231.5	232.5 ± 1.4	+0.43

N = 12 analyses for each element.

Further work is currently underway or planned which will hopefully reduce the imprecision by using ^{236}U as the spike for U and ^{240}Pu for Pu. Much of the fractionation effects from small samples using the sequential analysis procedure may be eliminated using these

isotopes, which are nearer in mass to the major isotope in the sample. Preliminary measurements for U concentration have been carried out, and results look very encouraging. Also, an isotopic equilibration test for Pu is underway in which reduced ^{233}Pu and oxidized ^{242}Pu have been mixed and valence adjustment made using KMnO_4 for oxidation. This is being compared with the $\text{HClO}_4\text{-HF}$ method that we are currently using.

SUMMARY

The principal advantages over conventional techniques offered by the resin bead method are the simplicity and ease of chemical separation and the reduction in the amount of sample required for shipment. Secondary benefits include more efficient ion collection and cleaner spectra. Disadvantages include the necessity of learning new technology (resin bead handling is much easier under a microscope) and the need to have mass spectrometers equipped with pulse-counting detection systems. However, manipulating the beads is much less formidable than it appears, and the techniques and equipment needed for ion counting are well known. By following the procedure outlined, no sacrifice in quality of results in comparison to those obtained by conventional techniques is observed. We thus feel that the resin bead technique can make useful contributions to both domestic and international safeguards programs in areas that are otherwise difficult to attack. In addition, it is a very useful technique for isotopic and concentration measurements in radioactive samples used in process control and development.

SEQUENTIAL ANALYSIS OF PU AND U
(RESIN BEAD METHOD)

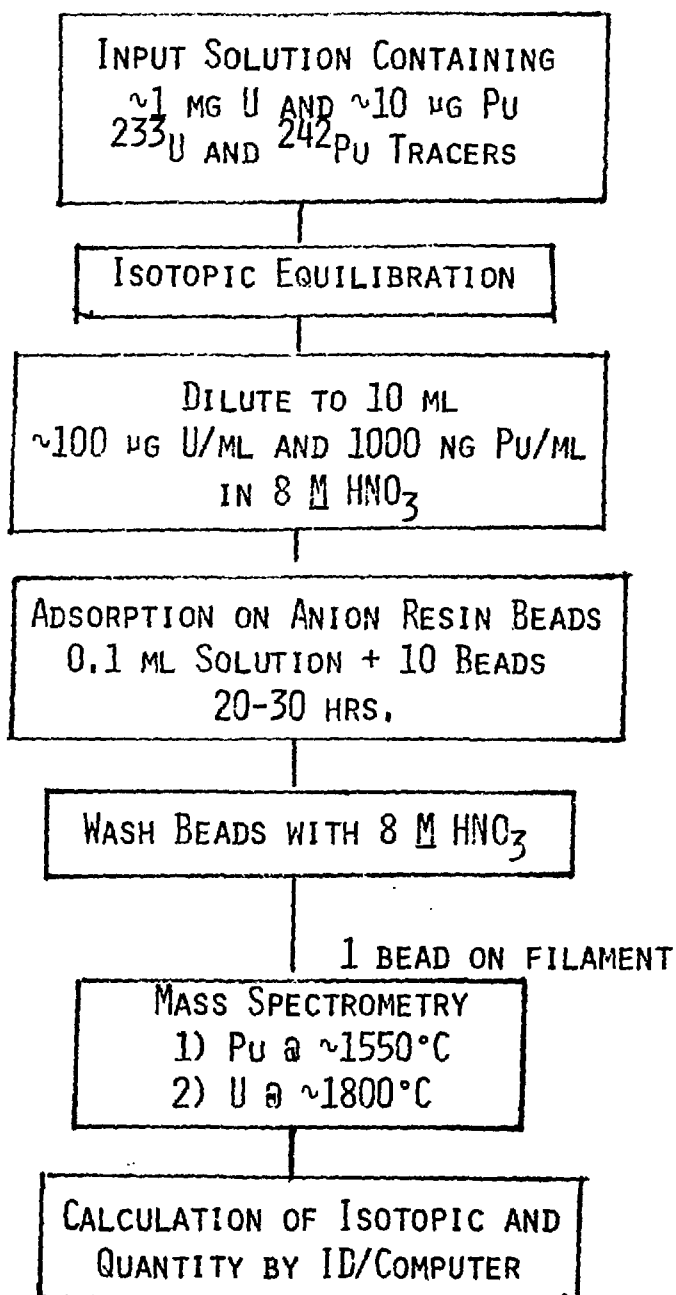


Fig. 1. Sequential Analysis of Pu and U (Resin Bead Method)

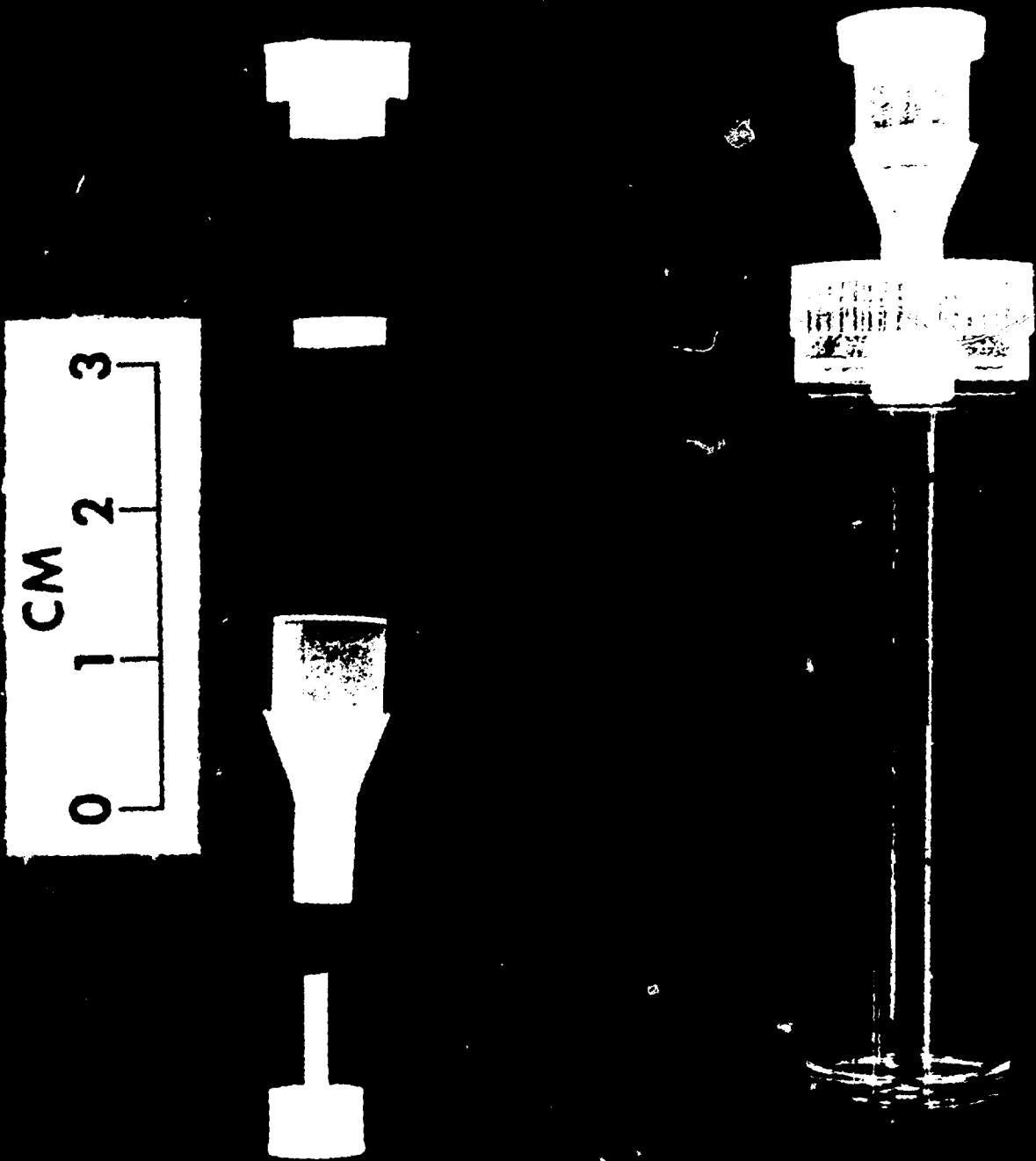


Fig. 2. Combination Adsorption and Shipping Apparatus