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PREPARATION OF URANIUM STANDARD SOLUTIONS
FOR X-RAY FLUORESCENCE ANALYSIS
A Safeguards Progress Report

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ABSTRACT

A method has been developed for preparing uranium standard solutions by weighing, to an accuracy of 0.1%. This method corrects for variation in aliquoting and for evaporation loss during weighing.

The standards are freeze-dried in a configuration suitable for x-ray fluorescence analysis.

Three high-precision pipets were compared and found to be unsatisfactory for 0.1% accuracy or precision.

INTRODUCTION

One of the primary considerations in preparing uranium standard solutions for x-ray fluorescence analysis is to develop a technique for dispensing 50 λ aliquots of solution with a precision of 0.1% and an accuracy of 0.1%. The 50 λ aliquot was chosen because this volume best meets the requirements of the sample mounting and counting procedure developed by Hazards Control Special Projects Section for x-ray fluorescence analysis of uranium-bearing solutions.¹ Briefly, this procedure consists of an adhesive Kapton film mounted in a 35-mm slide with a 1.27-cm-diam beeswax ring centered on the film. A liquid sample is then dispensed into the beeswax ring, weighed, freeze-dried, and analyzed by x-ray fluorescence.

DISPENSING PRECISION AND ACCURACY

Three high-precision microdispensers were investigated. The accuracy and precision of each were measured by weighing each aliquot on a Mettler H-16 balance. To standardize the effects of weight loss due to evaporation while weighing, the following procedure was used: (1) open vial; (2) start electric timer; (3) pipet 50 λ aliquot of

1. W. L. Pickles and J. L. Cate, Jr. Quantitative Nondispersive X-Ray Fluorescence Analysis of Highly Radioactive Samples for Uranium and Plutonium Concentration, Lawrence Livermore Laboratory, Rept. UCRL-74717 (1973); and in Advances in X-Ray Analysis, vol. 17, C. L. Grant, C. S. Barrett, J. B. Newkirk, and Co. O. Rudd, Eds. (Plenum Press, New York, 1974), pp. 337-347.

distilled water; (4) dispense sample into vial; (5) place on balance pan; (6) weigh; (7) read weight when timer is exactly 1.00 min. The Brand A pipet proved to be far superior to the Brand B and Brand C pipets, as is shown in Table 1. However, none of the three pipets are capable of delivering 0.1% accuracy or precision volumetrically. Therefore, the accuracy will have to be achieved gravimetrically, and every sample will have to be weighed individually.

Table 1. Pipet precision and accuracy for delivery of 50 λ water samples.

Pipet	Number of measurements	% accuracy ^a		Average % precision
		Range	Av	
Brand A	70	-1.38 to 1.72	-0.48	0.47
Brand B	60	-6.62 to 7.28	-2.27	3.03
Brand C	20	-9.46 to 1.16	-1.42	2.65

^aCorrected for H₂O density variation at room temperature (22°C).

WEIGHING ACCURACY

We also checked the H-16 Mettler balance and our weighing method to determine the consistency of the balance in weighing and the individual bias in reading the weights. First, one person alternately weighed an empty vial and a vial with 50 λ of distilled water in it. This was done ten times for each vial. Then two people did this weighing, rezeroing the balance and alternately reading the weights. The results in Table 2 show that the slight variance in weight read by different people or by the same person is not great enough to affect the 0.1% precision and accuracy of weight that we hope to achieve.

Table 2. Individual bias in reading weights.

	Empty vial	Vial + H ₂ O
Same person reading weights	1.14944 + 0.00002 g	1.19851 $\pm$ 0.00003 g
Two people reading weights	1.14945 $\pm$ 0.00003 g	1.19858 $\pm$ 0.00005 g

EVAPORATION CORRECTION IN WEIGHING

The evaporation rate of 50 λ aliquots of several solutions was determined by repeated weighings over a 5-min time interval for each sample. It is apparent from Fig. 1 that the evaporation loss becomes significant for a weighing time greater than 15 sec. The evaporation rates of 50 λ of pure water and of 100 ppm, and 19 000 ppm (in 0.25 N HNO₃) uranium solutions vary between 0.19 and 0.21 mg/min (a slightly lower rate, 0.15 mg/min, is observed for 6 N HNO₃). In actual practice, the minimum time required for conveniently dispensing (with an automatic pipet) and weighing the 50 λ aliquot is about 30 sec. Therefore, for solutions with the above evaporation rate, in 30 sec 0.10 mg of solution would have been volatilized, or 0.2% of a 50-mg aliquot. To achieve the accuracy of 0.1% as required in the Safeguards Program, it is necessary that this kind of correction be incorporated into the weighing procedure.

STANDARDS PREPARATION

To make our initial trial uranium standards, we obtained some depleted UO₂ from Materials Management of LLL. The UO₂ was about 15 yr old and was supposed to be 99.93% pure UO₂. This was sent to the Chemistry Department to be spectrographically analyzed for impurities, as was the beeswax to be used in the containment ring on the sample holder. These results are given in Tables 3 and 4.

The initial preparation of the uranium oxide was done according to the standard method, which is: (1) The oxides are converted to U₃O₈ by heating in a cleaned platinum crucible at 800°C for 1 hr; (2) the crucible is removed from the oven and the powder stirred and mixed well; (3) the crucible is returned to the oven and heated for 1 hr; and then (4) the U₃O₈ is allowed to cool in a desiccator and is weighed. The weight of the UO₂ before heating was 201.859 g; the weight of U₃O₈ after heating was 208.967 g; and the weight gain of 7.108 g indicates a 99.6% theoretical conversion of UO₂ to U₃O₈. According to the equation, $3 \text{ UO}_2 + \text{O}_2 \rightarrow \text{U}_3\text{O}_8$, the gain in weight should have been 7.973 g. This may indicate that the original UO₂ contained a small amount of U₃O₈. The stoichiometry as well as the isotopic composition are being established by mass spectroscopy in the Radiochemistry Department.

A weighed aliquot of the U₃O₈ was dissolved in sub-boiled distilled 8 N HNO₃ and a stock solution of 19.156 mg U per g of solution was prepared using sub-boiled distilled H₂O and sub-boiled distilled HNO₃. We prepared sub-standards of 9.7611 mg U per g of solution to 0.098752 mg U per g of solution from the stock solution.

All aliquots and dilutions were made by weight. All initial weighing of UO₂ and U₃O₈ powder was done with aluminum foil pans and funnels to eliminate the static charge the powder exhibited. Next, these solutions will be pipetted, weighed, freeze-dried and analyzed according to our procedure for uranium calibrations by x-ray fluorescence.

Fig. 1. Weight changes during weighing.

Table 3. Spectrochemical analysis report.

Sample description: UO_2		Plate No.:	3224
		Sample No.:	SS-1148
Key:	Values are approximate ppm by weight for the impurity elements listed.		
Analysis:	The following elements were not detected in either.		
	Fe	100 ppm	sample (detection limits are for UO_2):
	Ni	30	
	Ca	20	<30 Ba
	Mo	20	<10 Zr
	Cr	15	<3 Nb, Sb
	Si	15	<1 Bi, Co
	Al	5	<0.3 Cd
	Mg	5	
	Cu	4	
	Mn	3	
	Sn	3	
	Zn	2	
	B	$\bar{<1}$	
	Sr	$\bar{<1}$	
	Pb	0.5	
	Ti	<0.3	
	Be	<0.1	
	V	1	

Table 4. Spectrochemical analysis report.

Sample description: Beeswax		Plate No.:	3225
		Sample No.:	SS-1151
Key:	Values are approximate ppm by weight for the elements listed.		
Analysis:	The following elements were not detected:		
	Fe	8 ppm	<4 Na
	Si	4	<1 Nb, Sb, Zr
	Ca	2	<0.4 Ba, Ge, Ni, V, Zn
	Al	1	<0.1 Bi, Cd, In, Sn
	B	0.4	<0.04 Be, Co, Cr, Mo
	Cu	0.4	
	Ti	0.4	
	Pb	0.2	
	Mg	0.1	
	Mn	0.1	
	Ag	0.04	
	Sr	<0.04	

FUTURE WORK

Subsequent to the preparation of these trial standards, we obtained a preprint from Dr. Stanley S. Yamamura of Allied Chemical Corporation in Idaho Falls. He has been actively pursuing research on standards for the AEC Safeguards Program for some time, and his paper contains several useful suggestions which we plan to institute in our future work. He recommends: (1) Some NBS uranium source materials which we are going to compare with our own source UO_2 ; (2) standardized procedures for preparing working calibration and test solutions; (3) methods for packaging and storing standard solutions; and (4) standardization and statistical evaluation of the working standards.²

We have also obtained some IAEA (International Atomic Energy Agency) uranium standard solution from I. M. Fisenne of AEC Health and Safety Laboratories in New York which we plan to compare with our standards.

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2. S. S. Yamamura, Preparation of Working Calibration and Test Materials for Intra- and Interlaboratory Surveillance of Nuclear Materials Measurement Methods - Uranium Nitrate Solutions, 1974 (in press).

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