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Spectrophotometer for Uranium
Determination at Submilligram Levels**

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EVALUATION OF THE LASL AUTOMATED SPECTROPHOTOMETER FOR URANIUM DETERMINATION AT SUBMILLIGRAM LEVELS

by

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ABSTRACT

The LASL automated spectrophotometer, designed for determination of 1 to 14 mg of uranium and 0.5 to 14 mg of plutonium, has been evaluated for determination of lower levels of uranium to 0.12 mg. The essentially linear response of absorbance is maintained and the standard deviation for a single measurement is constant at about 0.013 mg of uranium, corresponding to a maximum uncertainty of about 10% at the 0.12-mg limit. The instrument was applied to the analysis of a series of low-level-concentration, 0.07- to 0.8-mg/mL uranium samples. The results were not statistically different from those obtained by a manual spectrophotometric method.

I. INTRODUCTION

The Los Alamos Scientific Laboratory (LASL) automated spectrophotometer was developed in 1975 for the determination of uranium and plutonium. A detailed report¹ describes the mechanical and electrical features, the hardware and software of the microcomputer control system, instrument operation, chemical procedures for instrument calibration and analysis of samples, and data showing accuracy and precision capability for determining 1 to 12 mg of uranium. The instrument was designed primarily for the analysis of scrap-type materials, usually characterized by low uranium and/or plutonium contents, high contents of many impurity elements, and heterogeneity. The design emphasized high specificity, moderate precision capability of 0.010 to 0.020 mg standard deviation, a throughput rate of 5 min per sample, and mechanical simplicity.

The chemical procedure used in the instrument involves the extraction of tetrapropylammonium uranyl and plutonyl trinitrate complexes into 2-nitropropane and measurement of the optical absorbances in the organic phase at unique peak wavelengths. The instrument features a turntable that rotates as many as 24 samples in tubes made from precision-bore tubing to a series of stations for the sequential chemical operations and absorbance measurements. All operations, including the absorbance measurement, are done without transfer of the sample. Output is a paper tape printout of three series of numbers, one proportional to the absorbance of the uranium or plutonium complex, a second designating turntable position for sample identification, and the third designating whether uranium or plutonium was determined.

The analyst delivers the sample to a tube as a volume or weight aliquot and the tube is transferred

to the turntable. The maximum sample volume is 0.5 mL. Larger volumes of samples containing low concentrations of uranium or plutonium may be evaporated in the tubes before transfer to the instrument. The evaporation of samples in tubes is not labor-consuming; however, there can be a technical disadvantage. For samples containing high amounts of impurities relative to uranium or plutonium, the residue can be difficult to dissolve completely in 0.5 mL of acid. Undissolved residue can retain small amounts of uranium or plutonium.

To extend the applicability of the automated spectrophotometer, we are currently adapting another uranium spectrophotometric method that has sensitivity to low microgram levels.² Meanwhile, the need to analyze samples from various uranium recovery processes in which the concentrations of uranium generally are within the range of 0.05 to 1 mg/mL prompted an evaluation of the instrument, without chemical or instrumental modifications, for lower level uranium analyses. This evaluation consisted of a 15-day processing of standard solutions containing 0.12 to 1.5 mg of uranium as well as the analysis of 32 uranium samples from a recovery process. The 32 samples also were analyzed by an experienced analyst who used a well-proven, manual spectrophotometric method.³

II. INSTRUMENT EVALUATION FOR SUB-MILLIGRAM URANIUM LEVELS

On each of 15 days over an elapsed time of almost a month, six weight aliquots at each of four levels of 0.12, 0.27, 0.56, and 1.5 mg of uranium were processed using the automated spectrophotometer. Also processed each day were four blank solutions—a total of 420 measurements. The aliquots were taken from solutions that had been prepared by nitric acid dissolution of a well-characterized, >99.9% pure uranium metal.

Using all the data, a calibration equation was computed by least squares fitting for the four-digit output number that is proportional to absorbance, in turn proportional to the milligrams of uranium. The equation, a second-order polynomial, was almost linear, as was the equation obtained previously for the range of 1 to 14 mg of uranium. We used this equation to calculate the milligrams of uranium corresponding to each output number. The

variance of the 90 values at each of the four levels of 0.12, 0.27, 0.56, and 1.5 mg uranium was computed. Bartlett's test for comparison of more than two variances showed no difference, indicating a constant precision over the range. The pooled standard deviation (for a single measurement) was 0.013 mg of uranium. The corresponding relative standard deviations ranged from 10.4% at 0.12 mg of uranium to 0.87% at 1.5 mg of uranium.

An analysis of variance of the data indicated a difference at the 95% significance level for between-day measurements relative to the within-day measurements. Although significant, the difference is small. The averages of the deviations of the 24 results for the day of highest and the day of lowest results, relative to the grand average of results for all 15-day data, were +0.021 mg and -0.024 mg, respectively. This effect can be decreased by adjusting the calibration on the basis of results obtained for concurrently analyzed standards. For the data obtained in this evaluation, an adjustment based on daily processing of two standards each at the upper and lower ends of the range would decrease the above obtained averages of the deviations to +0.004 and -0.001 mg.

III. ANALYSIS OF LOW-CONCENTRATION URANIUM SAMPLES

A series of 32 routine samples, containing 0.07 to 0.8 mg/mL uranium concentrations, was analyzed with the automated spectrophotometer as well as by a skilled analyst using a well-proven manual spectrophotometric method.³ The samples were solutions from a stage in a uranium recovery process. They contained significant quantities of various impurities and some had fine suspended material. About half were in a nitric acid medium and half were in sulfuric acid.

The maximum sample volume is 0.5 mL. Half of the samples contained <0.3 mg/mL of uranium. To attain more reliable results, we analyzed 10-mL volumes having a uranium range of 0.7 to 8 mg. Two sequential 5-mL volumes were evaporated in the tubes. A 0.5-mL volume of 8M HNO₃ was added to dissolve the residue and the tubes were transferred to the instrument. Duplicates were analyzed.

The instrument was calibrated just before sample analysis by processing a series of 28 weight aliquots

of standard solutions, prepared with >99.9% pure uranium metal, over the range of 0.25 to 14 mg of uranium. A regression line was fitted to the data by a least squares computation. As in the past,¹ a second-order polynomial, although almost a straight line, fitted the data better. During sample analysis, standards were processed daily to confirm satisfactory operation. The calibration was not adjusted.

Two types of statistical tests, "t" and Wilcoxon-Signed Ranks, were applied to compare the results obtained from use of the automated spectrophotometer to those obtained by the manual spectrophotometric method (Table I). Neither test showed a significant difference. The algebraic grand average difference was 0.0017 mg of uranium. The grand average difference calculated without regard to sign was only 0.0037 mg of uranium.

The standard deviation for a single measurement of the automated spectrophotometer results, computed from the duplicate analysis results, was 0.039 mg of uranium, corresponding to 6% and 0.5% at the 0.7-mg and 8-mg extremes.

ACKNOWLEDGMENT

Ludie Pulliam performed the manual spectrophotometric analysis.

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TABLE I
RESULTS OF URANIUM SAMPLES
ANALYZED BY THE AUTOMATED
SPECTROPHOTOMETER AND A MANUAL
SPECTROPHOTOMETRIC METHOD

Sample	Automated Spectrophotometer (mg/ml) ^a	Manual Spectrophotometric Method (mg/ml)	Difference
1	0.380	0.374	+0.006
2	0.374	0.373	+0.001
3	0.262	0.251	+0.011
4	0.253	0.251	+0.002
5	0.348	0.352	-0.004
6	0.354	0.352	+0.002
7	0.456	0.460	-0.004
8	0.459	0.459	-0.001
9	0.626	0.625	+0.001
10	0.627	0.625	+0.002
11	0.702	0.707	-0.005
12	0.711	0.707	+0.004
13	0.385	0.385	0.000
14	0.386	0.387	-0.001
15	0.232	0.232	0.000
16	0.233	0.232	+0.001
17	0.145	0.149	-0.004
18	0.147	0.149	-0.002
19	0.050	0.051	-0.001
20	0.048	0.051	-0.003
21	0.237	0.241	-0.004
22	0.237	0.241	-0.004
23	0.126	0.125	+0.001
24	0.125	0.125	0.000
25	0.066	0.070	-0.004
26	0.066	0.068	-0.002
27	0.111	0.114	-0.003
28	0.116	0.114	+0.002
29	0.770	0.787	-0.017
30	0.766	0.788	-0.022
31	0.434	0.436	-0.002
32	0.432	0.436	-0.004

^aAverage of duplicates.