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AUTOMATED SPIKE PREPARATION SYSTEM FOR ISOTOPE DILUTION MASS SPECTROMETRY (IDMS) (U)

by

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AUTOMATED SPIKE PREPARATION SYSTEM FOR ISOTOPE DILUTION MASS SPECTROMETRY (U)

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ABSTRACT

Isotope Dilution Mass Spectrometry (IDMS) is a method frequently employed to measure dissolved, irradiated nuclear materials. A known quantity of a unique isotope of the element to be measured (referred to as the "spike") is added to the solution containing the analyte. The resulting solution is chemically purified then analyzed by mass spectrometry. By measuring the magnitude of the response for each isotope and the response for the "unique spike" then relating this to the known quantity of the "spike", the quantity of the nuclear material can be determined.

An automated spike preparation system was developed at the Savannah River Site (SRS) to dispense spikes for use in IDMS analytical methods. Prior to this development, technicians weighed each individual spike manually to achieve the accuracy required. This procedure was time-consuming and subjected the master stock solution to evaporation. The new system employs a high precision SMI Model 300 Unipump dispenser interfaced with an electronic balance and a portable Epson HX-20 notebook computer to automate spike preparation. Using the computer to collect dupicate net weights on a predetermined number of spike containers, dispensing accuracy is confirmed by a statistically-based sampling plan. The density of the spike solution, the volume setting on the Unipump dispenser, and the calculated net weights of the spikes, the average weight of the spikes are calculated along with the observed variance estimate. If the observed variance meets control limits, the spikes are released and treated as having equal quantities of the "spiked" isotope within the calculated uncertainty estimate. This feature eliminates a whole layer of bookkeeping and the need to track individual spike containers and their individual quantities of the spiked isotope.

INTRODUCTION

Isotope Dilution Mass Spectrometry (IDMS) is an analytical method frequently employed to measure irradiated nuclear materials after dissolution for chemical processing. At the Savannah River Site, it is used to perform measurements for material accountability of enriched uranium dissolved in H Canyon and plutonium dissolved in F Canyon. A known quantity of either Uranium ^{233} or Plutonium^{244} is combined with the solution containing the analyte. The resulting solution is chemically purified then analyzed by mass spectrometry. The magnitude of the response of each isotope in the analyte solution and the response of the known spike is measured. By ratioing these responses, using the known quantity of the introduced spike, the quantity of the nuclear material in the analyte can be easily determined. The measurement reliability of the nuclear material accountability is directly dependent on the reliability of the spike quantities used in each analysis. The U^{233} or Pu^{244} is combined with the sample then purified to remove fission products in shielded cells (Figure 1) prior to analysis by thermal ionization mass spectrometry (Figure 2). The

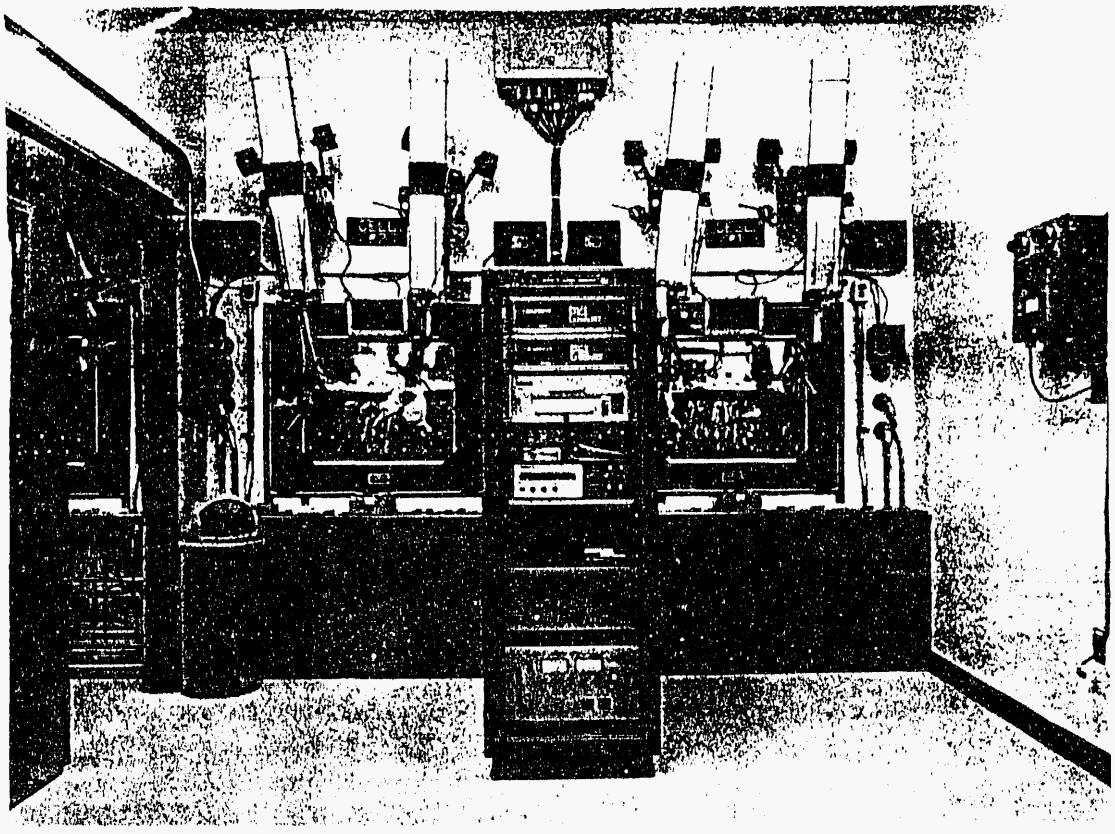

Figure 1 - Shielded Analytical Cells

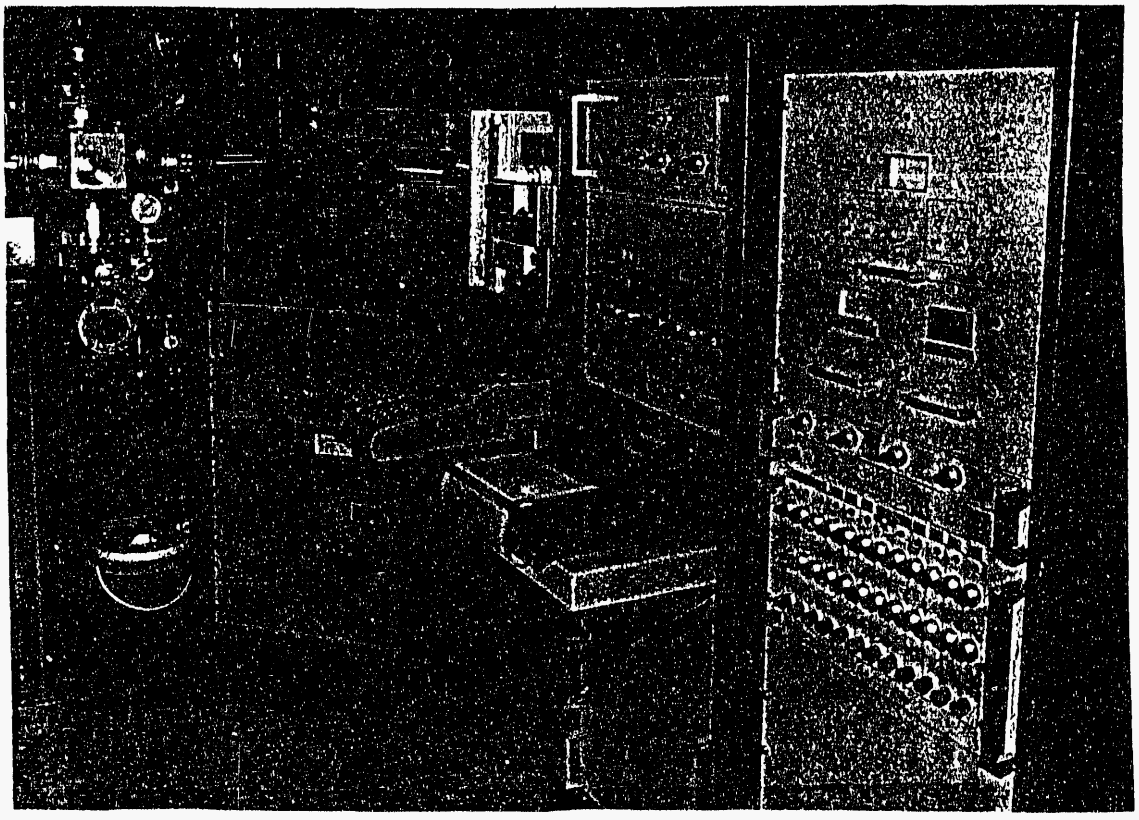

Figure 2 - Finnigan Mass Spectrometer

reliability of the IDMS measurement is dependent on the accuracy of the spike quantity used in each analysis.

The automated spike preparation system was developed at the Savannah River Site (SRS) to reduce the time required to prepare Uranium ^{233} and Plutonium^{244} spikes, provide comprehensive statistical evaluation of the spike standards, and to improve the quality of the IDMS technique.

BACKGROUND

Prior to the development of this automated system, technicians weighed each individual spike manually to achieve the high reliability required. This procedure was tedious, time-consuming and subjected the master stock solution to evaporation. A need to streamline the operation was recognized and a new method of spike preparation was developed.

Automated Spike Preparation

Rather than tediously weighing each spike quantity individually, a high precision volumetric dispenser [reliable to 0.1% Relative Standard Deviation (RSD) for a single dispensing] is employed to streamline the preparation. The system employs an SMI Model 300 Unipump dispenser, an electronic analytical balance and a portable Epson HX-20 notebook computer to facilitate spike preparation (Figure 3). Using the computer to collect duplicate net weights on a predetermined number of spike containers, dispensing accuracy is confirmed using a statistically-based sampling plan. The density of the spike solution, the volume setting on the Unipump dispenser, and the calculated net weights of the spikes, the average weight of the spikes are calulated along with an observed variance estimate. If the observed variance is within the control limits, the spikes are released and treated as having equal quantities of the isotope spike within the calculated uncertainty estimate. This feature eliminates a whole layer of bookkeeping and the need to track individual spike containers.

Epson HX-20 Computer Control

The system features data acquisition by an inexpensive Epson HS-20 portable computer with an interactive dialogue which prompts the operator through the preparation procedure and therefore reduces operator error. The system employs a double weighing routine which requires additional duplicate net weights which must agree with a set limit, typically 0.2%. Uncertainty estimates at the 95% confidence level are provided for each set of spikes dispensed. To ensure the reliability of mass measurements using the Mettler AE-163 electronic balance, the computer requires checkout with two traceable mass standards prior to use (Appendix A-1). A control chart is maintained to track balance performance over time (Appendix A-2). These mass measurement control features are consistent with mass standard controls already used at SRS.[1]

SMI Unipump Dispenser

The SMI Unipump 300 dispenser is used to dispense quantities of a known isotope solution into vials for use in both uranium and plutonium IDMS methods. The dispenser is microprocessor-based and has keypad control. The reproducibility of a single dispensing is better than 0.1% over a range of 1 microliter to 10 milliliters. To prepare uranium-233 spikes, 200 microliters is dispensed containing approximately 140 micrograms of U-233.

Figure 3 - Automated Spike Preparation System

Plutonium-244 spikes, in contrast, contain only about 3 micrograms of the isotope, due to the increased ionization efficiency of plutonium relative to uranium.

To test the SMI Unipump performance prior to spike dispensings, the dispenser must first deliver two successive volumes within ±0.35% of the target volume. Typically, one of every 10 spikes dispensed are tested gravimetrically, and spikes are only released for use if the spikes dispensed are bracketed by weighed spikes which meet a 0.25% bias test. Further dispensing of spikes is locked out if two successive spikes tested fail to meet the ±0.25% bias test. However, earlier data is saved and calculated to provide an average spike weight per vial dispensed, with uncertainty estimates at the 95% confidence level provided.

Double Weighing Routine

Spikes are weighed using a double weighing routine to ensure the accuracy of the weighed spike. The following sequence is followed:

- Zero balance
- Weigh vial (tare weight)
- Zero Balance
- Reweigh vial (tare weight): must agree within set limit
- Zero balance with vial on balance
- Dispense spike volume
- Weigh spike (direct "STD" weight)
- Remove spike vial
- Zero balance
- Weigh vial + spike (gross weight)
- Remove vial
- Zero balance
- Reweigh vial + spike: must agree within set limit.

Calculations

The computer performs calculations, printed after each spike which show (1) the net weight, which is the average gross weight minus the average tare weight, (2) the direct weight, which is the weight of the spike displayed after taring the balance just prior to dispensing the spike into the vial, (3) the percent relative difference between the net weight and the direct weight (4) The average spike weight, which is obtained by first adding the net weight to the direct weight and then dividing by 2, (5) spike volume, which is the average spike weight divided by the density of the spike solution, and (6) the percent bias from the target volume.

The printout shown in Appendix A-3 illustrates typical test results for an individual spike tested using the double weighing routine. Note that the difference between the net weight and direct ("STD") weight is only 0.072% RSD and that the bias from the target volume is only -0.05%.

The calculations, after each set of vials is completed, assigns a value for the set of spikes prepared which gives an average quantity of total uranium and uranium^{233} per vial or average quantity of total plutonium and plutonium ^{244} per vial in milligrams. Additional details including uncertainty estimates given are summarized in the Data Summary Printout section below.

Data Summary Printout

- Spike stock solution (mg/g)
- % isotope/spike element
- Temperature
- Density of spike solution (25°C)
- Density of spike solution (ambient T)
- Number of vials prepared
- Reprint of individual spike weights in set
- Average weight of spike element per vial in set
- Average weight of isotope per vial in set
- Uncertainty estimate for average
- ±% Relative Standard Deviation of an individual dispensing, X_i
- ±% Relative Standard Deviation of average dispensing, X_{bar}
- Degrees of freedom
- T-Table value
- 95% confidence interval in percent
- 95% confidence interval in milligrams

A printout of typical spike preparation results is shown in Appendix A-4. Eleven standards were tested; over 100 spikes were dispensed. The U-233 % of total uranium is 98.1979% and the target volume is 0.2 milliliters or about 0.14 grams. A U-233 value of 0.1479 grams is assigned for the entire set of vials. The relative standard deviation of the mean value is 0.023%, the confidence limits at the 95% level are ±0.049%.

ACKNOWLEDGEMENTS

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REFERENCES

1. S.L. Maxwell,III and J.P. Clark, "A Portable, Automated, Inexpensive Mass and Balance Calibration System". *Proceedings of the 28th Annual meeting of the Institute for Nuclear Materials Management,* Newport Beach, CA -July 12-15, 1987.

AUTOMATED STANDARD
DISPENSING PROGRAM

01/20/90 08:27:58

SLM 6823

CONTROL LIMIT
1 RSD = .01

STANDARD VALUES

STD 1 IS 20.00000 g
STD 2 IS 2.00000 g

PLOT OF STD DATA

SD'S	-3-2-1 0 1 2 3
WEIGHT	-+-+-+-+-+-+-+-
20.00003	1
2.00005	2

AUG. SD = 0.1

BALANCE CALIBRATED

M90jul008.01
7-11-90

Appendix A-1
Balance Checkout

06/09/90 11:49:39

SLM 6823
CONTROL LIMIT
1 RSD = 0.010%

STANDARD VALUES

STD	1	MEASURED	021787
STD	2	MEASURED	021787
STD	3	MEASURED	021887
STD	4	MEASURED	021887
STD	5	MEASURED	031387
STD	6	MEASURED	031387
STD	7	MEASURED	031387
STD	8	MEASURED	031387
STD	9	MEASURED	031487
STD	10	MEASURED	031487
STD	11	MEASURED	040787
STD	12	MEASURED	040787
STD	13	MEASURED	040887
STD	14	MEASURED	040887
STD	15	MEASURED	040887
STD	16	MEASURED	040887
STD	17	MEASURED	042187
STD	18	MEASURED	042187
STD	19	MEASURED	042287
STD	20	MEASURED	042287

PLOT OF STD DATA

SD'S	-3 -2 -1 0 1 2 3
WEIGHT	-+ -+ -+ -+ -+ -+ -+
30.00150	1
2.37050	2+
30.00220	3
2.37060	4
30.00250	5
2.37070	6
30.00230	7
2.37070	8
30.00220	9
2.37070	10
30.00180	11
2.37050	12+
30.00170	13
2.36990	< +
30.00200	15
2.37030	16+
30.00210	17
2.37070	18
30.00150	19
2.37080	+20

AVG. SD = 0.4

M90jul008.02
7-11-90

Appendix A-2
Historical Record of Balance Performance Documentation

VITAL	2 WT =	13.95547	g
STD	2 WT =	0.19984	g
GRS	2 WT =	14.15551	g
NET WT	2 =	0.20004	g
NET - ST	2 =	+0.00020	g
RSD(%)	2 =	0.07250	
AVG WT	2 =	0.19994	g
TARG. VOL	=	0.20000	mL
VOLUME	2 =	0.19990	mL
BIAS %	2 =	-0.05174	

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7-11-90

Appendix A-3
Double Weighing Routine Printout

123 VIALS 05/25/88
USTK (MG/G) = 0.705390
U233/TOTU = 98.1979 %

OPERATOR
TEMPERATURE = 22.0 DEG C
DENSITY 25C = 1.0295g/mL
DENS 22.0 C = 1.0307g/mL

NO. OF STDS = 11
STD 1 = 0.19974 mL
STD 2 = 0.20008 mL
STD 3 = 0.20003 mL
STD 4 = 0.20020 mL
STD 5 = 0.19994 mL
STD 6 = 0.20018 mL
STD 7 = 0.19989 mL
STD 8 = 0.20001 mL
STD 9 = 0.19989 mL
STD 10 = 0.19989 mL
STD 11 = 0.20020 mL

TARGET VOL = 0.19974 mL
AVERAGE VOL = 0.20001 mL
AVG STD WT = 0.206145g

TOT URANIUM = 0.145413mg
TOT U233 = 0.142792mg

RSD Xi = +/- 0.00076 %
RSD Xbar = +/- 0.00023 %
DEGREE F = 10
TABLE - T = 2.150
95% C. L. = 0.049%
95% C. L. = 0.00007
****
M90jul008.04
7-11-90

Appendix A-4
Typical Results for U-233 Spike Preparation

END

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6/15/92