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ORNL

FOREIGN TRIP REPORT

ORNL/CSD/FTR-3622

DATE: June 6, 1990

SUBJECT: Report of Foreign Travel by C. K. Bayne, Staff Member, Computing and Telecommunications Division.

TO: Alvin W. Trivelpiece

FROM: C. K. Bayne

ORNL/CSD/FTR--3622

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PURPOSE: To participate in the quality control programs for isotope dilution mass spectrometry under ISPO Task D.66 for the Safeguards Analytical Laboratory (SAL) at Seibersdorf, Austria.

SITES VISITED:

04/23-04/27/1990	SAL, Seibersdorf, Austria	
04/30-05/04/1990	Head of SAL	S. Deron
05/07-05/11/1990	Head of Chemical Analysis	G. Bagliano
	Head of Mass Spectrometry	J. Cappis
	Head of Radiometry	J. Parus
05/02/1990	International Atomic Energy Agency Vienna, Austria	
	Statistician	A. Goldman
	Statistician	G. Laszlo

ABSTRACT: This visit to the Safeguards Analytical Laboratory (SAL) examined a preliminary computer simulation program to study isotope dilution analysis by mass spectrometry (IDMS). Although the general simulation methods were acceptable, specific parameter values used in the simulation did not represent SAL's uranium and plutonium samples. These characterization parameters will be updated, and the simulation will be repeated. This simulation program will be used to analyze the effects of different components of the measurement errors on the final uranium and plutonium concentration calculations.

REPORT OF FOREIGN TRAVEL

ISPO TASK D.66 ON QUALITY-CONTROL PROGRAM FOR SAL

C. K. Bayne
Seibersdorf, Austria
April 23, 1990 -- May 11, 1990

1. Introduction

This foreign travel is related to the extension of ISPO task D.66 for quality-assurance (QA) and quality-control (QC) programs at the Safeguards Analytical Laboratory (SAL), Seibersdorf, Austria. Previous efforts under this task [*1-7*] have applied statistical process control to mass spectrometer, titration, and radiometry procedures. The primary focus for this extension is to develop a statistical QC program for isotopic dilution analysis by mass spectrometry (IDMS). This technique is used routinely at SAL to obtain elemental concentrations of uranium and plutonium in nuclear material when titration methods are not practical to use, usually due to limited sample quantity. The primary source of samples for IDMS analysis is spent fuel. The time spent at SAL was used to characterize the parameters for a computer simulation program of the IDMS technique. The IDMS computer simulation will be used to investigate the effects of different error components (e.g., isotopic ratio measurements, weighing, ratio of tracer to sample, etc.) on the error of the final calculated elemental concentration.

A secondary purpose is to review problems detected by QC charts. Two detected problems required additional statistical analyses. First, a procedure change was suspected of producing erroneous uranium assay values. In fact, the problem was due to incorrect isotopic ratio values used in the calculation of the uranium assay values. Second, the calibration of ^{235}U measurements by radiometry showed a dependency on the type of standard reference material used. Calibrations using National Bureau Standards (NBS) and British Nuclear Fuel (BNF) standard reference material show significant statistical differences. However, we did not resolve the reason for these differences.

2. Isotope Dilution Analysis by Mass Spectrometry

2.1 General Principles

Isotope dilution mass spectrometry (IDMS) is a method of measuring the elemental concentrations of materials that occur in very small quantities. IDMS is applied at SAL to measure the concentrations of uranium (0.5-10 mg) and plutonium (0.001-4 mg) usually in spent fuels or in products where titration methods are not practical. A known amount of sample with a measured isotopic composition is quantitatively mixed with a known amount of tracer of the same element as the sample. The tracer is a reference material with a well-characterized elemental concentration and isotopic distribution. The tracer material is fabricated with one or more isotopic spikes that occur at negligible abundance (e.g., ^{233}U, ^{236}U, ^{242}Pu, and ^{244}Pu) in the sample. The resulting isotope distribution of the mixture is measured. The concentration of the element in the sample can then be calculated by comparing the isotopic ratio of the spike in the mixture to the isotopic ratio of the known quantity of spike in the tracer. Figure 1 is a schematic diagram indicating the IDMS measurement sources.

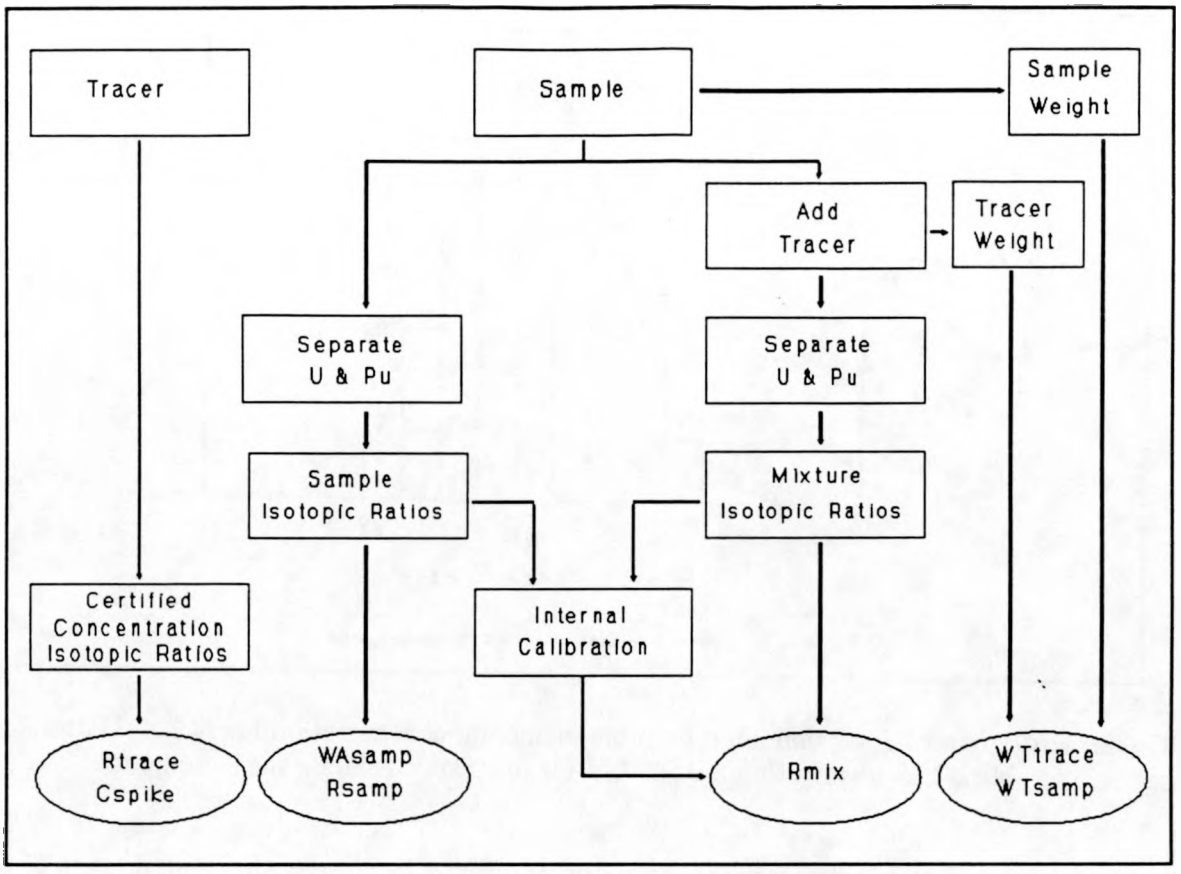

Fig. 1. IDMS measurement sources to calculate concentrations.

2.2 IDMS Computer Simulation Study

A computer simulation program for IDMS calculations has been developed to generate random, multivariate normal vectors for a given isotopic composition. This random generator is used to simulate mass spectrometry measurements for both simulated samples and simulated mixtures. Three simulation samples and three tracers are used in the simulation computer program. Typical samples are represented by (1) mixed-oxides samples with uranium:plutonium ratio > 10:1 (MOX_U), (2) mixed-oxides samples with uranium:plutonium ratio < 10:1 (MOX_Pu), and (3) spent fuel solutions from light-water reactors (LWR). These samples are paired with three tracers to form five cases: MOX_PU with NBL-116 and LWR with QS-87 for uranium samples, and MOX_U with NBL-126, MOX_Pu with NBL-126, and LWR with QS-87 for plutonium samples.

The simulation procedure for each case involves the following steps: (1) select a property to study (e.g., effects of mass spectrometry precision), (2) fix the other IDMS measurement sources at nominal values, (3) generate random mass spectrometry sample measurements (i.e., 1000 samples) and the corresponding random mass spectrometry mixture measurements, (4) calculate the elemental fractions from the IDMS calculation for each simulation run. For example, the frequency distribution is given in Fig. 2 of the simulated uranium elemental concentration for MOX_U with NBL-116. Figure 2 shows the distribution of uranium elemental concentration when a 0.5% coefficient of variation [CV = 100% X (standard deviation)/mean] is used for mass spectrometry measurements.

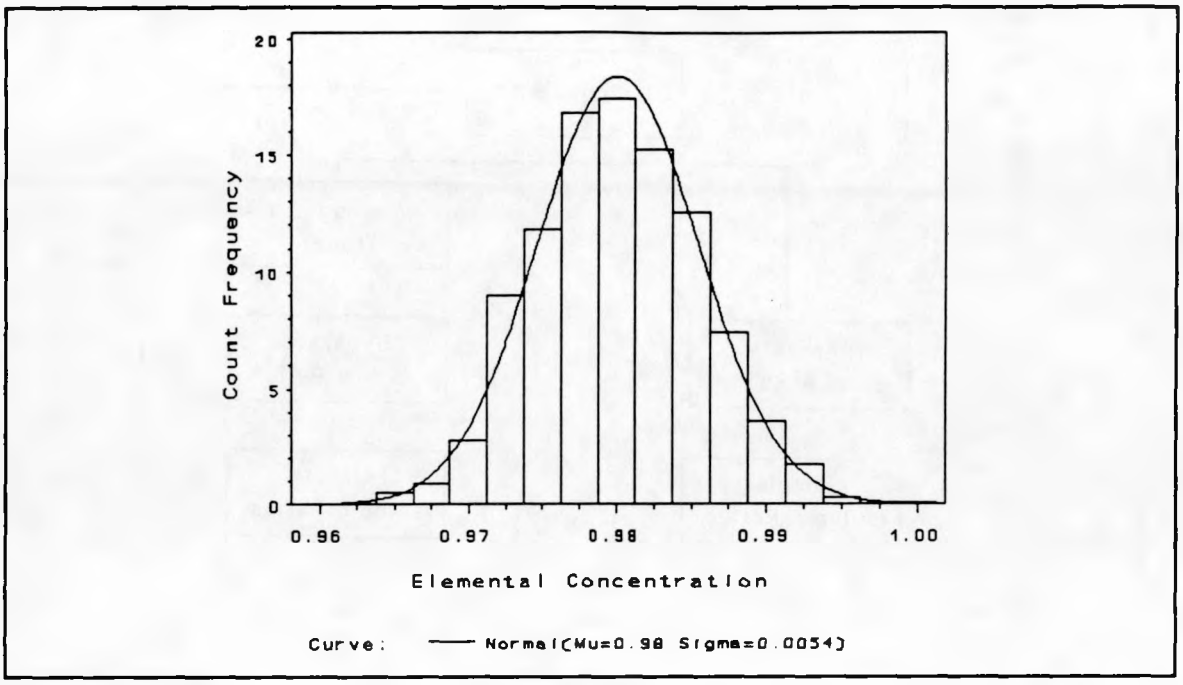

Fig. 2. Histogram of 1000 simulated uranium elemental concentration for MOX_U sample with NBL-116 tracer using a 0.5% CV for mass spectrometry measurements.

Studying the IDMS error sources in the laboratory is difficult because of the limited range of mixture composition of samples and the interaction of different error sources. The computer simulation study of the IDMS analysis method has the advantage that exact values for a set of conditions can be fixed and only the measurement sources of interest are randomly varied. The simulated results will be ideal because only those specified error sources are varied. In addition, many computer simulation runs can be made to study the effect of the error sources. These ideal results, tempered with practical experience, can be used as a guide to improve the IDMS procedure.

2.3 Computer Simulation Parameters

The effects of IDMS measurement sources on the precision and accuracy of elemental concentrations will be studied using the IDMS simulation program. The specified effects are the precision of mass spectrometry measurements, the precision of sample and tracer weighings, and the mixture weight ratios of sample to tracer. An important influence on mass spectrometry measurements is fractionation. Fractionation refers to the variable rate that ions volatilize for different nuclidic masses during mass spectrometry measurements. This phenomenon will not be simulated and may require a separate study.

Typical sample characteristics were identified based on SAL's data. These characteristics included elemental concentrations, sample weights, and correlations among the measured isotopic ratios. SAL is also concerned with the optimal sample:tracer mixture ratio used for IDMS. Guidelines for this optimization have been suggested by DeBièvre [*8*] using rather complicated graphs that do not cover all cases. Goldman et al. [*9*] have developed a computer program that provides results for any desired blend. This computer program selects the mixture ratio that minimizes the variance of the

term in the IDMS formula involving the ratios of spike isotope to reference isotope for the tracer, sample, and mixture. The IDMS simulation results will be compared with these optimal mixture ratios.

Weights for the sample and tracer are frequently measured at the nuclear facility and reported to SAL for their IDMS calculations. Although SAL cannot control the precision and accuracy of these weights, their contribution is important to the final elemental concentrations. Simulating IDMS elemental concentrations with different precision for both weighing and mass spectrometric measurements will identify the major error components.

3. QC Control Charts

SAL uses Shewhart and cumsum quality control (QC) charts [*6*] to track the accuracy and precision of control samples. These QC charts are made for titration, mass spectrometry, and radiometry measurements. Weekly meetings are held to analyze the QC charts and to discuss solutions to any indicated problems. The following actions have resulted from this QC program:

a. Improved method for the preparation of uranium solutions from uranium rods of standard reference material. The new preparation method accounts for variations in surface oxidation on different uranium rods.

b. Detected volume drifts by an automatic titrator in the uranium laboratory. The automatic titrator was replaced before the volume drift was out of specifications.

c. Detected faulty volume read-out of an automatic titrator in the plutonium laboratory. The titrator displayed the incorrect volume dispensed. The electronics were repaired.

d. Detected when calibrations of mass spectrometers were required. Calibrations are required about every 3 months.

e. Detected the need to calibrate specific detector cups in the multicollector mass spectrometer. Revised detector cup calibration procedure.

f. Detected a nonlinear response for a detector cup due to an amplifier overheating. The cooling system for the amplifier was repaired.

g. Detected contamination from insulation evaporation when THQ/MS filaments were temporarily substituted for MAT/MS filaments in the MAT mass spectrometers.

h. Detected that a chemical reagent was improperly prepared in a sample preparation laboratory. The faulty reagent caused bad recoveries of the plutonium fractions.

Some problems detected by the QC charts require additional statistical analyses to determine the causes. For example, a change in the procedure for preparing uranium samples for IDMS was suspected to be the cause of high assay values. A plot of the ratios [(Measured Assay)/(True Assay)] vs [(Measured $^{235}U/^{238}U$)/(True $^{235}U/^{238}U$)] for the mixture showed the actual cause was due to using old information on the isotopic ratios of the control sample. The additional analysis indicated that the information on the control samples needs to be constantly updated.

Another investigation during my visit was the calibration of ^{235}U radiometry measurements. A regression analysis showed significant differences between calibration lines based on NBS and BNF standard reference material. The regression analysis also showed that NBS-030 and BNF-050 require additional investigation as outlier samples. This problem wasn't completely solved at the end of my visit.

4. SAL and ORNL D.66 Projects

Several projects were outlined to be completed before my next visit to SAL. The SAL projects involve running mass spectrometry experiments to gather data for IDMS studies and multicollector calibrations. These data should be sent to ORNL by mid-July 1990. The ORNL projects involve reporting on the results of the IDMS simulation computer program based on SAL's characterization of typical sample parameters.

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APPENDIX A

ITINERARY AND CONTACTS

SAL: 1990 04/23-05/11.

S. Deron, Head, Safeguards Analytical Laboratory
J. Cappis, Head, Isotopic Analysis
G. Bagliano, Head, Chemical Analysis
J. Parus, Supervisor, Radiometry
H. Aigner, Coordinator, Analytical Quality Assurance
N. Doubek, Senior Technician, Plutonium Laboratory
W. Raab, Senior Technician, Radiometry

Vienna International Center: 05/02/90

A. Goldman, Statistician, Department of Safeguards
G. Laszlo, Statistician, Department of Safeguards

APPENDIX B

ACQUIRED LITERATURE

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