DETERMINATION OF TOTAL AND ISOTOPIC URANIUM
BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY
AT THE FERNALD ENVIRONMENTAL MANAGEMENT PROJECT

BY

FRANK L. MILLER
ROBERT N. BOLIN
MICHAEL T. FELLER
RAYMOND J. DANAHY

FERMCO*
Fernald Environmental Management Project
P. O. Box 538704
Cincinnati, OH 45253-8704

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(Authors: Frank L. Miller, Robert N. Bolin, Michael T. Feller
and Raymond J. Danahy)

At the Fernald Environmental Management Project (FEMP) in southwestern Ohio, ICP-mass spectrometry (ICP-MS), with sample introduction by peristaltic pumping, is used to determine total and isotopic uranium (U-234, U-235, U-236 and U-238) in soil samples. These analyses are conducted in support of the environmental cleanup of the FEMP site. Various aspects of the sample preparation and instrumental analysis will be discussed.

Initial sample preparation consists of oven drying to determine moisture content, and grinding and rolling to homogenize the sample. This is followed by a nitric/hydrofluoric acid digestion to bring the uranium in the sample into solution. Bismuth is added to the sample prior to digestion to monitor for losses. The total uranium (U-238) content of this solution and the $U^{235}/U^{238}$ ratio are measured on the first pass through the ICP-MS. To determine the concentration of the less abundant U$^{234}$ and U$^{236}$ isotopes, the digestate is further concentrated by using Eichrom TRU-Spec extraction columns before the second pass through the ICP-MS.

Quality controls for both the sample preparation and instrumental protocols will also be discussed.

Finally, an explanation of the calculations used to report the data in either weight percent or activity units will be given.

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OUTLINE FOR GATLINBURG CONFERENCE  
by Frank Miller

I. INTRODUCTION

A. Name and Occupation / Stand in for Michael Feller

B. Fernald
   1. Used to be Uranium Production Site
   2. ERMC site / cleanup

C. Use of ICP-MS to benefit Fernald

II. METHOD

A. Soil Sample Preparation
   1. Amount taken (wt.)
      a. Dried at 110°C for ≈18 hours (also for % moisture)
      b. Ground with ‘Jaw Tooth’ crusher
      c. Rolled to homogenize
   2. Muffle Furnace
      a. Breakdown of remaining organics
      b. Without this step leaves residue on beakers
   3. Hydrofluoric Acid
      a. Breakdown of silicon
      b. Aid in filtration
   4. Nitric Acid
      a. Dissolution of the heavy metals
      b. Ideal matrix solution for ICP-MS
   5. Hydrogen Peroxide / Oxidation of analytes of interest
   6. Hot Plate / Teflon Beakers
      a. Keep temperature between 150°C and 200°C
      b. Teflon beakers used because of HF
B. Instrumental Analysis

1. Total Uranium Analysis
   a. Based on $U^{238}$
   b. Bismuth used as the Internal (Surrogate) Standard
   c. Acquire time

2. $U^{235}/U^{238}$ Ratio
   a. Use of NBL Standards
   b. Derived from Total Data or Independent Run

3. $U^{234}/U^{235}$ and $U^{236}/U^{235}$ Ratios
   a. Use of NBL Standards
   b. Higher concentration for instrument to see peaks

C. Conversions / Calculations

1. Using Lotus Spreadsheet to calculate isotopic wt%
2. Back calculating Total U using wt% of $U^{238}$
3. Using individual isotopic wt% and Total U to give ppm
4. Specific Activity Conversions for isotopic activity

III. Further Developments

A. Quicker Digestion yet same sensitivity
   1. Smaller aliquot
   2. Which Acids
   3. Use of glass erlenmeyer flasks
   4. Use of an infrared hotplate (quick heat)

B. Shorter Acquire Time

IV. Conclusion
SAMPLE PREP / ANALYSIS FLOWCHART

SAMPLE

DRIED @ 110°C & GROUND

MUFFLE FURNACE

ACID DIGESTION

FILTER & DILUTE

( CONTINUED )

HF
HNO₃
H₂O₂
DILUTION

FIRST PASS THROUGH INSTRUMENT FOR U238 & U235/U238 RATIO

CONCENTRATE

PASS THROUGH EICHROM COLUMNS

SECOND PASS THROUGH INSTRUMENT U234/U235 & U236/U235 RATIOS
$^{235}\text{U} : ^{238}\text{U}$ Scan
$U^{234} : U^{235} : U^{236}$ Scan
MASS DISCRIMINATION
BIAS FACTOR

\[ B = \left\{ \frac{1}{c} \left[ \frac{\bar{R}}{R_s} - 1 \right] \right\} \]

where,

\[ c = \frac{\Delta M}{M} \text{ for the ratio used} \]

\[ (\text{ie. for } U^{235} / U^{238}, \ c = (238 - 235) / 238) \]

\[ \bar{R} = \text{Average ratio from 12 sets of 8 analyses} \]

\[ R_s = \text{Certified value for the standard used} \]
CORRECTED RATIO

\[ \bar{R}' = \frac{\bar{R}}{(1 + c B)} \]

where,

\[ \bar{R} = \text{Average raw ratio} \]
\[ c = \frac{\Delta M}{M} \text{ for each ratio to be corrected} \]
\[ B = \text{Mass Discrimination Bias Factor} \]

(ie. \[ \bar{R}'_{45} = \frac{\bar{R}_{45}}{(1 + (235^M-234^M/235) \cdot B)} \])
WEIGHT PERCENT

\[ W = \frac{100 \ M \ \bar{R}'_x}{238 + 234 \bar{R}'_{48} + 235 \bar{R}'_{58} + 236 \bar{R}'_{68}} \]

where,

- \( M \) = Mass of isotope of interest
- \( \bar{R}' \) = Ratio of isotope of interest related to \( \text{U}^{238} \)
- \( \bar{R}'_x \) = \( \bar{R}'_{48} \times \bar{R}'_{58} \)
- \( \bar{R}'_{48} \) = \( \bar{R}'_{45} \times \bar{R}'_{48} \)
- \( \bar{R}'_{68} \) = \( \bar{R}'_{65} \times \bar{R}'_{58} \)
ACTIVITY CALCULATION

\[ U^n \text{ Activity} = \frac{A_s \cdot W \cdot T_U}{222} = \text{pCi/g} \]

where,

- \( U^n \) = Isotope of interest
- \( A_s \) = Specific Activity (d/m\text{–ug})
- \( W \) = Weight Percent of \( U^n \)
- \( T_u \) = Total Uranium (ppm)
- 222 = Conversion from d/m to pCi (2.22 d/m = 1 pCi)
  (multiply by 100 to give value to wt%)
FURTHER DEVELOPMENTS

A. FASTER DIGESTION

- Smaller Aliquot
- HNO$_3$ + HCLO$_4$
- Use of glass
- Infrared Hotplate
- Varying column resins

B. SHORTER ACQUIRE TIME