ICP-OES Method for Material Accountancy Measurements

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Introduction:

Processes being developed by the Department of Energy for treating spent nuclear fuel require timely and reliable chemical analysis data to maintain Material Control and Accountability (MC&A) inventories that track the amounts and locations of uranium, plutonium, and other fissile materials in the treatment system.

Current analysis methods for MC&A, like isotope dilution mass spectrometry (IDMS), provide very accurate data (0.25%RSD) but take a long time to do and use specialized equipment.

This proof-of-concept LDRD project looked at whether a method based on Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) could produce comparable performance while taking less time and using equipment that is commonly employed for analyzing other kinds of process samples.

Why Did We Consider ICP-OES ?

ICP-OES measures the light emitted by an element in a sample Introduced to a high-temperature argon plasma. Each element emits at specific wavelengths. The intensity of the emission is proportional to the number of atoms and, therefore, to the element concentration.

- Simpler Sample Preparation
- Faster Analysis
- Instrument Used for Other Process Measurements

BUT… ICP-OES is not generally known for high accuracy!

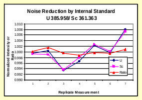
High-Performance ICP-OES

Short-term variations in **signal (noise)** and longer-term **signal drift** limit the precision of conventional ICP-OES measurements.

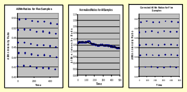
A high-performance approach to such measurements was developed at the National Institute of Standards and Technology (NIST) and applied to certifying Standard Reference Materials [M. L. Salit et al., *Anal. Chem.*, **1998**, *70*, 3184-3190].

The NIST Approach:

Reduces noise by taking ratios of the analyte signal to a simultaneously measured signal from an added internal-standard element (most noise sources affect both lines).



Compensates for drift by making repetitive measurements and using a fitted curve to provide drift correction.



Drift Compensation with NIST Algorithm

Achieves measurement precision on the order of 0.1% RSD.

High precision and good standards produce accurate data.

Applying the NIST Approach to Uranium Materials Control and Accountability (MC&A)

Work plan to implement and evaluate high-performance ICP-OES method for uranium MC&A

- Select internal standard, analysis wavelengths, plasma operating conditions
- Prepare and analyze solutions made from reference materials
- Compile statistics to evaluate method performance

Method Implementation

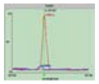
Perkin Elmer 3300 DV ICP-OES Instrument

Select Internal Standard

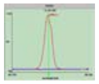
Properties of ideal internal standard
- Absent from samples
- Free of analyte
- Compatible chemistry
- Similar excitation energy
- No spectral overlap with analyte

Scandium selected

357.253 nm (U Interferes)



361.383 nm (Good)



424.683 nm (Good)

Select Uranium Wavelengths

Properties of ideal analyte line
- Strong line
- High signal to background ratio
- No spectral overlap with non-analyte sources

Uranium lines selected

385.958 nm

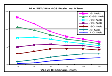
409.014 nm

424.167 nm

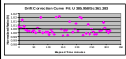
Optimize Operating Conditions

Optimum depends on:
- RF power
- View distance
- Carrier gas flow

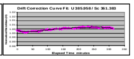
ANL optimization strategy uses ionic-to-atomic line intensities to profile plasma for selection of view distance and carrier flow



Plasma conditions affect method performance



RF Power 1300 Watts
Radial View (12 mm)
"Compromised" Gas Flow



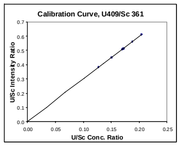
RF Power 1450 Watts
Radial View (12 mm)
Optimized Gas Flow

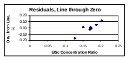
Performance Study

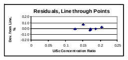
- Seven solutions made from NBS SRM 950, U_3O_8 Uranium Assay Standard
- U from 100 to 170 mg/kg (ppm); Sc at 1 mg/kg (ppm)
- Calculated calibration line in two ways:

  Straight line through zero (6 degrees of freedom)

  Straight line through measured points (5 degrees of freedom)
- Used RMS percent residual (% RSD) to indicate precision.







Rel. Std. Dev. From Seven Solutions, % RSD Calibration as Line Through Zero (6 degrees of freedom)		
	Sc 424	**Sc 361**
U 385	0.059	0.035
U 409	0.031	0.086
U 424	0.061	0.089

Rel. Std. Dev. From Seven Solutions, % RSD Calibration as Line Through Points (5 degrees of freedom)		
	Sc 424	**Sc 361**
U 385	0.041	0.034
U 409	0.027	0.036
U 424	0.064	0.056

- For all combinations of uranium and scandium lines, RSD better than 0.1% was achieved – comparable to isotope dilution.

Conclusions

The ICP-OES method performs as well as isotope dilution for clean matrix (U_3O_8 standards); RSDs on the order of 0.05% were achieved with best combinations of internal standard and uranium wavelengths.

Method should be easily adapted for assay of product materials

Method might be improved, but already at a level where sample weighing and handling introduce uncertainty comparable to measurements.

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