Sulfur Limits of Detection and Spectral Interference Corrections for DWPF Sludge Matrices by Inductively Coupled Plasma Emission Spectrometry (U)

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Savannah River Technology Center
Measurement Technology Department
Analytical Development Section

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ADS	Analytical Development Section
DWPF	Defense Waste Processing Facility
IUPAC	International Union of Pure and Applied Chemistry
LOD	Limit of Detection
NIST	National Institute of Science and Technology
S	Sulfur
SRTC	Savannah River Technology Center
WSRC	Westinghouse Savannah River Company

Introduction

The Analytical Development Section (ADS) of the Savannah River Technology Center (SRTC) has been requested to perform sulfur (S) analysis on digested Defense Waste Processing Facility (DWPF) radioactive sludge and supernatant samples by Inductively Coupled Plasma Emission Spectrometry (ICP-ES). The amount of sulfur is a concern because there are sulfur limits for the incoming feed to DWPF, due to glass melter, process vessel, and off-gas line corrosion concerns and limited sulfur solubility in the glass wasteform. Recent changes in the Tank Farm washing strategy and H-Canyon stream additions change the amount of sulfur in the sludge. Increasing the sulfur concentration in the sludge challenges the current limits, so accurately determining the amount of sulfur present in a sludge batch is paramount.

There are two important figures of merit that need to be evaluated for this analysis. The first is the detection limit (LOD), the smallest concentration of an element that can be detected with a defined certainty. This issue is important since the sulfur concentration in these process streams is low. Another critical analytical parameter is the effect on the S quantitation from potential spectral interferences. Spectral interferences are caused by background emission from plasma recombination events, scattered and stray light from the line emission of high concentration elements, or molecular band emission and from direct or tailing spectral line overlap from a matrix element. Any existing spectral overlaps could give false positives or increase the measured S concentrations in these matrices. The purpose of this study was to document the Analytical Development Sections's contained ICP-ES performance in these two areas.

Experimental

The instrument used for these measurements is a Horiba Jobin Yvon Model 170C Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-ES) with a 1.5 kW, 40 MHz solid-state generator and torch box assembly contained in a radiological fume hood[1]. The spectrometer section of the instrument consists of a 1-meter Czerny-Turner monochromator with a 1-m focal length, 80 x 110 mm, and 2400 grooves/mm grating with 5 pm resolution (2nd order full width half max) at 182 nm and a 0.5-meter polychromator. The polychromator uses a Paschen-Rungen (Rowland Circle) design with a 0.5-m focal length (3000 grooves/mm) grating in first order and with a flat-field segment to detect Na, Li and K. All measurements were made in the Gaussian peak mode, with nine points sampled across the S emission line peak shape. Although lower LODs could be acquired in the single or "median" (5 points) modes, the Gaussian mode provides higher precision data, since more points on the emission profile are measured. In addition, there is acceleration in the calibration curve drift in the single or "median" modes. All data were acquired following procedure ADS-1564, "Contained ICP-ES for Radioactive Sample Analysis, JY170C"[2]. A 5 μg/mL chromium (Cr) instrument profile standard was measured daily to properly align the polychromator entrance

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[1] F. M. Pennebaker and J.C. Hart, WSRC-TR-2003-00063, "Final Report on Jobin Yvon Contained Inductively Coupled Plasma Emission Spectrometer (ICP-ES)", Westinghouse Savannah River Site 2/6/03.

[2] L16.1-ADS-1564, "Contained ICP-ES for Radioactive Sample Analysis, JY170C", Westinghouse Savannah River Site, 9/01/03

slit with the plasma analytical zone. Carbon emission from excited air was used to align the monochromator entrance slit. The three main sulfur optical emission wavelengths are 180.676, 181.974, and 182.568 nm. Only the last two lines were studied due to time constraints at the initiation of this investigation. The 182.568 line was rejected after a preliminary survey, primarily because it is not very sensitive and suffers severe spectral interferences from matrix elements in a digested surrogate waste glass. For this report, sulfur measurements were made at the 181.97 nm wavelength both sequentially on the monochromator and on the simultaneous polychromator channel with no background correction points. Continuous background emission (either flat or sloping) across the sulfur peak may be removed by subtracting the off-peak background intensity or an intensity linearly interpolated between two selected wavelengths on either side of the line emission. This protocol will not correct for the direct line overlaps on sulfur that are present during the analysis of complex sludge and glass digestates. And since additional measurements must be made to perform background correction, both the analysis time and expended sample volume increase. A 2 µg/mL scandium (Sc) in 2% HNO_3 internal standard was added to all solutions to compensate for minor fluctuations in the plasma and sample introduction system. Scandium intensity was measured simultaneous to sulfur using a fixed channel on the polychromator.

Limits of Detection have been determined utilizing the International Union of Pure and Applied Chemistry (IUPAC)[3] methodology as follows:

$$\mathbf{X_L = \bar{X}_{bl} + ks_{bl}}$$

$$\mathbf{C_L = (X_L - \bar{X}_{bl})/S}$$

where

- $\mathbf{X_L}$: **Smallest measure detected with reasonable certainty**
- $\bar{X}_{bl}$: **Mean of blank measures**
- **k: Uncertainty factor**
- $\mathbf{s_{bl}}$: **Standard deviation of blank measures**
- $\mathbf{C_L}$: **Limit of Detection**
- **S: Sensitivity (Slope of the Calibration Curve)**

Note: "A value of 3 for k . . . is strongly recommended; for this value, a 99.6% confidence level applies only for a strictly one sided Gaussian distribution. At low concentrations, non-Gaussian distributions are more likely. Moreover, the values of $\bar{X}_{bl}$ and S_{bl} are themselves only estimates based on limited measurements. Therefore, in a practical sense, the 3 S_{bl} value usually corresponds to a confidence level of about 90%."[3] ADS has chosen to use k = 5 to increase the confidence interval above 90%.

For the LOD determination twenty replicate blank measurements of the 2% nitric acid solution were collected. The number of replicate blank measurements is not specified by

[3] IUPAC Compendium of Analytical Nomenclature, Definitive Rules, 3rd Edition, Section 10.3.3.3.1 "Limit of Detection" (1997).

IUPAC for the LOD determination, but literature references recommend twenty[4, 5]. The S sensitivity (slope of the calibration curve) was calculated from the intensities of the 2% HNO_3 blank, 5 µg/mL and 10 µg/mL sulfur standard solutions. To better quantify S at low concentrations, the calibration curve was forced through the origin and the blank intensity was subtracted from the sample value. Standards were made from a 1000 µg/mL NIST traceable stock solution diluted in the 2% HNO_3 matrix blank.

For the spectral interference study, several single element standards at the nominal DWPF sludge concentrations were analyzed on both S lines to determine the equivalent S detected in µg/mL in 2% HNO_3. As for the LOD study, all the standards were diluted from a 1000 µg/mL NIST traceable stock solution and spiked with 2 µg/mL Sc added as an internal standard. To eliminate carry-over, a 2% HNO_3 solution was flushed through the system between interferent solutions until the background intensity was reduced to the blank level.

Results and Discussion

The sulfur detection limit results for both emission lines explored are listed in Tables 1. The LOD for the monochromator line is 5x better than the polychromator line even though their atomic transition (wavelength) is the same. Although the 1-meter monochromator will have better stray and scattered light rejection, the difference in sensitivity (intensity per unit concentration) between the two spectrometers is surprising. The polychromator photomultiplier tube may be defective or improperly adjusted. If sulfur is present, the monochromator is the spectrometer of choice for low-level sulfur analysis.

Table 1. Sulfur Limits of Detection in a 2% HNO_3 Matrix.

	Polychromator 181.974 nm	Monochromator 181.978 nm
Blank Avg. (20)	0.00728	0.0127
Blank Stdev. (20)	0.00046	0.00037
S (Intensity/(µg/mL))	0.018386	0.07102
IUPAC 3σ LOD (µg/mL)	0.07	0.016
IUPAC 5σ LOD (µg/mL)	**0.13**	**0.026**

Typical spectral interferences on both S emission lines in µg/mL in 2% HNO_3, are listed in Table 2 for the major DWPF sludge elements. These listed ratios should be re-determined periodically since plasma and sample introduction conditions, and spectrometer alignment vary over time. The interferences are considerably lower for the monochromator line than the polychromator fixed channel and only significant for Mn, Al, and U. In contrast, the interferences on the polychromator channel are severe, especially for Fe, Mn, U, and Al with factors as much as 15x higher. Interelement overlaps may vary for the same emission line among spectrometers due to differences in resolution, as determined by spectrometer focal

[4] P. W. J. M Boumans, Inductively Coupled Plasma Emission Spectroscopy, Part 1, Methodology, Instrumentation, and Performance, (John Wiley & Sons, New York ,1987), p 106.
[5] J. D. Winefordner, Trace Analysis, Spectroscopic Methods for Elements, (John Wiley & Sons, New York, 1976), p 5.

length, grating line density, the entrance and exit slit widths, and by line dispersion. By using the JY170C monochomator, sulfur spectral interference corrections are minimized.

Table 2. Typical Equivalent S (μg/ml) in 2% HNO_3 Matrix

Interferent	Polychromator 181.974	Monochromator 181.978
Al - 200 μg/ml	**0.249**	**0.055**
Ca - 100 μg/ml	**0.103**	0.007*
Fe - 400 μg/ml	**1.45**	0.016*
Mg- 100 μg/ml	0.064*	0.015*
Mn - 100 μg/ml	**1.93**	**0.146**
Na - 400 μg/ml	0.042*	0.011*
Ni - 100 μg/ml	0.043*	0.012*
P - 100 μg/ml	0.001*	0.002*
Si - 100 μg/ml	0.084*	0.002*
Sr - 100 μg/ml	0.083*	0.008*
U - 200 μg/ml	**0.308**	**0.068**

* Values below the sulfur LOD.

Quadruplicate samples of dried DWPF radioactive sludge, both Sludge Batchs 2 & 3, were digested for 2 hrs at 100^{o} C in aqua regia (3:1 HCl/HNO_3) in sealed Teflon vessels. These acid digestates were analyzed on both emission lines with results summary listed in Table 3. Complete detailed spectral interference corrections for all major elements in these sludge samples, plus blanks and controls are listed in Tables 4 and 5. These results were not corrected for dilutions performed in the SRTC High-Activity Cells. Correction factors were determined from single element standards on the day each of the two batches of samples were analyzed. After correction ratios are applied, sulfur concentrations converge with an average difference of only 13%. Considering the propagated errors associated with this number, the difference between the two is small. This variation reduces to only 10%, if sample AR-1-T40-Qual-3 is removed from the average. The average polychromator sulfur correction was 81% while the monochromator's adjustment was only 4.8% (a 15x difference). Clearly the monochromator analytical results would be more accurate and the spectrometer of choice for this measurement. The final official results (on a wt% dried sludge basis) for Sludge Batches 2 & 3 and additional information on sulfur analysis of DWPF feed streams can be found in Bibler and Hay [6]. Finally, equivalent sulfur concentrations for a series of 50 to 900 μg/mL Fe standards were determined to prove that the correction factors on the sulfur lines are linear with increasing interferent. The linear relationship is presented in Figure 1. This relationship should be similar for all the other interfering elements. It would not be necessary to measurement correction ratios at more than one concentration.

[6] N. E. Bibler and M. S. Hay, WSRC-TR-2004-00092, "Total and Soluble Sulfur in a Sample from Tank 40 (Sludge Batch 2) and a Composite of Samples from Tank 51 (Sludge Batch 3)", Westinghouse Savannah River Site, 2/20/04

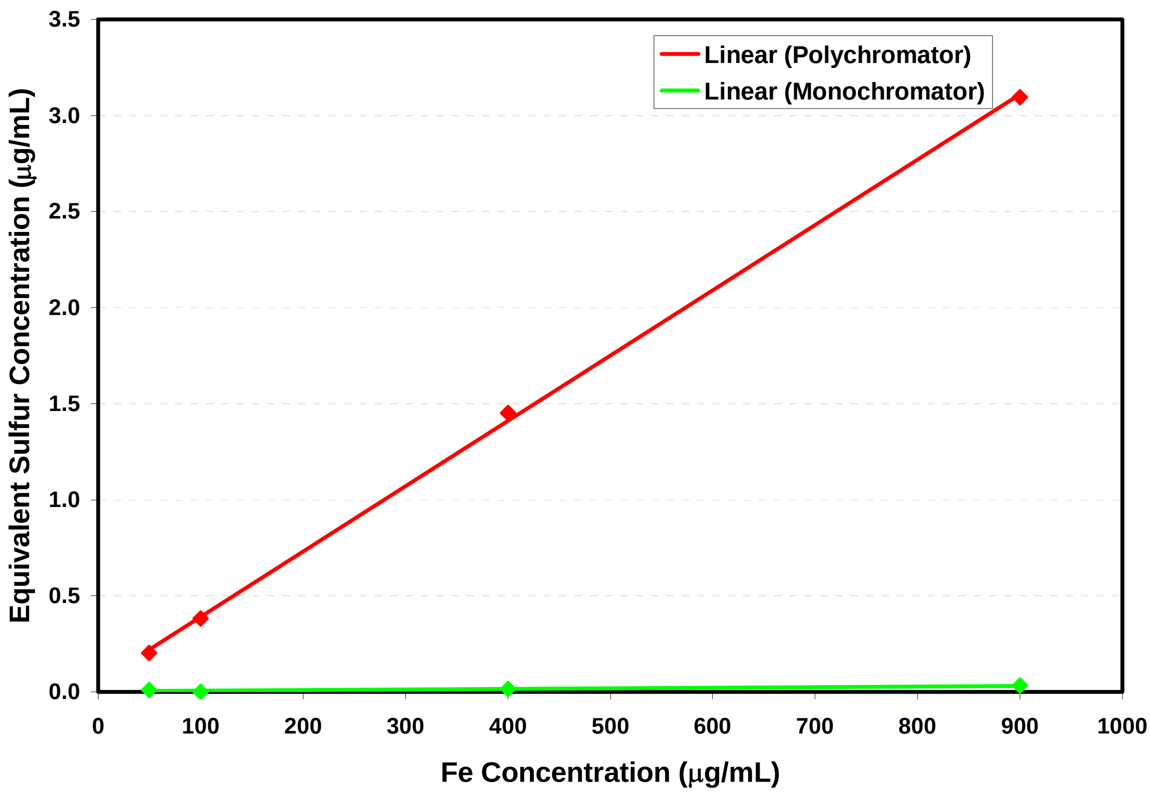

Figure 1. Iron spectral interference on sulfur concentration

Conclusions & Path Forward

The monochromator 181.97 nm atomic emission line is superior for both examined figures of merit, LOD and spectral interference minimization. This spectrometer has a 5-fold better detection limit and requires only minimal overlap corrections (~5%), making it the line of choice for sulfur analysis in radioactive sludge. As time permits, future studies will be conducted on the final sulfur emission line at 180.676 nm. This wavelength may have negligible spectral overlaps from concomitant matrix elements, eliminating the need for any spectral interference corrections. The poor signal to noise response for the sulfur polychromator channel will also be examined to see if the difference between the two spectrometers at the same sulfur line is real or an equipment malfunction in the polychromator.

Table 3. Digested Radioactive Sludge Sulfur Concentrations (μg/ml)

Customer ID	S Mono 181.978 Uncorrected	S Mono 181.978 Corrected	% Correction	S Poly 181.978 Uncorrected	S Poly 181.978 Corrected	% Correction	% Difference Mon vs. Poly
Sludge Batch 2							
AR-1-T40-Qual-1	3.956	3.774	4.8	6.746	3.492	93	7
AR-1-T40-Qual-2	3.908	3.729	4.8	6.550	3.343	96	10
AR-1-T40-Qual-3	3.584	3.416	4.9	7.424	4.436	67	30
AR-1-T40-Qual-4	3.763	3.586	4.9	6.449	3.276	97	9
Sludge Batch3							
AR-1-T51-Qual-1	6.973	6.659	4.7	10.438	6.059	72	9
AR-1-T51-Qual-2	7.657	7.320	4.6	11.095	6.382	74	13
AR-1-T51-Qual-3	7.737	7.400	4.6	11.228	6.535	72	12
AR-1-T51-Qual-4	7.472	7.140	4.7	10.993	6.337	73	11
Average:			**4.8**			**81**	**13**

Table 4. Sludge Batch 2 Sulfur Concentrations (μg/mL) for both ICP-ES Emission Lines.

		S Mono 181.978	Spectral Interference Correction on Sulfur											S Mono 181.978
LIMS #	Customer ID	Uncorrected	Al	Ca	Fe	Mg	Mn	Na	Ni	P	Si	Sr	U	Corrected
205573	AR1-BLK-1-T40	0.051	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.051
205574	S-1	0.020	0.001	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	<0.02
205575	AR-1-T40-Qual-1	3.956	0.027	0.003	0.018	0.005	0.089	0.004	0.003	0.000	0.000	0.001	0.032	3.774
205576	AR-1-ARG-1-T40	1.034	0.018	0.002	0.012	0.002	0.065	0.007	0.003	0.000	0.000	0.001	0.000	0.925
205577	AR1-T40-Qual-2	3.908	0.027	0.003	0.017	0.005	0.088	0.004	0.003	0.000	0.000	0.001	0.031	3.729
205578	S-2	0.043	0.001	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.040
205579	AR-1-ARG-T40	1.032	0.018	0.002	0.012	0.002	0.064	0.007	0.003	0.000	0.000	0.001	0.000	0.923
205580	AR-1-T40-Qual-3	3.584	0.026	0.003	0.016	0.005	0.082	0.004	0.003	0.000	0.000	0.001	0.029	3.416
205581	AR-1-ARG-3T40	1.020	0.018	0.002	0.011	0.002	0.063	0.007	0.003	0.000	0.000	0.001	0.000	0.914
205582	AR-1-T40-Qual-4	3.763	0.027	0.003	0.017	0.005	0.087	0.004	0.003	0.000	0.000	0.001	0.030	3.586
205583	S-3	0.025	0.001	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.022

		S Poly 181.978	Spectral Interference Correction on Sulfur											S Poly 181.978
LIMS #	Customer ID	Uncorrected	Al	Ca	Fe	Mg	Mn	Na	Ni	P	Si	Sr	U	Corrected
205573	AR1-BLK-1-T40	0.014	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	<0.1
205574	S-1	0.127	0.005	0.000	0.015	0.000	0.000	0.008	0.000	0.000	0.048	0.000	0.000	<0.1
205575	AR-1-T40-Qual-1	6.746	0.124	0.043	1.617	0.023	1.181	0.014	0.010	0.000	0.013	0.008	0.220	3.492
205576	AR-1-ARG-1-T40	3.229	0.082	0.031	1.064	0.010	0.854	0.026	0.011	0.000	0.002	0.006	0.000	1.144
205577	AR1-T40-Qual-2	6.550	0.122	0.042	1.597	0.023	1.168	0.014	0.010	0.000	0.012	0.008	0.212	3.343
205578	S-2	0.160	0.004	0.000	0.015	0.000	0.000	0.008	0.000	0.000	0.048	0.000	0.000	<0.1
205579	AR-1-ARG-T40	2.947	0.082	0.030	1.058	0.010	0.849	0.026	0.011	0.000	0.002	0.006	0.000	0.874
205580	AR-1-T40-Qual-3	7.424	0.118	0.040	1.482	0.021	1.084	0.014	0.009	0.000	0.012	0.008	0.201	4.436
205581	AR-1-ARG-3T40	2.994	0.081	0.029	1.027	0.010	0.830	0.025	0.010	0.000	0.002	0.005	0.000	0.975
205582	AR-1-T40-Qual-4	6.449	0.123	0.041	1.579	0.022	1.153	0.014	0.010	0.000	0.012	0.008	0.212	3.276
205583	S-3	0.089	0.004	0.000	0.015	0.000	0.000	0.008	0.000	0.000	0.048	0.000	0.000	<0.1

Table 5. Sludge Batch 3 Sulfur Concentrations (μg/mL) for both ICP-ES Emission Lines.

		S Mono 181.978	Spectral Interference Correction on Sulfur											S Mono 181.978
LIMS #	Customer ID	Uncorrected	Al	Ca	Fe	Mg	Mn	Na	Ni	P	Si	Sr	U	Corrected
205708	AR1-BLK-1-T51	0.075	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.075
205709	S-1	1.032	0.020	0.002	0.011	0.002	0.065	0.007	0.003	0.000	0.000	0.001	0.000	0.921
205710	AR-1-T51-Qual-1	6.973	0.048	0.002	0.016	0.006	0.175	0.009	0.003	0.000	0.000	0.001	0.054	6.659
205711	AR-1-ARG-1-T51	0.922	0.018	0.002	0.010	0.002	0.060	0.006	0.003	0.000	0.000	0.001	0.000	0.820
205712	AR1-T51-Qual-2	7.657	0.052	0.003	0.017	0.007	0.188	0.010	0.004	0.000	0.000	0.001	0.057	7.320
NOT IN	S-2													
205713	AR-1-ARG-T51	0.843	0.016	0.002	0.009	0.002	0.054	0.006	0.002	0.000	0.000	0.000	0.000	0.751
205714	AR-1-T51-Qual-3	7.737	0.051	0.003	0.017	0.007	0.187	0.010	0.004	0.000	0.000	0.001	0.058	7.400
205715	AR-1-ARG-3T51	0.810	0.016	0.002	0.009	0.002	0.054	0.006	0.002	0.000	0.000	0.000	0.000	0.719
205716	AR-1-T51-Qual-4	7.472	0.051	0.003	0.017	0.007	0.186	0.010	0.003	0.000	0.000	0.001	0.056	7.140
NOT IN	S-3													

		S Poly 181.978	Spectral Interference Correction on Sulfur											S Poly 181.978
LIMS #	Customer ID	Uncorrected	Al	Ca	Fe	Mg	Mn	Na	Ni	P	Si	Sr	U	Corrected
205708	AR1-BLK-1-T51	0.090	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.089
205709	S-1	3.044	0.082	0.030	1.031	0.010	0.868	0.026	0.010	0.000	0.000	0.006	0.000	0.980
205710	AR-1-T51-Qual-1	10.438	0.197	0.036	1.433	0.026	2.345	0.036	0.011	0.000	0.015	0.007	0.273	6.059
205711	AR-1-ARG-1-T51	2.671	0.075	0.028	0.952	0.009	0.802	0.024	0.010	0.000	0.025	0.005	0.001	0.741
205712	AR1-T51-Qual-2	11.095	0.214	0.038	1.545	0.028	2.524	0.039	0.012	0.000	0.017	0.008	0.288	6.382
NOT IN	S-2													
205713	AR-1-ARG-T51	2.429	0.068	0.025	0.861	0.008	0.724	0.022	0.009	0.000	0.015	0.005	0.000	0.692
205714	AR-1-T51-Qual-3	11.228	0.213	0.038	1.535	0.028	2.510	0.039	0.012	0.000	0.015	0.008	0.294	6.535
205715	AR-1-ARG-3T51	2.425	0.067	0.025	0.860	0.008	0.722	0.022	0.009	0.000	0.019	0.005	0.000	0.689
205716	AR-1-T51-Qual-4	10.993	0.211	0.038	1.537	0.028	2.488	0.038	0.012	0.000	0.014	0.007	0.284	6.337
NOT IN	S-3													