

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

**Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/help/index.asp>**

**Available electronically at <http://www.osti.gov/bridge>
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov**

March 3, 2004

**Keywords: DWPF Sludge Feed,
Sulfur Determinations,
Sludge Analyses**

**Determination of Sulfur in High-Level Waste Sludge by Inductively
Coupled Plasma-Atomic Emission Spectroscopy and
Ion Chromatography**

March 3, 2004

Keywords: DWPF Sludge Feed,
Sulfur Determinations,
Sludge Analyses

Determination of Sulfur in High-Level Waste Sludge by Inductively Coupled Plasma-Atomic Emission Spectroscopy and Ion Chromatography

Summary

Significant differences (~ 30 %) have been observed in the sulfur measurements in high-level waste sludge by the Analytical Development Section (ADS) when using both the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ion chromatography (IC) methods. Since the measured concentrations of sulfur in the sludge may approach the maximum concentration that can be processed in the DWPF, experiments were performed to determine the source of the differences and assess the true accuracy of sulfur measurements. The data and observations support the following conclusions:

- Spectral interferences from several sludge elements including Fe, Mn, Al, and U on the sulfur analytical line used for ICP-AES determinations can account within experimental uncertainties for the differences in ICP-AES and IC measurements in some samples that were dissolved in strong acid. The spectral interferences increased the ICP-AES sulfur measurements in high-level sludge to create a positive bias versus IC determinations. Minimizing spectral interferences reduces the positive bias in ICP-AES determinations.
- For some samples, statistically significant differences between ICP-AES and IC for sulfur determinations still have been observed even after the reduction of emission spectral interference. One possible source of disagreement of sulfur measurements from ICP-AES and IC methods is the existence, not yet verified, of non-sulfate forms of sulfur that would be transparent to IC measurements. Another possible source of disagreement is simply increased analytical errors from sulfur measurements near the IC detection limit in a complex chemical matrix.
- Cross-checks of the calibration standards used for ICP-AES and IC sulfur measurements revealed no problem with the standards.

- Standard addition of sulfate to a dissolved glass matrix containing sludge elements common in SRS sludge showed no inherent bias for the IC method to be able to measure sulfur in the form of sulfate. ICP-AES determinations of sulfur significantly above the detection limit were also accurate, indicating that spectral interferences would only affect sulfur determinations at low concentrations in the sludge.

Recommendations for Sulfur Determinations of High-level Waste Sludge at SRTC

1. The sludge should be completely dissolved in a hot bath of strong acids, such as boiling aqua regia (3:1, v/v, HCl/HNO₃) to help oxidize and dissolve all forms of sulfur that may be in the waste as a precursor to ICP-AES determinations. This recommendation is made even though analyses indicate that sulfur in SRS high-level waste is predominantly in the form of soluble sulfates¹. Since the hot aqua regia digestion is already currently used for Sludge Batch characterization, this recommendation primarily serves to specify the hot aqua regia digestion as the preferred sample preparation step for sulfur measurements.

The ADS protocol for dissolving high-level sludge with hot aqua regia for sulfur determinations is included in this report.

2. SRTC should use ICP-AES exclusively as the reference method to measure sulfur in each Sludge Batch feed to the DWPF. The ICP-AES method measures total sulfur, versus IC that measures only sulfate. Therefore, ICP-AES is inherently less likely than IC to under-report total sulfur in the Sludge Batch should it contain insoluble or non-sulfate forms of sulfur. The ICP-AES method also has important advantages of being more sensitive and less affected by strong acid solutions than IC.

Development work to account for matrix and acid effects from the aqua regia digestion would be required for IC to be considered equivalent to ICP-AES for sulfur measurements. In contrast, measurements of sulfate in the caustic liquid fraction is considered a relatively straightforward application of the ADS IC method and can often serve as a useful cross-check of the reference ICP-AES for total sulfur in waste samples.

The ADS protocols for both ICP-AES and IC determinations of sulfur in high-level sludge are included in this report. The IC protocol is included in case it is needed as a backup or cross-check to ICP-AES.

3. ICP-AES determinations of sulfur in high-level waste should employ the optimal analytical line/spectrometer system for minimizing spectral interferences that can bias sulfur measurements. Spectral interference checks should be part of the quality control program for ICP-AES sulfur determinations of high-level waste. Sulfur measurements by ICP-AES will require development for each different Sludge Batch feed to the DWPF.

4. Matrix-matched blanks and standards should be prepared and analyzed as part of the quality control protocol for sulfur determinations by ICP-AES (and IC as well, should this method be used as a back-up to ICP-AES).

Introduction

Limits are imposed on the sulfur concentration in the DWPF sludge feed because of its potential for affecting glass processing and increasing corrosion of DWPF metal surfaces. Samples of Tank 51 and blends of Sludge Batch 2/Sludge Batch 3 were analyzed by both ICP-AES and IC methods for sulfur. ICP-AES sulfur determinations have been, in general, about 30 % higher than from IC. Since sulfur is an important minor element in the sludge, determining the source of differences in sulfur measurements by ICP-AES versus IC was undertaken.

Discussion

Resolution of Differences in Sulfur Determinations from ICP-AES and IC

Investigations into the source of the differences in ICP-AES and IC sulfur measurements and determination of the accuracy of the methods for measuring sulfur in high-level sludge proceeded along two major paths:

- (1) Determine if there was a systematic quality control problem with one of the methods. The experimental program included extensive cross-checks of calibration standards, and also included selected analyses of samples by the Immobilization Technology Mobile Laboratory as an independent laboratory cross-check.
- (2) Assess both ICP-AES and IC methods to determine if there were inherent flaws that would bias sulfur determinations. This assessment included standard addition experiments with sulfur spiked into a simulated high-level sludge matrix followed by ICP-AES and IC analyses.

Evaluation of ICP-AES and IC Sulfur Calibration Standards

The ICP-AES and IC calibration standards used to measure sulfur were not the problem, as shown in the results of standards cross-checks in Table 1. Both ICP-AES ² and IC ³ methods are considered within quality control if the determinations are within 10 % of the standard value. The ADS IC did have one measurement that was 11 % low versus the standard value, but subsequent analyses were within the 10 % quality control limits. The results of this study showed no significant bias by either ICP-AES or IC for measuring calibration standards from various sources.

Table 1 Comparison of ADS ^a and Mobile Lab ^b Determinations of Sulfur Calibration Standards						
Sulfate Concen. in Standard	Lot #	Source Of Standard	ADS ICP-AES Results (% Difference- Measured vs. Standard)	ADS IC Results (% Difference- Measured vs. Standard)	Mobile Lab ICP-AES Results (% Difference- Measured vs. Standard)	Mobile Lab IC Results (% Difference- Measured vs. Standard)
3,000 mg/L	309720	ADS ICP-AES	Not measured	-11 %	- 3 %	+ 5 %
3,000 mg/L	310621	ADS ICP-AES	Not measured	-2 %	- 2 %	+ 6 %
3,000 mg/L	9-645	ADS ICP-AES	Not measured	+ 4 %	- 3 %	+ 7 %
1,000 mg/L	B3055098	Mobile Lab	+ 6 %	+ 6 %	Not measured	Not measured
1,000 mg/L	HP234530	Mobile Lab	+ 6 %	+ 6 %	Not measured	Not measured
1,000 mg/L	HP136105	Mobile Lab	- 4 %	- 5 %	- 2 %	Not measured
1,000 mg/L	ACC2044 10	Mobile Lab	+ 7 %	Not measured	- 1 %	+ 8 %
a ADS IC determinations were performed under the direction of R.J. Ray. ADS ICP-AES determinations were performed under the direction of J.C. Hart.						
b Mobile Lab IC and ICP-AES determinations were performed under the direction of D.R. Best.						

Evaluation of ICP-AES and IC Methods for Matrix Interferences

High-level sludge is a complex chemical matrix that can create analytical interferences. A non-radioactive matrix similar to that of dissolved high-level sludge was produced by boiling a three-gram portion of -200 mesh Analytical Reference Glass-1 (ARG-1) ⁴ in aqua regia for four hours. The acid solution was then filtered to remove the insoluble silica and diluted to 1L to produce a solution that approximates the composition of dissolved high-level sludge (Table 2), assuming quantitative leach of sludge elements from the glass. Note that this solution has much higher concentrations of B and Li (from

the glass-making chemicals) than is found in high-level sludge, but lacks the uranium found in all SRS sludges, so it is not a perfect simulated sludge.

Table 2 Simulated High-Level Sludge Matrix Created by Leaching 3 Grams of ARG-1 Reference Glass in Boiling Aqua Regia and Diluting to 1 Liter			
Element	Concentration in matrix (mg/L)	Element	Concentration in matrix (mg/L)
Al	75	Mn	44
B	81	Na	256
Ba	2	Ni	25
Ca	31	P	3
Cr	2	Si	3 ^a
Cu	< 1	Sr	< 1
Fe	290	Ti	21
K	68	Zn	< 1
Li	45	Zr	3
Mg	16		
^a The silicon concentration is estimated based on the very low solubility of silicon in this acid matrix.			

This stock solution was then used to dilute a 1000 mg/L ICP-AES sulfur standard (sulfate form) for preparing quality control sulfur standards in a simulated high-level sludge matrix. The target concentrations for sulfur in the four standards prepared were 38 mg/L, 75 mg/L, 150 mg/L, and 300 mg/L. These standards were analyzed by the ADS IC lab, the ADS ICP-AES lab, and the Mobile ICP-AES lab. Results of these analyses are shown in Table 3.

Table 3			
Comparison of Sulfur Determinations in Dissolved ARG-1 Glass Spiked with Sulfur by ADS IC Lab, ADS ICP-AES Lab, and Mobile Lab ICP-AES Lab			
(Shown in parentheses are the differences in the sulfur determinations and the target sulfur concentration in the matrix standards after correcting for sulfur readings in the blank glass.)			
Target Sulfur Concentration in Matrix Standard (mg/L)	ADS IC Sulfur Determination ^a <u>Without</u> Blank Correction (mg/L)	ADS ICP-AES Sulfur Determination ^b <u>Without</u> Blank Correction (mg/L)	Mobile Lab-ICP-AES Sulfur Determination ^c <u>Without</u> Blank Correction (mg/L)
0 (Blank)	2.6	3.2	1.6
13	16	16	15
25	29	29	28
50	50	56	54
100	87	107	105
Target Sulfur Concentration in Matrix Standard (mg/L)	ADS IC Sulfur Determination <u>With</u> Blank Correction (mg/L)	ADS ICP-AES Sulfur Determination <u>With</u> Blank Correction (mg/L)	Mobile Lab-ICP-AES Sulfur Determination <u>With</u> Blank Correction (mg/L)
13	13 (0 %)	13 (0 %)	13 (0 %)
25	26 (+4 %)	26 (+4 %)	26 (+4 %)
50	48 (-4 %)	53 (+6 %)	53 (+6 %)
100	85 (-15 %)	104 (+4 %)	103 (+3 %)
<p>a ADS IC analyses were performed under the direction of R.J. Ray. The IC method measures sulfate ion in mg/L. The conversion factor was used (3 mg/L sulfate = 1 mg/L elemental sulfur) to express the sulfate determinations in terms of mg/L elemental sulfur.</p> <p>b ADS ICP-AES analyses were performed under the direction of J.C. Hart.</p> <p>c Mobile Lab ICP-AES analyses were performed under the direction of D.R. Best.</p>			

These data indicate that both IC and ICP-AES techniques provide accurate sulfur determinations when the sulfur concentration is well above detection limits. The ARG-1 glass standard contains about 0.05 weight % sulfur that was subtracted from the raw measured values to provide the blank-corrected values in Table 3. The standard addition experiment demonstrated that the high-level waste matrix had no effect on the stability of sulfate as shown by good IC determinations. The IC determination of the 100 mg/L standard was 85 mg/L, outside the normal QC limits of ± 10 %. The 15 % error for this analysis was a technique issue on that particular sample as opposed to a systematic problem. ICP-AES determinations on the matrix standards were provided by both the ADS and the Mobile Lab. Both laboratories accurately analyzed the sulfate spiked into matrix standards.

Evaluation of ICP-AES for Matrix Spectral Interferences

High biases in ICP-AES determinations may result from overlap of emission lines produced by the elements in the sample matrix. Jurgensen, Hart, and Farrow⁵ evaluated the sulfur analytical line at 181.97 nm for spectral interferences by preparing a series of

single element standards with the approximate concentration of these elements in dissolved sludge. Complete details of this evaluation are discussed in reference 5, but the results are also summarized here by permission of the authors. Spectral interferences from iron, manganese, aluminum, and uranium at the 181.97 analytical line can result in high biases (Table 4). However, by using the analytical flexibility of the RADICPES system, the higher spectral resolving power of the 1.0 meter focal length monochromator significantly reduced spectral interferences compared to those observed with the 0.5 meter focal length polychromator.

Table 4 Comparison of Spectral Interferences at the 181.97 nm Sulfur Analytical Line From Common High-Level Sludge Elements When Using the - 0.5 meter focal length polychromator system - 1.0 meter focal length monochromator system (Spectral interference data used by permission and taken from the report by Jurgensen, Hart, and Farrow- WSRC-TR-2004-00090)							
Measured Sulfur Interference	Fe 400 mg/L	Al 200 mg/L	Ca 100 mg/L	Mg 100 mg/L	Mn 100 mg/L	Ni 100 mg/L	U 200 mg/L
Measured Sulfur in mg/L using Polychromator (focal length=0.5 meter)	1.453	0.249	0.103	<0.1	1.930	<0.1	0.308
Measured Sulfur in mg/L using Monochromator (focal length=1.0 meter)	<0.02	0.055	<0.02	<0.02	0.146	<0.02	0.044

Application of Improved ICP-AES Spectral Resolution to Sulfur Determinations

Reduction of spectral interferences in sulfur determinations by ICP-AES should minimize the differences between ICP-AES and IC. Table 5 shows sulfur analysis data on Tank 40 and Tank 51 supernatant fraction as compiled by Bibler and Hay ¹. The ICP-AES monochromator and the 181.97 nm analytical line were used to measure sulfur in these samples. However, a statistically significant discrepancy still exists between the two methods for measuring sulfur in the supernatant fraction in both Tank 40 (~27 %) and Tank 51 (~12 %). Known spectral interferences in the ICP-AES analyses of supernatant fraction samples do not account for higher sulfur determinations from this method. Also, since these measurements were performed on filtered supernatant samples, insoluble forms of sulfur cannot explain differences in these measurements. As discussed by Bibler

and Hay ¹, one possible source of the differences is non-sulfate form of sulfur that would be transparent in the sulfate determinations by IC with anionic chromatographic columns, but would be measured as total sulfur by ICP-AES. Note that the “non-sulfate” theory for these differences in sulfur determinations of the caustic supernatant fraction has not yet been proven, nor has any non-sulfate species been identified as part of this study.

Table 5 Measured Supernatant Sulfur Concentrations in -Tank 40 (Sludge Batch 2) -Tank 51 (Sludge Batch 3) (Data used by permission and taken from the report by Bibler and Hay- WSRC-TR-2004-00092) (% relative standard deviation is shown in parentheses for each result)		
Supernatant Sulfur (Molarity)	Tank 40 Sample Molarity of Sulfur ^a	Tank 51 Sample Molarity of Sulfur ^a
Sulfur Measured by ICP-AES	1.13 E-2 (4.0)	2.63 E -2 (0.6)
Sulfur Measured by IC	8.93 E-3 (8.6)	2.35 E-2 (3.9)
a. Average result based on analyses of three aliquots of the filtered supernatant.		

Discussion of ICP-AES versus IC for Sulfur Determinations of Dissolved High-level Sludge

Despite initial spectral interference problems with the ICP-AES method for sulfur determinations, this method is recommended as the SRTC reference method for characterizing the Macro-batch or Sludge Batch feeds to the DWPF. The ICP-AES has three principal advantages vis-à-vis IC:

1. The ICP-AES determinations are on total sulfur, whereas the IC determinations are sulfate. Since it is the total sulfur concentration that has consequences on DWPF processing, the ICP-AES total sulfur measurement is inherently advantageous. Data from the report by Bibler and Hay ¹ indicate that non-sulfate forms of sulfur may be present in some sludge samples that would not be detectable by IC without a sample preparation step to convert non-sulfate forms of sulfur to sulfate.
2. The ICP-AES method can directly analyze the strong acid solutions produced from the aqua regia digestion, versus the IC method that must adjust the solution pH to ≥ 5

to achieve good chromatographic column performance. The pH adjustment is tantamount to an additional dilution requirement for IC determinations.

3. The ICP-AES method has a detection limit for elemental sulfur of about 0.02 mg/L, versus the IC detection limit for sulfate of about 0.5 mg/L (or about 0.2 mg/L on an elemental sulfur basis). For example, if a sludge sample contains about 0.25 wt % sulfur on a dried solids basis, the concentration in a solution of 0.25 grams of sludge dissolved and diluted to 100 mL is on a mg/L basis:

$$\frac{250 \text{ mg sludge} \times 0.25 \text{ g S} / 100 \text{ g sludge}}{0.1 \text{ L solution (cell dilution volume)}} = 6.25 \text{ mg/L S or } 18.75 \text{ mg/L sulfate}$$

The IC method must dilute this solution by a factor of 10 to adjust the pH and make it compatible with the anion column, which reduces the sulfate concentration to 1.87 mg/L. This sulfate concentration is detectable by IC, but is well below the IC calibration range of 10-50 mg/L sulfate. The IC method would require testing to determine if the detector and column response is linear below 10 mg/L sulfate.

That being said, the IC method has at least two advantages over ICP-AES:

1. The sulfate peak is well separated from other ions common in dissolved sludge, minimizing the chance for significant positive biases.
2. The IC method requires much less sample. Only 50 μ L are required for injection into the sample loop for an IC run versus at least 5-10 mL required for ICP-AES determinations. This means that a larger sludge sample could be dissolved for IC analyses to help neutralize the inherent ICP-AES sensitivity advantage. For example, a 2.5 g portion of sludge could be dissolved and diluted to 100 mL. With this amount of dissolved sludge, the normal 10 mL aliquot solution removed from the shielded cells for ICP-AES analysis would likely exceed the permitted dose rate for work in hoods. However, the IC method can easily get by with only 500 μ L (for at least three replicate analyses) of the pH adjusted sample removed from cells, even with up to 10 times more sludge dissolved. This low sample volume would have roughly the same dose as the 10 mL of the more dilute sludge solution removed from the cells for ICP-AES analysis. Therefore, using the same hypothetical sludge that contains 0.25 wt. % sulfur, 2.5 grams of sludge dissolved and diluted to 100 mL would contain 187.5 mg/L sulfate or 18.75 mg/L sulfate after the nominal 10-fold dilution required to adjust the pH. Sulfate at this concentration is ideal for measurements by IC, but development work would still be required to determine if the higher concentration of metal ions affects IC response and performance.

Matrix-Matched Quality Control Standard for Sulfur Determinations by ICP-AES and IC

Concurrent analysis of matrix-matched standards is one of the best techniques for quality control of analytical methods. A matrix-matched standard that contains the approximate concentration of metals, sulfur, and acid as dissolved sludge can be prepared to achieve the following concentrations:

Fe	350 mg/L	
Al	200 mg/L	
Mn	100 mg/L	
U	200 mg/L	
S (in sulfate form)	5 mg/L	(15 mg/L sulfate)

Aqua Regia 9 mL HCl (concentrated) and 3 mL HNO₃ (concentrated)

This matrix contains elements that are either present in high concentration in dissolved sludge and/or exhibit some degree of spectral interference even when using the high-resolving power of the monochromator system at the 181.97 nm line. The concentration of sulfur spike is equivalent to dissolving 0.25 grams of dried sludge that contains 0.20 % sulfur and diluting the solution to 100 mL prior to analysis. The ICP-AES and IC Task Supervisors may develop other matrix standards as required for establishing method accuracy.

Procedure For Preparing a Matrix Standard for Sulfur Determinations by ICP-AES and IC

1. To a 100 mL volumetric flask, add the following volumes using calibrated pipettes:

Fe	35 mL of 1000 mg/L ICP-AES single element Fe standard
Al	20 mL of 1000 mg/L ICP-AES single element Al standard
Mn	10 mL of 1000 mg/L ICP-AES single element Mn standard
U	20 mL of 1000 mg/L ICP-AES single element U standard

S (in the sulfate form) 0.500 mL of 1000 mg/L ICP-AES single element S standard

2. Add 9 mL HCl (concentrated) and 3 mL HNO₃ (concentrated) to the flask. Let solution cool for 15 minutes before filling flask to the mark.
3. Fill the flask to the mark with de-ionized water, cap, and mix well by inverting several times. Transfer this solution to a labeled plastic or Teflon bottle. Label the bottle as "5.00 mg/L Sulfur Standard in Simulated Dissolved Sludge Matrix"

Procedure For Preparing Matrix Blank for Sulfur Determinations Laboratory Quality Control (same procedure as for matrix standard, but no sulfur is added)

1. To a 100 mL volumetric flask, add using calibrated pipettes:

Fe	35 mL of 1000 mg/L ICP-AES single element Fe standard
Al	20 mL of 1000 mg/L ICP-AES single element Al standard
Mn	10 mL of 1000 mg/L ICP-AES single element Mn standard
U	20 mL of 1000 mg/L ICP-AES single element U standard

2. Add 9 mL HCl (concentrated) and 3 mL HNO₃ (concentrated) to the flask. Let solution cool for 15 minutes before filling flask to the mark.
3. Fill the flask to the mark with de-ionized water, cap, and mix well by inverting several times. Transfer this solution to a labeled plastic or Teflon bottle. Label as "Blank Dissolved Sludge Matrix".

ADS Protocols for Sulfur Determinations in High-Level Sludge

The following discussion of recommended protocols for sulfur determinations of high-level sludge are not complete ADS analytical procedures, but they convey the general steps performed and include the parameters currently used to optimize sulfur determinations.

ADS Protocol for Hot Aqua Regia Digestion of Sludge for Sulfur Analyses

General ADS Procedure for Aqua Regia Digestions:

"Aqua Regia Dissolution of Sludge for Elemental Analysis"

ADS Procedure Number: ADS-2226

Author: C.J. Coleman

Effective Date: 2/25/03

Table 6	
Recommended Protocol for Hot Aqua Regia Digestion of High-Level Waste Sludge Samples for Sulfur Determinations	
Parameter	ADS Protocol For Analysis
Sample Size	0.25 –0.50 g solid; 1-3 mL slurry
Acid Mixture	9 mL con. HCl, 3 mL con. HNO ₃ ; reagent grade
Heating Temperature	115 ± 5 ° C
Heating Duration	At least 2 hours but no more than 4 hours after oven temperature re-equilibrates to 115 ± 5 ° C
Source of Heat	Conventional Drying Oven
Digestion Vessels	CEM Corporation 120 PFA Teflon microwave digestion vessel with cap; CEM catalog # 221001
Capping Station for Digestion Vessels	CEM capping station; CEM catalog # 920030
Cooling time before opening vessels after heating	At least 30 minutes
Dilution vessel/Final volume	Plastic volumetric flask/ 100 mL
Diluting solution	De-ionized water

The basic steps in the hot aqua regia digestion of high-level sludge for sulfur determinations are:

1. Pre-heat the drying oven to 115 ± 5 °C in the cell where the digestion will be performed.
2. Perform the balance calibration check in the cell where the work will be performed and record the data in the calibration log book.
3. Tare the bottom of a clean, dry Teflon pressure vessel bottom on the balance pan.
4. Using either dried sludge or slurry as directed by the researcher or task supervisor, add 0.25- 0.5 g dried powder or 1-3 mL of slurry to the Teflon pressure vessel.
5. Immediately weigh and record in the notebook or data sheet the amount of sample transferred to the pressure vessel.
6. Add the contents of the separate bottles that contain pre-measured 9 mL concentrated HCl and 3 mL concentrated HNO₃.
7. Immediately cap the Teflon pressure vessel with the capping station.
8. Repeat Steps 3-7 for all the number of replicates as prescribed by the researcher or task supervisor.

9. Place the Teflon Pressure Vessels in the oven.
10. Monitor the temperature and note the time that the temperature re-equilibrates at 115 ± 5 °C.
11. Heat the vessels at 115 ± 5 °C for at least 2 hours but no more than 4 hours.
12. Remove the vessels from the oven and let them cool for at least 30 minutes before opening to allow the pressure to subside in the vessel. Opening the vessels before they have cooled (still under pressure) can result in a dangerous evolution of gases and hot solution.
13. Use the capping station to uncap the vessel.
14. Transfer the solution in the pressure vessel to a clean 100 mL plastic volumetric flask, using several rinses of the vessel with de-ionized water to ensure quantitative transfer.
15. Fill the volumetric flask to the mark with de-ionized water.
16. Cap the volumetric flask and mix thoroughly by inverting the flask several times.
17. Transfer the solution in the flask into a labeled 125 mL narrow-mouth plastic bottle.
18. Transfer about 10 mL of the solution into a green shielded bottle for analysis by instrumental methods. Repeat for all replicates, blanks, and standards and remove from the cells for instrumental analysis.

ADS Protocol for Sulfur Determinations by ICP-AES

General ADS Procedure for Elemental Analysis by ICP-AES:

“Contained Inductively Couple Plasma-Atomic Emission Spectrometer for Radioactive Sample Analysis”

ADS Procedure Number: ADS-1564

Author: J.C. Hart

Revision: 2

Effective Date: 9/30/03

<p align="center">Table 7</p> <p align="center">Recommended ICP-AES Protocol for Determinations of Sulfur in High-Level Sludge after Hot Aqua Regia Digestion</p>	
Parameter	ADS Protocol For Analysis
Instrument Setup	Routine instrument conditions in terms of reflected power, wavelength profiling, sample integration times, peristaltic pump, nebulizer, and torch configuration will be used for sulfur determinations.
Calibration standards- 3 point calibration scheme	Mixed element standard with sulfur concentrations 0 mg/L (blank), 5 mg/L, 10 mg/L
Spectrometer	Scanning monochromator with 1.0 meter focal length
Monochromator wavelength (analytical line)	181.97 nm (or as directed by the ICP-AES Task Supervisor)
Spectral interference check	Analyze the following solutions for spectral interference on the sulfur analytical line: Fe- 350 mg/L; Al-200 mg/L, , Mn-100 mg/L, U- 200 mg/L.
Laboratory Control Blanks and Standards (Matrix matched)	Analyze the matrix-matched standard containing 5.00 mg/L sulfur standard to assess the accuracy of the method in a realistic chemical matrix (see report text for instructions on preparing matrix-matched blanks and standards).

The basic steps in the ICP-AES determinations of sulfur in high-level waste are:

1. Obtain the aqua regia digestion of the high-level sludge including any blanks and standards that were digested concurrently with the sludge samples.
2. Complete the routine setup and calibration of the ICP-AES instrument (this includes the setup and calibration of the monochromator at the 181.97 nm analytical line for sulfur determinations or as directed by the Task Supervisor).
3. Perform the matrix interference check on the sulfur analytical line using the following single element standards:

Fe- 350 mg/L
Al- 200 mg/L
Mn-100 mg/L
U- 200 mg/L

4. The Task Supervisor will review the spectral interference data on the sulfur analytical line and advise on whether to proceed with the analysis.

5. Perform any dilutions as directed by the Task Supervisor to obtain sulfur concentrations in the proper range for ICP-AES determinations.
6. Analyze the matrix-matched blanks and standards according to the ICP-AES protocol listed in Table 7. The Task Supervisor will determine whether the results of blanks and standards analyses are acceptable.
7. Analyze the samples according to the ICP-AES protocol listed in Table 7.

ADS Protocol for Sulfur Determinations by IC

General ADS Procedure for Ion Analysis by IC: “Analysis of Solutions by Ion Chromatography”

ADS Procedure Number: ADS-2306

Author: R.J. Ray

Revision: 8

Effective Date: 6/15/03

Table 8	
Recommended IC Protocol for Determinations of Sulfur in High-Level Sludge after Hot Aqua Regia Digestion	
Parameter	ADS Protocol For Analysis
Sample Volume for Dilution	500 μ L
Sample diluent	77 mM carbonate/22mM bicarbonate in distilled/de-ionized water
Initial dilution for pH adjustment	500 μ L sample into 5 mL of diluent
pH of solution injected into IC	> 5
Preferred instrumental dynamic range for sulfate determinations	10-50 μ g/mL
Typical serial dilutions required for sludge samples with less than 1 wt % sulfate content	10 fold, 100 fold
Sample Volume Injected into IC	50 μ L sample loop
IC Instrument	DX-500 Ion Chromatograph or equivalent
Detection Mode	Conductivity
Analytical Column(s)	Dionex AS14G 4mm x 50mm (guard column), AS14 4mm x 250mm (separator column)
Isocratic Flowrate	1.2 mL/minute
Eluent	3.5 mM carbonate/1mM bicarbonate in distilled/de-ionized water
Autosampler	Dionex AS-40 or equivalent
Suppression	Dionex ASRS anion self-regeneration suppressor
Laboratory Control Blanks and Standards (Matrix matched)	Analyze the matrix-matched standard containing 5.00 mg/L sulfur standard to assess the accuracy of the method in a realistic chemical matrix (see report text for instructions on preparing matrix-matched blanks and standards).

The basic steps in the IC determinations of sulfur in high-level waste are:

1. Obtain the aqua regia digestion of the high-level sludge including any blanks and standards that were digested concurrently with the sludge samples.
2. Dilute a 500 μ L aliquot of digested sample into 4.5 mL of 77 mM carbonate/22 mM bicarbonate solution.

Note: The pH of the dilution must be > 5. If the pH is around 2, a more concentrated carbonate/bicarbonate diluent must be used to obtain a pH > 5. Consult with the IC Task Supervisor for guidance and instructions on preparing a more concentrated carbonate/bicarbonate diluent if the pH is < 5.

3. Filter the solution after pH adjustment through a 0.22 μ m porosity filter.

4. Make serial dilutions, 10-fold, 100-fold, 1000-fold, as necessary to obtain a sulfate concentration in the range of 10 ug/mL to 50 ug/mL. Use the 77 mM carbonate/bicarbonate solution as the diluent. Note: For most high-level waste samples, the 10-fold dilution will be most appropriate for sulfate measurements.
5. Analyze the solutions with the ion chromatograph using the conditions specified in Table 8.

References

1. N.E. Bibler and M.S. Hay, "Total and Soluble Sulfur in a Sample from Tank 40 (Sludge Batch 2) and a Composite of Sample from Tank 51 (Sludge Batch 3)", WSRC-TR-2004-00092, March, 2004.
2. J.C. Hart, ADS Procedure-1564, "Contained Inductively Couple Plasma-Atomic Emission Spectrometer for Radioactive Sample Analysis"; effective date: September 30, 2003.
3. R.J. Ray, ADS Procedure- ADS-2306 "Analysis of Solutions by Ion Chromatography"
Revision: 8
Effective Date: 6/15/03
4. C.J. Coleman, et al, "SRL's Performance in Round Robin # 6- Analyses of Simulated Defense Waste Glass", WSRC-TR-1991-00187, May 31, 1991.
5. A.R. Jurgensen, J.C. Hart, L.L. Farrow, "Sulfur Limits of Detection and Spectral Interference Corrections for DWPF Sludge Matrices by Inductively Coupled Plasma Emission Spectrometry", WSRC-TR-2004-00090, March, 2004.