

Actinide, Elemental, and Fission Product Measurements by ICPMS at the Savannah River Site

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ACTINIDE, ELEMENTAL, AND FISSION PRODUCT MEASUREMENTS BY ICPMS AT THE SAVANNAH RIVER SITE

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ABSTRACT: A Fisons/VG Elemental Inductively coupled plasma-mass spectrometer (ICPMS), PlasmaQuad 1 (PQ1) Model No. 4, installed in a radiohood, is used by the Savannah River Technology Center to provide non-routine mass measurements for environmental monitoring, waste tank characterization studies, isotope ratios for criticality determinations, and the measurement of elemental, fission product, and actinide mass distributions of the glass product from the Defense Waste Processing Facility (DWPF).

Modifications to improve instrument reliability, sample preparation, and data handling, as well as modifications to the laboratory that permit measurements in a radioactive environment will be discussed. Based on our operating experience, two laboratory facilities are being prepared for additional instruments to operate in a radioactive environment. A separate instrument is being installed for non-radioactive measurements and method development.

KEYWORDS: ICP-MS, radiochemical methods, actinides, fission products, high level radioactive waste

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Inductively coupled plasma mass spectrometry (ICPMS) is used across the Savannah River Site (SRS) to provide information for many site missions such as waste processing, environmental remediation, and reactor basin stabilization. The procedures developed over the last seven years provide site customers with relatively fast and reliable analyses to satisfy their process needs. The Savannah River Technology Center (the research and development laboratory for the site) currently has three instruments, a Fisons/VG Elemental first generation PQ1 #4 and 2 Fisons/VG Elemental PQ2+'s. The PQ1 and one of the PQ2's are housed in hoods and used for both radioactive and non-radioactive samples. The second PQ2 is used exclusively for research, procedure development and non regulatory environmental samples.

The production environment at the SRS necessitates minimizing sample analysis time while maximizing quality from the analytical laboratory. SRS high level waste samples are typically high in salt content (~ 5 molar) and may contain large amounts of aluminum, iron, and organic species. These complex matrices complicate the radionuclide characterization of the sample by conventional counting methods [1] and therefore would normally require time consuming sample pretreatment to eliminate matrix effects. However, in previous reported work [1,2], ICPMS was shown to provide rapid reliable analysis for actinides and fission products in the SRS high level wastes with minimal sample pretreatment. For the analysis of actinides and fission products, a Quickbasic™ [3] program was written to extract mass spectral data from the binary format of the ICPMS instrument data files. This data could then be imported to Grams/386™ [4] for visual examination or to an EXCEL™ [3] spreadsheet for quantitative analysis. The lack of readily available certified standards or known isotopic mixtures for all possible radioactive analytes posed a problem in the quantitative analysis of actinides and fission products. The analytical procedure developed to overcome this problem included a knowledge of nuclear properties, process information, and instrumental response. Common multielement standards were used to calibrate for natural abundance elements. The assumption was then made that the mass sensitivities over a small mass range are quite similar and therefore the mass bias is small over that range. The uncalibrated masses can then be estimated using the calibrated mass sensitivities. The application of this analysis method to SRS high level waste samples resulted in the determination of actinide and fission product concentrations with 25% precision at the 1 ppb level.

Since commercial software did not exist for the analysis of non-natural and variable isotopic abundance elements, this first generation data reduction method provided a significant advantage in the analysis of SRS high level waste. Still, data handling required a high degree of human interaction with many manual manipulations in the EXCEL spreadsheet. Reduction in analysis time and the need for an audit trail of the calculations required a more user friendly and automated data reduction package.

In this paper, we present refinements to the first generation software that automates data reduction as well as hardware enhancements that improve instrument reliability and sensitivity. Experimental data is also presented to support the mass sensitivity assumption used in previous work [1,2]. The efficiency gained from these improvements proved beneficial in analyses performed for low activity and high level waste processing treatability studies for the Hanford Tank Waste Remediation program. For this program, chemical, radionuclide, and physical property characterization was

required on various Hanford waste streams. Like SRS high level waste, the Hanford waste streams are typically high in salt content, aluminum and organics and therefore the characterization is complicated by matrix effects.

ANALYTICAL PROCEDURES AND INSTRUMENTATION

Instrumentation

The containment hoods on the PQ1 and PQ2+ enclose the torch box, sampling cones, slide valve, peristaltic pump and optional autosampler. The sample effluent is collected in waste bottles or sent directly to the low level drain as required by the waste handling requirements of the sample. Electronics and vacuum pumps are located outside of the radioactive hood. Reported [2,5] and repeated in-house experience in vacuum system cleaning has demonstrated that the instrument pumps, detector region, quadrupole region and lens stack vacuum housing is free from detectable radioactive contamination. Fixed and smearable contamination is found on the cones. Within the lens stack, the photostop and first two lenses receive the majority of the contamination.

Routine sample introduction is accomplished with a Meinhard nebulizer, water cooled Scott spray chamber, and peristaltic pump operating at 1mL per minute. Typically, uptake times of 120 seconds, 60 second acquisition times, and 0 rinse time is used for analysis of samples. The long uptake time is used to wash the previous sample from the introduction system. With the "dirty matrices" that we encounter, this method of sample introduction appears to work better than rinsing with 1% nitric acid or deionized water.

Detector lifetime is substantially increased by operating in the pulse counting mode only, and eliminating any response in excess of 1000000 in any single channel. As a rule of thumb, we measure only trace masses at or above mass 41. The instrument software has several measurement possibilities. Sample data may be collected in the scan mode, the peak jumping mode or the single ion monitoring mode. Both single ion monitoring and peak jumping require prior knowledge of the sample composition. The scan mode can detect all masses from mass 4 through mass 250, and is routinely used for unknown samples. Normally, a scan involves 1300 watts RF power, 20 channels/amu, 320 microsecond dwell/channel, and a minimum of 3 scans per sample.

The PQ1 instrument operational availability was significantly improved, from < 50% available to > 80% available, by upgrading the quadrupole rf generator and control electronics to equivalent PQ2+ components.

Recently, a plasmascreen upgrade was performed on the PQ2+. This upgrade allows the instrument to operate in the cool plasma mode reducing the argon molecular ion interferences substantially. Thus iron, potassium, calcium, magnesium, lithium, etc. have greater sensitivities than without the plasmascreen. Future benefits to be realized from this upgrade are the extension of our analysis range and the ability to do larger dilutions to reduce matrix interferences

Dissolutions

Glass and sludge samples are dissolved using aqua regia, fusion, and microwave dissolutions. High level waste and radioactive glass samples are dissolved in the "high level caves" and diluted to within radioactivity control limits for analysis outside the remote facilities. Further dilution prior to ICPMS analysis is based on dissolved solids content, effects of matrix elements, and analyte concentration. As a rule, the analyte concentration is made to be >1 ppb but < 100 ppb. When necessary, matrix matching and spike recovery techniques from submitted samples are performed to verify analytical methodology. All samples are diluted with 1% nitric acid and spiked with 50 to 100 ppb of internal standard (indium, bismuth, scandium, or thallium). The internal standard is used to correct for variations in signal caused by environmental changes and matrix effects.

RESULTS AND DISCUSSION

Multielement calibration solutions are a convenient way to calibrate the ICP-MS when a large number of elements or isotopes need to be determined simultaneously. In previous work [1,2], the assumption was made that reasonable estimates of sensitivities could be made for isotopes that are not present in calibration solutions. To support this assumption, the sensitivities of masses 130 through 180, 203 through 208, 232, 235, and 238 were determined independently. This mass region was chosen since the actinides and most of the high mass fission products fall within this range. Elemental concentration standards purchased from High Purity, Inc., Charleston, SC were used to determine the isotopic sensitivities. Solutions of 1, 10, and 100 ppb of each element were prepared from the certified standard. Each solution was spiked with 50 ppb indium as an internal standard. With the instrument optimized for response, each standard solution was run using a full mass scan to assure the data collection timing was the same for each sample. The raw data was normalized to the indium internal standard. Using linear regression, the slopes of the concentration response curve were obtained for each isotope and are plotted in Figures 1 and 2.

The data in Figures 1 and 2 demonstrate that the isotopic mass sensitivity is very similar for different elements having overlapping isobars and that isotopic sensitivities can indeed be estimated from a linear regression of data collected from neighboring isotopic concentration response data.

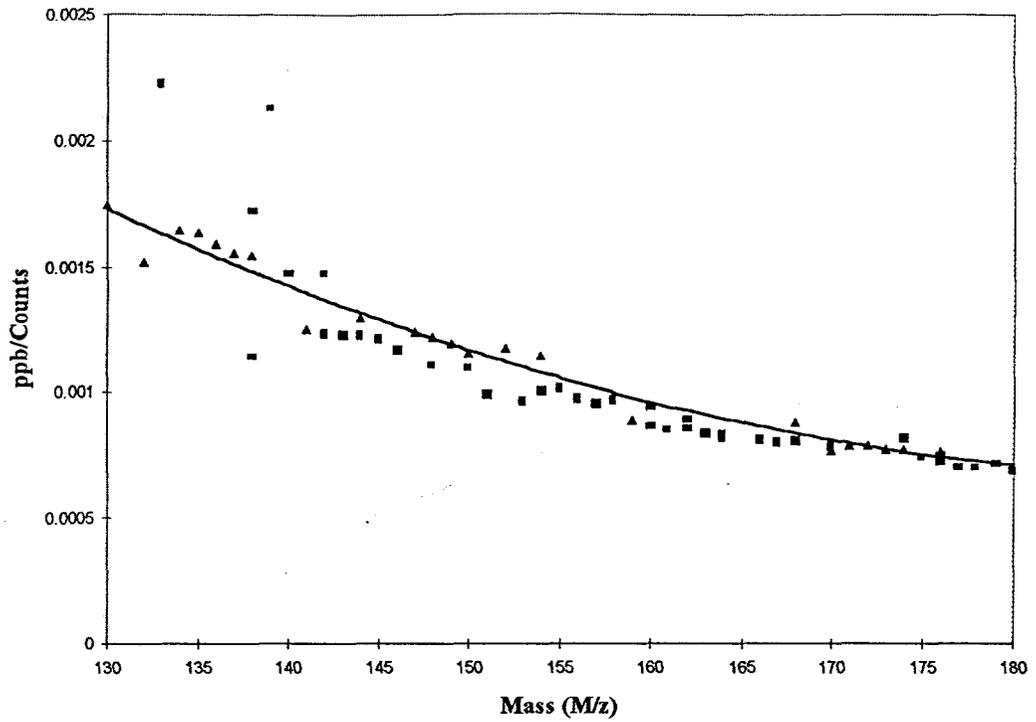


FIGURE 1 - ICPMS sensitivity versus mass for fission product region. Solid line is 2nd degree polynomial fit to the data.

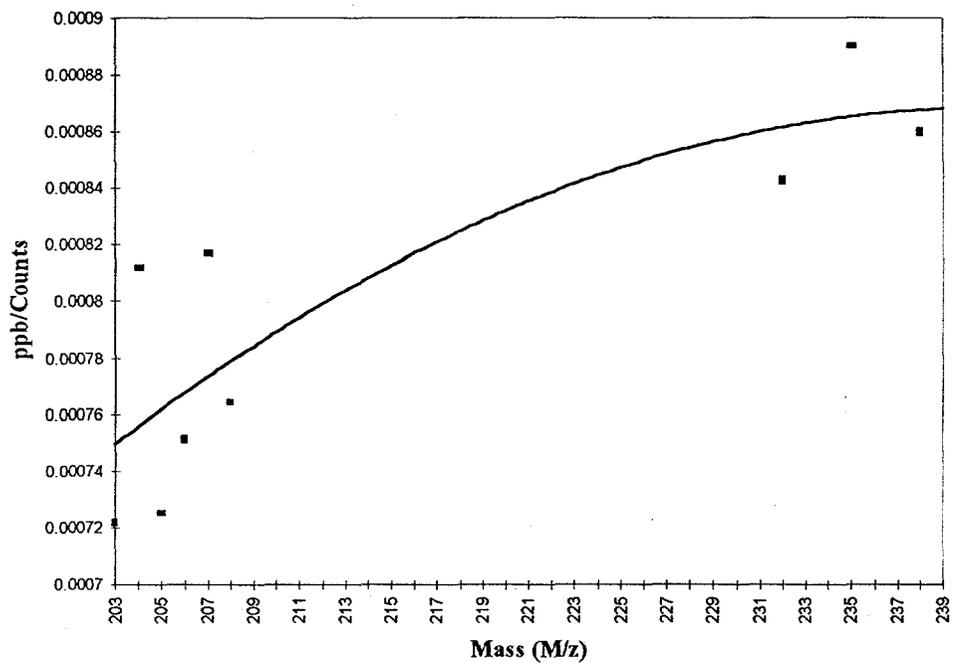


FIGURE 2 - ICPMS sensitivity versus mass for actinide region. Solid line is 2nd degree polynomial fit to the data.

ICPMS was used in support of the Hanford Tank Waste Remediation program. The goal of this program was testing and demonstration of waste processing strategies. Namely, pretreatment methods were developed for the removal of cesium, strontium, technetium, and transuranics from Hanford tank waste. Vitrification of the resultant low level waste was demonstrated as well as vitrification of the removed radionuclides combined with high level waste sludge. Radionuclide information from ICPMS was provided for each step of the development process. Strict program deadlines required rapid sample turn around times which precluded lengthy sample pretreatment.

Figure 3 shows an example of the ICPMS spectrum obtained for the untreated Hanford tank material diluted 2X in the ICPMS laboratory. This spectrum is used to demonstrate the analysis strategy used to meet the strict time requirements of this program.

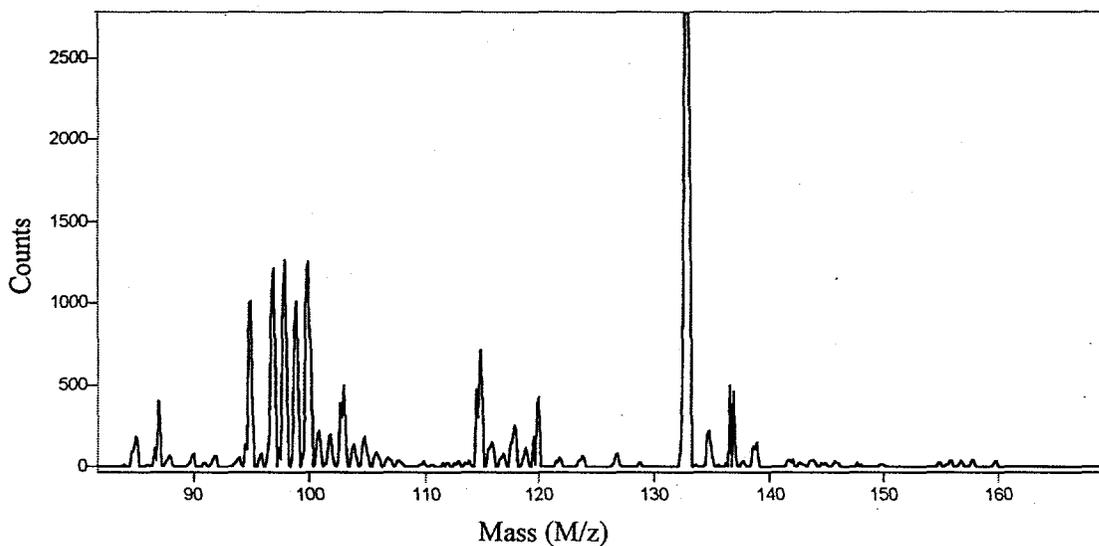


FIGURE 3 - ICPMS spectrum of untreated Hanford material.

In the mass region between mass 85 and mass 104, non-natural abundance distributions are measured for rubidium, molybdenum, and ruthenium. Likewise masses at 135 and 137 do not correspond to the natural abundance distribution for barium. Because of these anomalies in mass distributions, the standard software provided by the vendor cannot easily provide concentration data for the masses under investigation. Concentration data is obtained using the following strategy. The Quickbasic program, described previously in reference 2, extracts mass spectral data from the instrument generated binary files. The data is then imported into EXCEL for archival and quantitative analysis purposes and into GRAMS/32 for visual examination and comparison.

An Excel macro, developed in house and written in "Visual Basic for Applications" [3], performs quantitative analysis on the ICPMS spectral data. The software detects the presence of fission products and actinides and flags the user using the the following key indicators :

Rubidium	mass 87>mass 85 and mass 88
Cesium	mass 137>mass 138
enriched Uranium	masses 234,235,236, and 237 present
Plutonium-238	mass 234>mass 235

The program calculates the concentration of the actinides, estimates the isobaric concentrations of fission species, and also calculates elemental concentrations based on natural abundances. For fission products, slope sensitivities are calculated based on isotopic abundances of possible standard mass interferences. Slopes for uncalibrated masses are estimated from a linear regression of known sensitivities on mass. The concentration at each mass value is then calculated. The program automatically prints the data in formatted sheets. An example of a portion of the data sheet is shown in Table 1. The raw counting data is preserved in the spreadsheet so that analytical interferences and anomalies can be easily investigated. Plots of the internal standards are automatically generated so that any aberrations, such as signal suppression, can be readily observed.

CONCLUSION

Experimental evidence has been presented that supports the assumption of using a linear regression of neighboring mass sensitivities to calculate fission product and actinide concentrations for which certified standards are not readily available. An EXCEL macro is available that automates ICPMS data analysis of fission products and actinides using linear regression of calibrated neighboring mass sensitivities. The efficiency gained in the data analysis of ICPMS spectra allowed us to meet strict time requirements while providing quality data in support of the Hanford Tank Waste Remediation program.

TABLE 1 - Sample EXCEL macro printout of fission product calculations.
Concentrations are in ppb.

Fission product diagnostics		90849-10/5.5 fission Rb indicated, Tc indicated, fission Ru indicated, fission Cs indicated, enriched U indicated						
	<i>Element</i>	Zr	Nb	Zr	Mo	Mo	Mo	
	<i>% abund.</i>	17.1	100	17.5	15.9	16.7	9.5	
	<i>Element</i>	Mo		Mo		Ru		
	<i>% abund.</i>	14.8		9.1		5.5		
	<i>Element</i>					Zr		
	<i>% abund.</i>					2.8		
	<i>Fiss. Prod.</i>	Zr*	Zr+	Zr*	Mo*	Zr*	Mo*	
	<i>Fiss. Yield</i>	6.03	6.37	6.5	6.5	6.3	5.98	
	<i>Sensitivity</i>	313.259	312.142	311.025	309.908	316.167	307.673	
Sample	Dilution Factor	92	93	94	95	96	97	
blank 1	1							
std1 1	1	0.15	0.00	0.10	0.18	0.15	0.12	
std10 1	1	1.56	0.02	0.88	1.91	1.98	1.06	
std100 1	1	14.89		9.82	17.89	18.70	12.16	
std500 1	1	66.99	0.03	44.19	78.69	83.71	51.00	
90849-10/5.5	10	93.71	0.68	76.28	1365.52	86.60		
	<i>Element</i>	Mo	Ru	Ru	Ru	Ru	Rh	Ru
	<i>% abund.</i>	24.4	12.7	12.6	17.1	31.6	100	18.6
	<i>Element</i>	Ru		Mo		Pd		Pd
	<i>% abund.</i>	1.9		9.6		1		11
	<i>Element</i>							
	<i>% abund.</i>							
	<i>Fiss. Prod.</i>	Mo*	Tc+	Mo*	Ru*	Ru*	Rh*	Ru*
	<i>Fiss. Yield</i>	5.78	6.1	6.28	5.18	4.29	3.03	1.88
	<i>Sensitivity</i>	338.139	305.438	304.321	303.204	302.086	300.969	299.852
Sample	Dilution Factor	98	99	100	101	102	103	104
blank 1	1							
std1 1	1	0.32	0.00	0.15	0.07	0.01		0.10
std10 1	1	2.88	0.00	1.33	0.01	0.03		0.02
std100 1	1	28.15	0.02	13.17		0.01		0.04
std500 1	1	122.37	0.01	57.87		0.00		0.11
90849-10/5.5	10	1391.70	1250.77	1674.56	289.08	255.85	562.30	162.93

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