

Initial Report on the Application of Laser
Ablation - Inductively Coupled Plasma
Mass Spectrometry for the Analysis of
Radioactive Hanford Tank Waste Materials

M.R. Smith
J.S. Hartman
M.L. Alexander
A. Mendoza
E.H. Hirt

T.L. Stewart
M.A. Hansen
W.R. Park
T.J. Peters
B.J. Burghard

MASTER

December 1996

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Preface

This report will describe the results of initial chemical analysis testing on Hanford tank waste materials at the Pacific Northwest National Laboratory (Pacific Northwest) using Laser Ablation (LA) in conjunction with an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). (In this report the combined method will be referred to as LA/MS.) The practicality of using LA/MS methods for radioactive sample analysis was previously reported for nuclear fuel analysis (Garcia Alonso 1993). This project has extended the application of LA/MS methods to solids typical of the Hanford tank waste materials (including sludges, salt cake, etc.). The project has concentrated on issues required to provide robust LA/MS method performance and to allow useful data interpretation.

The tests described in this report were conducted as part of an on-going LA/MS method and technology development and deployment project which has been conducted at Pacific Northwest under joint funding provided by the U.S. Department of Energy (DOE) EM-50/Tanks Focus Area and the DOE EM-30/Tank Waste Remediation System (TWRS) Characterization Program. In Fiscal Year 1996, an LA/MS instrumentation system was designed and deployed in a Hanford production analytical chemistry hot cell laboratory on a "fast track" deployment program under an agreement of a number Hanford site stakeholders [dated August 11, 1995 and signed by staff from DOE, Richland Operations/Characterization Division, TWRS; DOE, Richland Operations/Analytical Services Program/Waste Programs Division; EM-50/Tanks Focus Area; WHC (Westinghouse Hanford Company)/Analytical Services; and Pacific Northwest]. The objective of the "fast track" deployment program was to rapidly enable the use of the LA/MS technology for semi-quantitative analysis of Hanford tank waste samples located within Hanford's analytical chemistry hot cells. The LA/MS system design and deployment activities were performed by an integrated project team of Pacific Northwest, Kaiser Hanford Company, and WHC staff. The deployed hot cell LA/MS system is now available to support sample analyses to meet the requirements of the EM-30 TWRS Characterization Program.

Complementary Pacific Northwest LA/MS Project activities have included laboratory testing and data analysis to determine:

- LA/MS experimental parameters which provide robust sample analyses for glass and waste simulant sludge samples,
- Practical expectations for the analysis capability of the LA/MS instrumentation and methods, and
- Practical test methods and protocols for the LA/MS analyses and for the reduction of LA/MS data to obtain needed sample composition results.

These tests have been performed using both a) non-radioactive glass and waste simulant samples and b) radioactive waste samples taken from the Hanford waste storage tanks. The findings of initial LA/MS analyses on the radioactive tank waste samples will be described in this report.

While the objective of the initial "fast track" project deployment was to provide an early semi-quantitative analyses capability, continuing method development tasks were planned (and are being carried out) to extend the LA/MS capability for tank waste sample analysis to allow quantitative interpretation of the LA/MS data. These efforts are in progress at this time.

The motivations for the development of the LA/MS capability included a need to provide significant reductions in the cost and time required to obtain elemental and isotopic constituent data for the radioactive tank waste materials and the need to provide an analysis method which is capable of meeting the analysis throughput requirements of the Characterization Program.

A preliminary, comparative analysis of the time and cost factors for radioactive solid sample analyses using a) LA/MS and b) solid sample dissolution followed by ICP/AES or ICP/MS analysis indicates that LA/MS usage will provide benefits which include:

- Direct analysis costs will be reduced (est. 20% - 67% savings)
- Minimum sample turn around times will be reduced significantly (i.e., for priority samples or during low analysis demand periods) (est. 85% reduction)
- Sample throughput during periods of heavy laboratory demand will be increased (est. increase of 16X to 160X).

In addition, a hot cell LA/MS method will allow significant reductions in:

- Chemical laboratory worker radiation exposures since analysis are performed with the removal of only minute quantities of sample from the hot cell and
- Secondary waste streams created during the chemical analysis activities since no sample dissolution processes are required.

LA/MS methods are applicable to a variety of near-term and long-term DOE applications including:

- Tank Waste Sample Characterization:

Rapid evaluation of core samples, selected subsamples, and composite samples to determine elemental and isotopic constituents and sample homogeneity.

- Tank Waste Material Retrieval:

Rapid evaluation of sludge washing efficiencies (solid and solution components). (ICP/MS can also be used for direct liquid sample analysis using a standard nebulizer to allow integrated tracking of constituents in both waste liquid and residual solids for sludge washing experiments.)

- Tank Waste Material Pretreatment:

Rapid analysis of starting and interim process sample materials from process development experiments. Access to timely results can expedite the pace of process evaluation and development. LA/MS instrumentation can provide direct LA/MS analysis of solid samples and direct ICP/MS analysis of associated liquid samples to provide a full picture of pretreatment process effectiveness. Rapid on-line analysis of Pretreatment Plant feed and product.

- Tank Waste Processing Support for Low-Level Waste (LLW) and High-Level Waste (HLW):

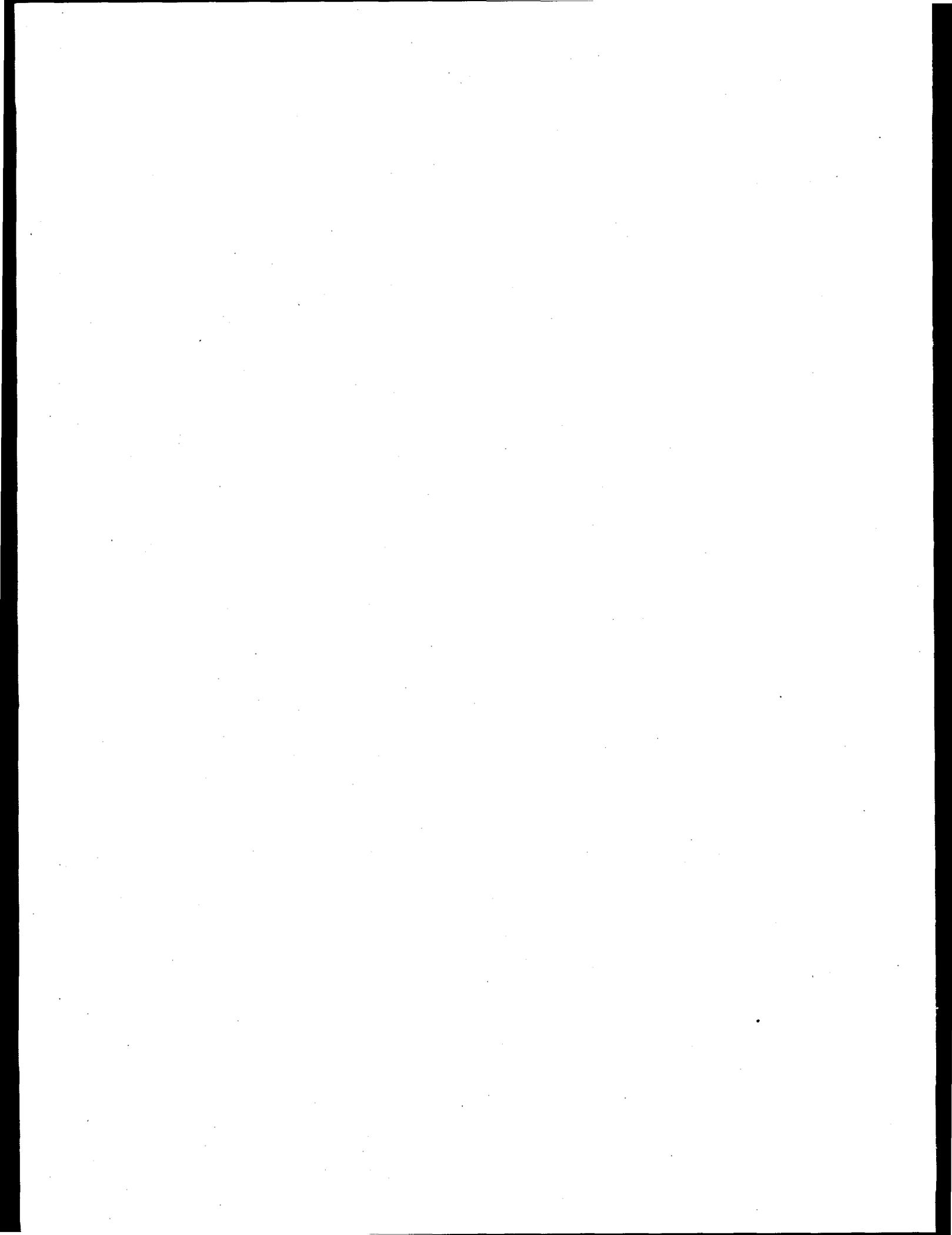
Rapid analysis of mixed waste materials prior to shipment to processing plants.

Recent discussions with staff supporting the Hanford Site Technology Coordination Group indicate a significant opportunity for the application of LA/MS technology for inclusion in an instrument suite being considered for deployment to support waste properties immediately prior to transfer to "privatization contractor pilot plants" for waste treatment.

Rapid analysis of LLW and HLW samples resulting from the final waste form development experiments. Rapid on-line analysis of vitrification plant feedstock and final glass product. Prior Hanford Waste Vitrification Plant (HWVP) LA/MS experience supports this application.

These potential LA/MS applications include opportunities at a variety of DOE sites including Hanford, Savannah River, Oak Ridge, and Idaho National Engineering Laboratory.

In addition, the LA/MS methods and technology offer similar time and cost advantages for the elemental and isotopic analysis of non-radioactive samples in applications ranging from environmental characterization, environmental clean-up verification, and industrial material analysis.



Executive Summary

The development of the Laser Ablation/Mass Spectroscopy (LA/MS) method to determine elemental and isotopic constituents in solid samples is being conducted to provide significant reductions in analysis cost and time. The LA/MS method is applicable for the analysis of a broad range of materials including radioactive solids in the U.S. Department of Energy inventory (including Hanford tank wastes) and non-radioactive materials encountered in environmental clean-up and industrial applications. Current methods employed for solids analysis often require sample dissolution and require significant time to execute. This project has extended the application of LA/MS methods to solid forms typical of the Hanford tank waste materials (including sludges, salt cake, etc.) and has concentrated on issues required to provide robust LA/MS method performance and to allow useful data interpretation.

For maximum effectiveness, chemical analysis methods applied for radioactive waste characterization should provide analysis results in a timely, cost-effective manner and should be capable of handling the sample throughput required for the program requirements. A preliminary analysis of the time and cost factors for radioactive solid sample analyses with a) LA/MS and b) solid sample dissolution followed by ICP/AES or ICP/MS analysis indicate that LA/MS usage benefits will include:

- Direct analysis costs will be reduced (est. 20% - 67% savings)
- Sample throughput during periods of heavy laboratory demand will be increased (est. increase of 16X to 160X)
- Minimum sample turn around times will be reduced (i.e., for priority samples or during low analysis demand periods) will be reduced (est. 85% reduction).

In addition, a hot cell LA/MS method will allow significant reductions in:

- Chemical laboratory worker radiation exposures since analysis are performed with the removal of only minute quantities of sample from the hot cell and
- Secondary waste streams created during the chemical analysis activities since no sample dissolution processes are required.

A hot cell LA/MS instrument system was deployed and demonstrated at Hanford in September 1996 to enable routine, semi-quantitative analysis of tank waste materials to determine elemental and isotopic constituents. LA/MS analysis has suitable sensitivity and dynamic range to provide data on constituent concentrations ranging from parts-per-million (ppm) to tens of percent with a single analysis. Although the current LA/MS capability for tank waste

analysis is semi-quantitative, method development is continuing under this project to advance the LA/MS method to enable quantitative analyses to be performed.

The deployed LA/MS capability for solids analysis at Hanford will allow time- and cost-effective analysis of tank samples to determine elemental/isotopic constituents to support a number of tank waste operation and remediation functions including:

- Safe operation of the tank farms prior to retrieval and remediation
- Resolution of possible tank safety questions prior to retrieval
- Development of robust processes and equipment for retrieval, pretreatment, and immobilization of the tank waste materials.

This report describes the results of initial chemical analysis of seven radioactive Hanford tank waste samples at the Pacific Northwest National Laboratory (Pacific Northwest) using LA/MS methods. Samples analyzed have included both raw tank wastes and samples which have been pretreated (washed) to remove soluble constituents. Analysis of the resulting LA/MS data allowed the determination of both a) general/non-radiogenic and b) radiogenic constituents in the waste samples. The ability to determine isotopic constituents using the LA/MS method yielded significant advantages over ICP/AES analysis by providing valuable information on fission products and radioactive constituents.

The experimental results described in this report have demonstrated that the LA/MS data can be used to provide rapid analysis of solid, radioactive Hanford tank waste samples to identify:

- Major, minor, and trace elemental and isotopic constituents and
- Fission products and radioactive isotopes.

The LA/MS capability for the rapid identification of major and minor components in solid (sludge) samples has been demonstrated successfully for radioactive waste samples. The LA/MS data contain both natural components (non-radiogenic, presumably materials used for processing the nuclear fuels) and radiogenic products (due to the nuclear fuel composition and irradiation history). Although current data reduction methods are limited to providing semi-quantitative results, the results obtained from these LA/MS analyses reported are consistent with previously reported values determined by current laboratory analytical methods for most sample constituent concentrations.

Data precision (i.e., relative standard deviations) for the LA/MS data for the majority of these initial waste samples was in the range of 4 - 12% for most sample constituents (with sufficient count rates for good data statistics). This is comparable to results obtained for homogeneous glass reference materials and indicates that the LA/MS raster scanning and data integration

periods employed for these initial tests were sufficient to provide useful averaging of sample constituents exposed on the sample's surface.

These initial analyses of radioactive tank waste samples using the LA/MS method have also demonstrated the ability for rapid determination of the fission products present in samples. The radioactivity levels due to the fission products can be estimated directly using known fission yields and the LA/MS mass spectral data. An analyst can determine a sample's bulk radiological contents introduced by fission based on the sample's LA/MS fission product spectra. Using a knowledge of stable isotopes and by determining the isotopic abundances of the various elements produced by fission, radioactive isotopes can be identified and their abundances calculated. This avoids the need to perform tedious and time-consuming radiochemical separations. For accurate quantification, it is necessary that the radionuclides must be sampled equally, including those which exist primarily in the soluble components of the sludge.

The LA/MS data for tank waste samples has provided direct information on the sample's actinide constituents. The actinides make another major contribution to the radioactivity of tank wastes. The initial results of tank waste analyses using LA/MS exhibited numerous isotopes of Th, U, Np, Pu and Am. These data, even if qualitative, can be used with known relative isotopic abundance information to provide an estimate of the bulk fissile material in the tank wastes. Relative abundances of the actinides can be determined which may be used to evaluate sample composition relative to tank safety criteria. In addition, these data can be used to project long-term radioactive constituents and levels in both low-level and high-level waste forms.

Although the current, semi-quantitative LA/MS method will be useful immediately for a number of applications, the value of the LA/MS will be enhanced by advancing the analytical capability to provide quantitative results. In order to enable the LA/MS technology and method to better support waste characterization needs, activities are continuing with the objective of advancing the capability to:

- Allow quantitative interpretation of LA/MS data for tank waste samples and
- Further improve the operational LA/MS capability for both data acquisition and data reduction to support routine use in the analysis of radioactive, solid sample materials.

Continuing project activities to provide quantitative results include LA/MS method development efforts using elementally spiked (i.e., broad mass range and concentration range) solids to allow improved characterization of the LA/MS instrument response. The elementally spiked solids have been designed to serve as reference materials suitable for LA/MS tank waste analysis. It is felt that their use will enable advances in data reduction to provide quantitative results. At this time, few if any changes to the installed LA/MS system equipment would be

anticipated to enable the data reduction to provide quantitative results once the method is established.

Specific near-term and long-term DOE applications where LA/MS methods offer advantages for chemical analysis include:

- Tank Waste Sample Characterization: Rapid evaluation of core samples, selected subsamples, and composited samples to determine elemental and isotopic constituents and sample homogeneity.
- Tank Waste Material Retrieval: Rapid evaluation of sludge washing efficiencies.
- Tank Waste Material Pretreatment: a) Rapid analysis of starting and interim process sample materials from process development experiments. (Access to timely results can expedite the pace of process evaluation and development.) b) Rapid on-line analysis of Pretreatment Plant feed and product.
- Tank Waste Processing Support for Low-Level Waste (LLW) and High-Level Waste (HLW): a) Rapid analysis of LLW and HLW samples resulting from the final waste form development experiments. b) Rapid on-line analysis of vitrification plant feedstock and final glass product.

In addition, recent discussions with staff supporting the Hanford Site Technology Coordination Group indicate a significant opportunity for the application of LA/MS technology for inclusion in an instrument suite being considered for deployment to support characterization of waste immediately prior to transfer to "privatization contractor pilot plants" for waste treatment.

These potential LA/MS applications include opportunities at a variety of DOE sites including Hanford, Savannah River, Oak Ridge, and Idaho National Engineering Laboratory.

In addition, the LA/MS methods and technology offer similar time and cost advantages for the elemental and isotopic analysis of non-radioactive samples in applications ranging from environmental characterization, environmental clean-up verification, and industrial material analysis.

Acknowledgments

This work was prepared with the support of the following contributors:

U.S. DOE Headquarters: Office of Science and Technology
EM-52
David Geiser

Focus Area/Program: Tanks Focus Area
Terri L. Stewart, Manager
Dr. Thomas R. Thomas, Characterization
Technology Integration Manager
Al Noonan, Characterization Program

Operations Office: Richland Operations Office
Science and Technology Programs Division
Maria C. Vargas, Technical Program Officer

Contractor: Pacific Northwest National Laboratory
Environmental Management
Technology Development Program
Steven C. Slate, Manager

In addition, the authors wish to acknowledge:

- The U.S. DOE Office of Environmental Management (EM-30), Tank Waste Remediation System (TWRS) Characterization Program under the auspices of the Westinghouse Hanford Company (WHC) for funding complementary LA/MS project tasks which included a) early LA/MS method development and instrument system integration activities and b) the design and implementation of hot cell facility modifications to accommodate the installation of the hot cell LA/MS system.
- The positive attitude brought to the FY 1996 "fast track" LA/MS technology deployment and demonstration effort by both project oversight [EM-30/DOE-RL (C.A.Babel), EM-50/TFA (T.R. Thomas and A.F. Noonan), and WHC (D.A. Dodd)] and project team members (Pacific Northwest National Laboratory, WHC, and ICF-Kaiser Hanford Company [ICF-KHC]). A number of funding, scheduling, and design option issues were resolved rapidly and positively as a result of a strong collaborative attitude and a common commitment to complete the FY 1996 work scope on schedule.

- The contributions of a number of staff serving the Hanford Maintenance and Operations contractor(s) (i.e., WHC and ICF-KHC) during FY 1996 who were valued LA/MS Project team members. They completed a broad range of tasks (e.g., instrumentation design option evaluation, design reviews, facility modification design development, facility modification implementation, and system installation) required for the hot cell LA/MS system installation on a very demanding schedule. Their contributions enabled the completion of the hot cell LA/MS system installation and demonstration with the U-105 tank waste analysis in September 1996. Specifically, we wish to recognize the following team members for their major contributions to the project success: Clifford T. Narquis, Daniel M. Thornton, Jon W. Ball, Richard L. Harris, Lanni L. Weaver, David A. Dodd, Thomas R. Oleson, Stephen L. Brey, Charles R. Zook, Raymond K. Fisher, Roderick S. Cook, and Frederick A. Hardy.
- Jon W. Ball (Numatec Hanford Company) who has assumed responsibility for the installed hot cell LA/MS system and for its application to meet ongoing TWRS Characterization Program needs. In addition, he selected and obtained the U-105 waste sample discussed in Section 6.2 of this report and collaborated on the acquisition LA/MS data for this sample.
- Drs. Wayne J. Martin and Jeffrey W. Griffin for their constructive technical review of this report.
- Kathy Kindall and Nell Cliff for their assistance with the preparation of this report.

Contents

Preface	iii
Executive Summary	vii
Acknowledgments	xi
List of Figures	xv
List of Tables	xix
1.0 Introduction	1.1
2.0 LA/MS Method Overview	2.1
2.1 Operating Principles	2.1
2.2 Potential Factors Affecting the LA/MS Analysis Results and Actions Taken to Minimize Effects	2.4
2.2.1 Factors Associated with Laser Ablation Sampling and Particle Dissociation by the ICP	2.4
2.2.2 Factors Associated with the Effectiveness of the ICP for Generating Singly Charged Atomic Ions	2.7
2.2.3 Factors Associated with MS Instrument Response	2.8
2.2.4 Combined Effects of ICP and Mass Spectrometer Response Factors	2.10
2.3 Summary of Factors Associated with the Application of LA/MS Methods for the Analysis of Solid Samples	2.12
3.0 Experimental Description	3.1
3.1 Practical Deployment Configurations	3.1
3.2 Tank Waste Samples Analyzed with LA/MS Instrumentation	3.1
3.3 Reference/Standard Samples Analyzed to Support Data Reduction	3.3
3.4 Experimental Conditions Employed for LA/MS Data Acquisition	3.4
3.4.1 Laser Ablation Conditions	3.4
3.4.2 Sample Environment for Laser Ablation	3.5
3.4.3 Plume Transfer Parameters	3.5
3.4.4 ICP/MS Operating Parameters	3.5
3.5 Data Recorded	3.6
3.6 Test Sequence	3.8
4.0 Data Reduction Procedures	4.1
4.1 Individual Data Set Processing	4.1

4.2	Background Corrections for MS Data	4.1
4.3	Replicate Data Set Processing	4.2
4.4	MS Instrument Mass Response Function Calculation	4.4
4.5	Calculation of Semi-Quantitative Sample Composition Results	4.6
5.0	Data Interpretation for Hanford Tank Waste Samples	5.1
5.1	Supplementary Information for Analysis of Samples with Radiogenic Constituents (Fission and Activation Products)	5.3
6.0	Experimental Results and Discussion	6.1
6.1	Sample Analyses Conducted with Laboratory LA/MS System for Radioactive Samples	6.1
6.1.1	Measurement Precision (Relative Standard Deviations)	6.1
6.1.2	General/Non-Radiogenic Chemical Analysis Results	6.3
6.1.3	Radiogenic Analysis (Fission and Activation Products)	6.3
6.2	Sample Analyses Conducted with Hot Cell LA/MS System for Radioactive Samples	6.26
6.2.1	Results of Rapid Determination of Major and Minor Waste Components	6.28
6.2.2	Measurement Precision (Relative Standard Deviations)	6.33
6.2.3	General/Non-Radiogenic Chemical Analysis Results	6.33
6.2.4	Radiogenic Analysis (Fission and Activation Products)	6.37
6.3	Summary of Initial LA/MS Analyses Conducted on Hanford Tank Waste Samples	6.38
7.0	Conclusions	7.1
8.0	Future Task Activities	8.1
9.0	References	9.1

List of Figures

2.1	Schematic illustration of primary LA/MS system components, including the laser source, sample, plume transfer line, ICP torch, and mass spectrometer	2.2
2.2	Projected LA/MS chemical analysis capability for Hanford tank waste materials . . .	2.3
2.3	Method for calculating the Mass Response Curve using known sample composition data and corresponding mass spectrometer data	2.11
2.4	Method for calculating the concentration of an analyte in an unknown sample using the instrument Mass Response Curve and the mass spectrometer data recorded for the unknown sample	2.11
4.1	Conceptual illustration of calculated mass response function showing examples of elements which are readily ionized by the ICP (e.g., A ₁ , A ₂ , and A ₃) and elements which are ineffectively ionized by the ICP (e.g., B ₁ and B ₂)	4.5
5.1	Typical fission yields of isotopes produced from fission of ²³⁵ U and ²³⁹ Pu via conventional (moderated neutron) reactors	5.5
6.1	Plot of LA/MS Relative Standard Deviation values versus elements for constituents of an untreated S-104 tank waste sample. Elements are plotted in the order of increasing concentration	6.4
6.2	Plot of LA/MS Relative Standard Deviation values versus elements for constituents of an untreated T-104 tank waste sample. Elements are plotted in the order of increasing concentration	6.5
6.3	Plot of LA/MS Relative Standard Deviation values versus elements for constituents of an untreated T-111 tank waste sample. Elements are plotted in the order of increasing concentration	6.6
6.4	Logarithmic plot of elemental concentrations in S-104 tank waste samples as determined by independent analysis (ICP/AES analysis of solution-based samples) and preliminary LA/MS analysis. Elements are shown in order of increasing concentration in the pretreated sample. a) Pretreated/washed waste and b) Raw/untreated waste	6.10
6.5	Logarithmic plot of elemental concentrations in T-104 tank waste samples as determined by independent analysis (ICP/AES analysis of solution-based samples)	

and preliminary LA/MS analysis. Elements are shown in order of **increasing** concentration in the pretreated sample.

a) Pretreated/washed waste and b) Raw/untreated waste 6.11

6.6 Logarithmic plot of elemental concentrations in T-111 tank waste samples as determined by independent analysis (ICP/AES analysis of solution-based samples) and preliminary LA/MS analysis. Elements are shown in order of **increasing** concentration in the pretreated sample.

a) Pretreated/washed waste and b) Raw/untreated waste 6.12

6.7 Logarithmic plot of mass spectrometer signal levels for isotopes in the lower fission product mass spectral region (80 - 110 amu) from LA/MS analysis of a tank S-104 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions 6.13

6.8 Logarithmic plot of mass spectrometer signal levels for isotopes in the upper fission product mass spectral region (125 - 160 amu) from LA/MS analysis of a tank S-104 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions 6.15

6.9 Logarithmic plot of mass spectrometer signal levels for isotopes in the lower fission product mass spectral region (80 - 110 amu) from LA/MS analysis of a washed (i.e., pretreated) tank T-111 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions 6.16

6.10 Logarithmic plot of mass spectrometer signal levels for isotopes in the upper fission product mass spectral region (125 - 160 amu) from LA/MS analysis of a washed (i.e., pretreated) tank T-111 sample. Fission yield curves are shown for U^{235} and Pu^{239} decay to facilitate comparison of observed signal strengths with primary simple fission product distributions 6.17

6.11 Logarithmic plot of mass spectrometer signal levels for isotopes in the lower fission product mass spectral region (80 - 110 amu) from LA/MS analysis of a tank T-104 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions 6.18

6.12 Logarithmic plot of mass spectrometer signal levels for isotopes in the upper fission product mass spectral region (125 - 160 amu) from LA/MS analysis of a tank T-104 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to

	facilitate comparison of observed signal strengths with primary simple fission product distributions	6.19
6.13	Mass concentration spectrum determined from LA/MS data for raw waste sample from tank S-104	6.22
6.14	Tank S-104 mass concentration spectrum (solid black bars) with amplitude adjusted fission yield data (grey bars)	6.23
6.15	Plot of difference values between S-104 peak amplitudes and amplitude adjusted fission yield values from Figure 6.14. (Negative values are not shown.)	6.24
6.16	Logarithmic plot of mass spectrometer signal levels for isotopes in the actinide mass spectral region (230 - 242 amu) from LA/MS analysis of three tank samples (S-104, T-104, and T-111)	6.27
6.17	Logarithmic plot of mass spectrometer signal level versus mass number for the mass range of 0 - 250 amu for U-105 tank waste sample. Data recorded using hot cell LA/MS instrument system	6.31
6.18	Logarithmic plot of mass spectrometer signal level versus mass number for the mass range of 0 - 80 amu for U-105 tank waste sample. Selected sample constituent peaks are identified. Data recorded using hot cell LA/MS instrument system	6.32
6.19	Logarithmic plot of mass spectrometer signal level versus mass number for the mass range of 75 - 160 amu for U-105 tank waste sample. Selected sample constituent peaks are identified. Data recorded using hot cell LA/MS instrument system	6.34
6.20	Logarithmic plot of mass spectrometer signal level versus mass number for the mass range of 150 - 250 amu for U-105 tank waste sample. Selected sample constituent peaks are identified. Data recorded using hot cell LA/MS instrument system	6.35
6.21	Plot of LA/MS Relative Standard Deviation values versus elements for constituents of an untreated U-105 tank waste sample. Elements are plotted in the order of increasing concentration	6.36
6.22	Logarithmic plot of elemental concentrations in U-105 tank waste samples as determined by independent analysis (ICP/AES analysis of solution based samples) and preliminary LA/MS analysis. Elements are shown in order of increasing concentration as determined from the LA/MS data	6.40

6.23 Logarithmic plot of estimated isotopic concentration levels versus mass number for the range of 80 - 160 amu's for the U-105 waste sample. Fission yield curves for ^{235}U and ^{239}Pu are shown with selected peaks identified 6.41

List of Tables

3.1.	LA/MS System Components Installed in Radiation Containment Enclosures	3.1
3.2.	Hanford Tank Waste Samples Analyzed Using LA/MS Instrumentation Systems . .	3.2
3.3.	Laser Ablation Parameters Employed During the Analysis of Hanford Tank Waste Samples	3.3
3.4.	Ablation Plume Transfer System Parameters Utilized for Actual Waste Sample Analyses	3.6
6.1	Tank S-104 Sludge Component Analysis Showing LA/MS Results with Independent Analysis Results Where Available (ppm per Dry Weight)	6.7
6.2	Tank T-104 Sludge Component Analysis Showing LA/MS Results with Independent Analysis Results Where Available (ppm per Dry Weight)	6.8
6.3	Tank T-111 Sludge Component Analysis Showing LA/MS Results with Independent Analysis Results Where Available (ppm per Dry Weight)	6.9
6.4	Estimated radiogenic and non-radiogenic isotopes/elements in the fission product mass spectral region in the raw tank S-104 waste	6.21
6.5	Independent Elemental Analysis Results for U-105 Tank Waste Sample (Fritts 1996). Elements Are Shown in the Order of Descending Concentration	6.29
6.6	Independent Radiochemical Analysis Results for U-105 Tank Waste Sample (Fritts 1996)	6.30
6.7	Tank U-105 Sludge Component Analysis Showing LA/MS Analysis Results with Independent Analysis Results (Fritts 1996) Where Available (ppm per Dry Weight)	6.39

1.0 Introduction

The cost-effective and timely analysis of solid samples to determine a broad range of elemental and isotopic chemical constituents presents a significant challenge to the analytical chemist.

Essentially all established chemical analysis methods for solid samples (e.g., formalized for U.S. Environmental Protection Agency-approved applications) involve sample dissolution followed by the analysis of the solutions using a variety of instruments [e.g., Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP/AES), Inductively Coupled Plasma-Mass Spectrometry (ICP/MS), etc.]. The sample dissolution process commonly results in significant dilution of the analytes to be measured. It is common for these analytical methods to rely heavily on the use of appropriate standards for aiding in the quantification of analyte concentrations in unknown samples. For applications where analyses are performed repetitively on very similar samples, a reliable set of standards can be prepared and used routinely to obtain the required quantitative results.

However, the sample dissolution process for many types of solid samples (e.g., geologic materials including soils, low-solubility precipitates, etc.) is a slow, time-consuming process which may effectively govern the overall method throughput and turn-around time for samples analyses. Also, for some types of samples the dissolution process can introduce analysis biases associated with incomplete sample dissolution.

In addition, for applications where the unknown samples may exhibit compositions which are highly variable (e.g., elemental/isotopic composition, molecular forms, and individual analyte concentration levels), the preparation of suitable standards becomes very challenging for the analytical laboratory staff and can become a major factor in overall sample throughput and analysis turn-around time.

The Hanford tank waste materials present a challenge to the analytical chemist where both of these issues (e.g., sample solubility and variability) are significant. Residual solids in the Hanford waste tanks have resulted from the formation of precipitates either as the result of a) planned precipitation or separation process steps during the active production and processing years at Hanford or b) incidental precipitation reactions that have occurred in the tanks over the years due to liquid phase reduction and on-going chemical reactions in the tanks including those driven by radiolytic mechanisms. In either case, the precipitates are stable in the chemical environment within the tanks and include some materials that are difficult to fully dissolve in a rapid manner. Also, significant waste chemical composition variations are known to occur within individual tanks (e.g., due to stratification, differences in historical processing sequences and feedstocks placed in the individual tanks, etc.) and often bulk chemical variations are observed between different tanks and different tank farms (e.g., due to historical

processing sequences, etc.). At a minimum, six different, major classes of tank waste material exist within the Hanford waste tanks (McCain 1996).

Previous laboratory analysis experience on this project for reference and unknown samples using Laser Ablation (LA) in conjunction with an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) provides reason to believe this analytical method (LA/MS) can be developed to allow the rapid, routine analysis of a broad range of tank waste materials. Experience with the LA/MS analysis of glass standards and final waste form simulants was obtained previously under Hanford Waste Vitrification (HWVP) Program funding (Smith 1992 and Wyse 1993). Additional experience with glass reference materials has been obtained by this LA/MS development project. Experience with the analysis of tank waste simulant materials, including specially prepared reference simulants which contain a broad range of chemical constituents, has also been obtained by this LA/MS development project. Sample analyses using the LA/MS method conducted within this project have been performed to:

- Determine LA/MS experimental parameters which provide robust sample analyses for glass and waste simulant sludge samples,
- Establish practical expectations for LA/MS chemical analysis of materials,
- Establish an approved method/procedure for LA/MS analysis, and
- Establish reliable methods for data reduction and transfer those methods for incorporation into the LA/MS system software.

This report will provide an introduction to a) the LA/MS analysis method and its operating principles and b) issues associated with LA/MS data reduction and interpretation. This will be followed by a discussion of initial LA/MS analyses performed on actual Hanford tank waste sample materials. The waste samples examined have included both raw waste materials (e.g., as taken from the tanks) and samples which have undergone simple washing processes to remove soluble components.

This report will not include discussions of the tasks conducted to establish robust LA/MS operating conditions or the testing conducted with non-radioactive glass and simulant samples.

2.0 LA/MS Method Overview

2.1 Operating Principles

The LA/MS instrumentation systems utilized on this project are based on commercial instruments and subsystems including a pulsed laser source and an Inductively Coupled Plasma/Mass Spectrometer (ICP/MS) instrument.

Figure 2.1 shows a simplified representation of the equipment required for sample analysis using LA/MS. The major components include the following: a laser (ablation laser) which produces optical pulses with sufficient energy to ablate material from a sample, laser beam transfer and focusing optics, a sample chamber with translation stages, an ablation plume pickup and transfer line used to transport the sample via carrier gas, an Inductively Coupled Plasma (ICP), and a Mass Spectrometer (MS). System operation is outlined below:

- The ablation laser is triggered to produce a pulse of optical energy that strikes the sample surface.
- The laser pulse interacts with the sample material causing a small plume of material to be ablated from the sample (i.e., typically nanograms of sample material per laser pulse).
- The plume of sample material is entrained in the carrier gas flowing over the sample and carried into the transfer line.
- The carrier gas transports the plume material from the sample into the ICP.
- The plasma (i.e., the ICP) vaporizes and dissociates the ablation plume particles into atomic species and finally ionizes the resulting atoms.
- The ionized atoms enter the MS and are mass analyzed to determine the number of atoms at each mass.

In summary, the laser ablation process is used to subsample the target material, and the ICP/MS instrument is used to perform the chemical analysis of the subsampled material. The resulting mass spectrometer data set (i.e., detected ion count during the signal integration period for each mass number) provides a direct indication of the elemental and isotopic species and their populations in the sample material entering the mass spectrometer. The range of analytical capability for the LA/MS method is shown in summary fashion in Figure 2.2.

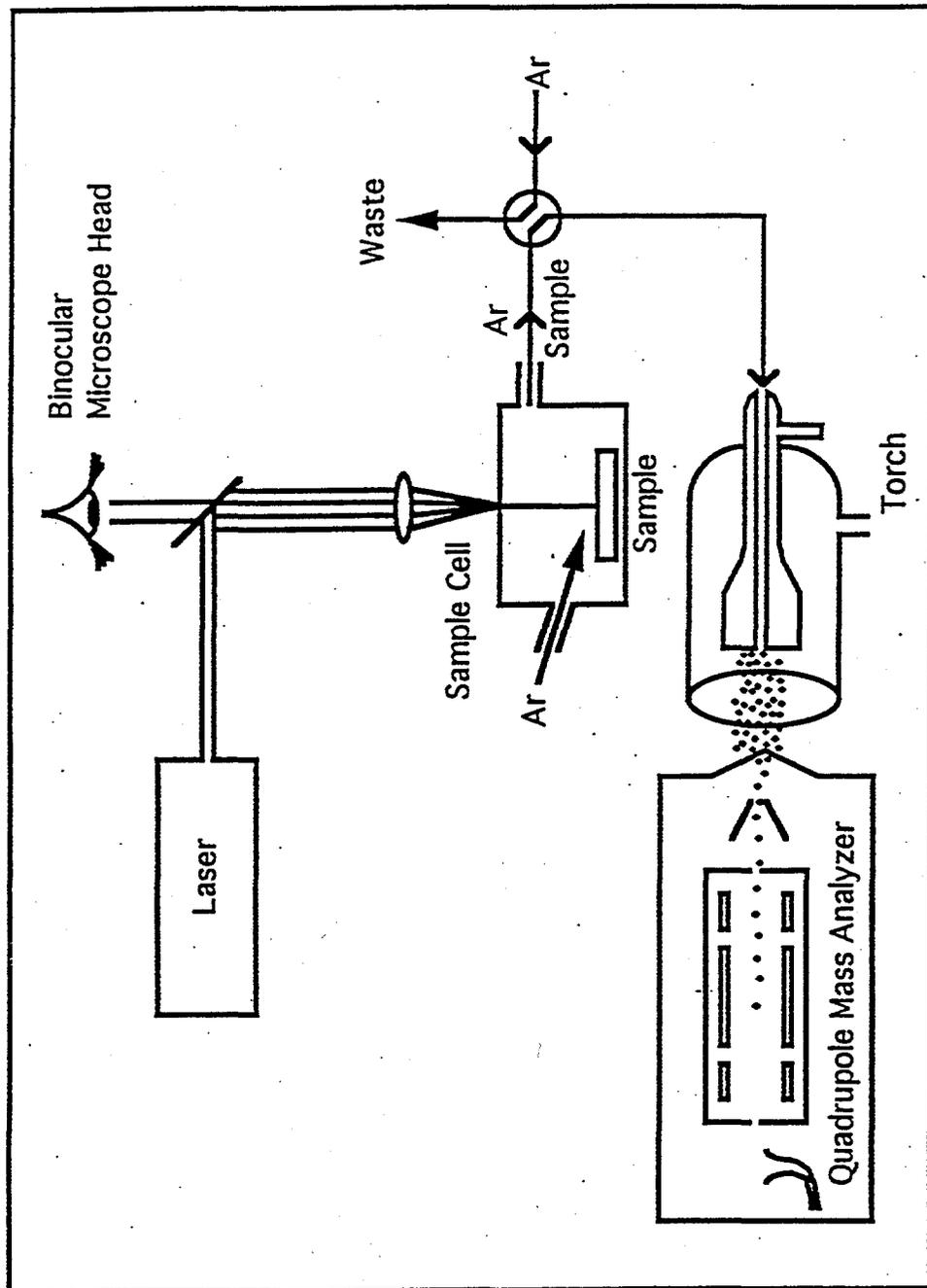


Figure 2.1 Schematic illustration of primary LA/MS system components, including the laser source, sample, plume transfer line, ICP torch, and mass spectrometer

2.2 Potential Factors Affecting the LA/MS Analysis Results and Actions Taken to Minimize Effects

The resulting mass spectrometer data set provides a direct indication of the elemental and isotopic species and their populations in the target sample if a number of criteria are met. These criteria include some associated with laser ablation sampling and particle dissociation in the ICP (e.g., laser ablation, ablated particle plume transport, and particle plume interaction with the ICP) plus other issues associated with the ICP/MS instrument including ion generation by the ICP and the mass spectrometer response. These two categories of criteria/issues will be discussed separately in consecutive sections which follow. In each case, the criteria/factors will be listed along with corresponding key findings from tests performed on this project using waste simulant materials and glass reference samples.

2.2.1 Factors Associated with Laser Ablation Sampling and Particle Dissociation by the ICP

- Criteria: The plume ablated by the laser pulse must contain a suitable proportion of all analytes in the sample (i.e., representative sampling with minimal fractionation).

Representative sampling and fractionation can be affected by spatial inhomogeneities in the sample and by the laser ablation process.

The effects of short-range sample spatial inhomogeneities are minimized by raster scanning the sample beneath the ablation laser beam and by integrating the mass spectrometer signal over a number of laser pulses. For samples with spatial inhomogeneities, compositional variations will occur in the material ablated from different positions on the samples. However, individual mass spectra data are integrated over a large number of laser pulses (and sample positions) to obtain a better estimate of the average composition for the sample. Typical test conditions often involve raster scanning over an area of roughly 2 mm x 2 mm and integrating data obtained from 900 laser pulses (ablation positions).

Previous test results have shown that laser ablation conditions can be chosen to effectively minimize sample fractionation during the ablation process. Specifically, the use of relatively short, low-power, ultraviolet laser pulses for the ablation process produces an ablation plume which is representative of the target material. (Actual parameters will be detailed in Section 3.4.1).

- Criteria: The particles in the ablation plume must be faithfully transported from the sample holder/ablation chamber to the ICP torch.

The transport efficiency for particulates is known to be a function of particle size and density, carrier gas density, and carrier gas flow conditions (Anand 1993). Large particles will rapidly fall from the carrier gas stream and be lost while very small particles will diffuse to the transfer tube walls and be lost.

Previous test results have shown that laser ablation conditions can be chosen to effectively produce ablation plume particle size distributions that are faithfully transferred from the sample holder to the ICP torch. Specifically, the use of low-power, ultraviolet laser pulses for the ablation process produces an ablation plume with particles sizes predominately in the 0.2 - 1.5 μm range. This particle size range can readily be transported over the distances required for LA/MS analysis.

- **Criteria:** Particles in the ablation plume must be effectively dissociated by the plasma to allow the production of atomic isotopes.

The ICP interaction with the ablation plume particles entering the plasma results in the "erosion" of the particles as they pass through the plasma region. The maximum amount of erosion from a particle is proportional to the particle residence time in the plasma. Thus the residence time required to fully break down a large particle is longer than the corresponding time for a small particle. Since the carrier gas flow rate through the plasma region is fixed, a practical size limit will exist for particles which can be effectively dissociated by the plasma interaction. Following removal from the particle, subsequent interaction with the plasma is required to dissociate molecules and ionize the resulting atoms.

Previous test results have shown that ablation plume particles in the size range of $\leq 1.5 \mu\text{m}$ are effectively processed by the ICP for subsequent mass spectrometer analysis. Again, this particle size range is produced by the use of low-power, ultraviolet laser pulses for the ablation process.

- **Criteria:** The atomic species ablated were distributed proportionally in the plume particulates (i.e., no plume particle size-related composition differences).

No evidence of particle-size dependent chemical composition has been noted in the results of previous laboratory testing with waste simulant materials.

- **Criteria:** Moist and dry samples can be ablated with comparable results (representative sampling).

Although LA/MS can be used for the analysis of liquid samples, there is little motivation to do this as the samples are already in a liquid form that can be readily analyzed using a nebulizer and routine methods for ICP/AES or ICP/MS analysis.

LA/MS analysis is suitable for both moist and dry samples. This does not present a serious constraint for tank waste sample analysis due to the protocols for handling the samples when they arrive in the Hanford hot cells. The process used in Hanford hot cells to remove tank core materials from the sampling tubes tends to reduce the amount of free liquid in the samples. The waste core materials are extruded from the waste sampling tube onto an open metal tray which has a drain outlet at its lowest point. The free liquid drains into the tray, then into a liquid collection bottle placed below the tray drain outlet. Any additional liquid that drains from the extruded core material during the time that it is in the tray is also gathered in the liquid collection bottle.

Previous test results do indicate that soluble components of some waste samples are found in lower concentrations in the solid samples than expected, but this is not unique to the LA/MS analysis method. It is felt that the "missing" soluble components may have been "lost" in the liquid supernate collected following the core extrusion. Thus, these soluble components would also be missing in the analysis of the dissolved solids with established methods unless the collected supernate was added to the dissolved sample solution.

If very wet samples are to be analyzed with the LA/MS method, the LA/MS system operator and analytical chemist must be cognizant of these factors as sample analyses are performed and the data analyzed.

In summary, a single set of system operating conditions can be chosen that will allow the acquisition of useful LA/MS data while minimizing the potential deleterious effects of the issues discussed above. Specifically, the operating conditions include the use of an ultraviolet wavelength ablation laser producing low-energy pulses for sample ablation.

One additional factor relating to the laser ablation process must be understood to support quantitative data interpretation. Nominally identical ablation laser pulses, when incident upon different samples, may cause the ablation of different amounts of material from each sample (i.e., nanograms of ablated sample per laser pulse). These differences in the amount of ablated material can occur from sample to sample and from run to run due to a number of factors including differences in the ablation efficiency for different samples (e.g., due to optical absorption differences, sample mechanical strength, etc.) and changes in experimental conditions (e.g., laser pulse energy fluctuations and laser focusing). Since the amount of material ablated from the sample directly affects the number of ions which ultimately enter the MS, information on the ablation efficiency will be required to quantify the analytical results obtained with the LA/MS instrument system. Candidate methods for ablation efficiency (i.e., signal strength) normalization being evaluated include normalization based on a) the total integrated ion count detected by the MS (i.e., summed across all mass numbers in the scan), b) the total mass detected in the ablation plume passing through the plume transfer line as

determined from particle size spectrometer data, and c) knowing the concentration of at least one of the elements detected by the LA/MS method (e.g., an internal standard in the samples).

2.2.2 Factors Associated with the Effectiveness of the ICP for Generating Singly Charged Atomic Ions

The ability of the Inductively Coupled Plasma to produce singly charged atomic ions from the atoms and molecules created from the ablation plume particles also plays a significant role in the overall instrument response. If the plasma effectively produced singly charged atomic ions from all ablation plume material, then the ions entering the mass spectrometer would faithfully replicate the composition of material entering the ICP from the transfer line. However, a number of factors, including those listed below, must be considered which can affect this ionization efficiency.

- **Elemental ionization potentials** - The ionization energy for an atom depends directly on which element the atom represents. Some elements have low ionization potentials (e.g., Na, K, Cs) and are readily ionized by the plasma ionization source. Other elements require significantly more energy to ionize (e.g., B, Si, P, S, Cd) and may not be effectively ionized by the plasma interaction. This effect is element specific and depends on the binding energy of highest energy electron and this follows the cyclic nature of the periodic table. It is not monotonic with increasing mass number.
- **Material dissociation energies** - The ablation plume material may contain constituents in a variety of forms ranging from loosely bound particles to tightly bound particles where the material may represent a specific material, chemical, or mineral phase (e.g., TiO_2 can occur in many crystalline phases including rutile, anatase, brookite, amorphous, etc.). Some material phases can readily be dissociated by the plasma interaction, while others are very robust and may be resistant to dissociation by the plasma (e.g., refractory oxide materials).
- **Molecular dissociation energies** - A given element in the waste may occur in a variety of molecular forms in both the waste and in the ablation plume. Some molecular forms require significant energy to dissociate the molecular components while other molecular forms may dissociate readily. Atomic species found in tightly bound molecular forms can be difficult to dissociate to free atomic ions or may rapidly recombine before entering the MS. Failure to produce free atomic ions for injection into the MS will result in suppressed signal levels for these molecular constituents (potential candidates include carbides and oxides).
- **Argon plasma energy** - The argon plasma and operating conditions have been chosen by the manufacturer for optimal production of singly charged atomic ions. However, the plasma torch (ICP) operating conditions do establish practical plasma energy conditions which govern the limits for elemental ionization potentials and molecular dissociations

which can be routinely achieved within the plasma. In addition, the argon plasma properties may not be optimal for digestion of ablation plume particles in the LA/MS application and the residence time of the particles in the ICP may not be long enough for complete particle breakdown. Thus, the carrier gas flow rate is an important factor.

- Plasma torch loading effects - The effectiveness of the plasma for dissociating and ionizing the incoming sample material is a function of the amount of sample material which enters the plasma for both solution-based samples and ablated particle plumes. In general terms, it appears that for input sample quantities above an observed threshold level, the plasma effectiveness for performing the desired functions is reduced. For input sample levels below the threshold level, the plasma effectively performs the desired functions. An empirical threshold level can be established and monitored to ensure that this effect does not degrade the LA/MS results.
- Particle size effects - Previously discussed in Section 2.2.1.

The impacts of these ionization effectiveness issues on the overall response of the ICP/MS instrument will be discussed in more detail following an overview discussion of the issues associated with the MS instrument response.

2.2.3 Factors Associated with MS Instrument Response

The final factor, the mass spectrometer response function (e.g., ion collection and counting efficiency of the instrument across the required mass spectral range), depends primarily on the MS instrument design and tuning during sample analysis. These issues are common to any analytical method which employs an ICP/MS as the analytical instrument for sample analysis.

When ICP/MS instruments are used for solution analyses, these issues are commonly dealt with effectively in an empirical manner by using element-specific calibration standard solutions derived from readily available reference standard stock solutions. When considering ICP/MS application to samples which include a) significant compositional variations from sample to sample and b) non-normal isotopic abundance distributions (e.g., Hanford tank waste samples where the radiological history has altered the natural isotopic abundance of some elements), knowledge of the mass spectrometer response function becomes a valuable tool for reducing experimental data.

In order to simplify the introduction of concepts used for LA/MS data reduction, **the factors associated with the MS response function will be introduced under the simplifying assumption that the instrument ICP provided for effective conversion of ALL material entering the ICP to singly charged atomic ions.** (The concepts will be extended beyond this simplifying assumption in Section 4.4 with the introduction of practical factors that must be considered for practical application of the method.)

- Under this assumption, the detected MS signal at each mass number will be directly proportional to the concentration of atoms at each mass number entering the ICP.
 - For each mass number, the proportionality constant will be the slope of a plot of the MS signal strength versus the analyte concentration entering the ICP in units of counts/ppm.
 - If the linear dependence of the MS signal strength on the analyte concentration is established over a broad analyte dynamic range, it provides the basis for the use of just one standard material to determine the proportionality constant at each mass number.

Previous project results with elementally spiked waste simulant materials (masses covering the target mass range) have demonstrated the required linear response of the instrument for a variety of mass numbers.

- Although the MS signal level observed at each mass number will be proportional to the corresponding incoming atomic concentration, the proportionality constant relating the MS signal strength to the analyte concentration may vary from analyte to analyte due to a number of instrument factors.
- A knowledge of the instrument response proportionality constants for all pertinent mass numbers can be used to generate an overall response function for the MS instrument.
 - The overall MS response function can be visualized by plotting the individual MS response proportionality constants versus mass number.
 - This overall instrument mass response plot is commonly referred to as the instrument Mass Response Function (or Mass Response Curve).
- Once the instrument mass response function is known, it can serve as the basis for converting the raw mass spectrometer signal detected at each mass number to quantitative analyte concentration levels in the material entering the ICP.

Under the simplifying assumption of this discussion (complete ionization of all materials entering the ICP) the Mass Response Curve for the ICP/MS would be expected to be a smoothly varying function of the atomic mass number which is independent of the concentration of specific analytes in the sample. Under this assumption, the analysis of broad-mass composition reference materials injected into the ICP/MS can be used to determine the Mass Response Curve as illustrated in Figure 2.3. (A smooth mass response curve is shown which is consistent with the assumption of idealized performance of the plasma torch functions.)

Once the mass response curve has been determined for the instrument (under a set of current operating conditions), Figure 2.4 illustrates how the curve can be used with data recorded on an unknown sample material to calculate the concentration of an analyte entering the ICP.

As noted above, Section 4.4 will extend these concepts beyond the simplified case discussed here to include the factors that must be included for practical applications.

2.2.4 Combined Effects of ICP and Mass Spectrometer Response Factors

When the effects of the ICP (Section 2.2.2) and the concept of the instrument Mass Response Function (Section 2.2.3) are combined, we enter the practical world where the analytical chemist must use the instrument system and interpret data. However, even with these combined effects, experimental data indicate that under proper analytical conditions many elements behave in a manner which allows the ICP/MS instrument response to them to be described using a relatively smooth mass response curve. (Laser ablation conditions must be used which result in ablation plume particle sizes that can effectively be processed by the ICP.) Elements in this category have ionization potentials which are sufficiently low relative to the argon plasma energy to allow effective atomic ionization and do not tend to be found in very stable material forms (e.g., refractory materials).

In addition, experimental data, from both solution-based ICP/MS and LA/MS experience, indicate that mass spectrometer response to a number of additional elements is proportionally related to the smooth mass response curve and their response can be described by the mass response curve when scaled with element specific scale factors. The scale factors for individual elements in this group are fairly constant and are not significantly affected by the sample matrix. The scale factors can be determined empirically using known reference materials to aid in data interpretation (assuming that sample matrix effects are acceptably small).

Finally, current experience indicates that the mass spectrometer response for some other elements is rather problematic. Some of these problem elements are generally observed for ICP/MS analysis whether the sample is presented in a nebulized solution form or as a laser ablated particle plume.

Thus, if the MS instrument response is shown to be linearly related to sample analyte concentrations, the mass response curve provides a very effective tool to characterize the ICP/MS instrument response (detection sensitivity) to different elemental species and to aid in the interpretation of data recorded using unknown samples. The value of the mass response curve and its range of applicability (i.e., mass numbers) will be greatly enhanced by the use of known reference materials which contain a sufficient variety of elemental species which span the mass range anticipated for the targeted unknown samples. It is for this reason that the elementally spiked waste simulant materials have been prepared and characterized.

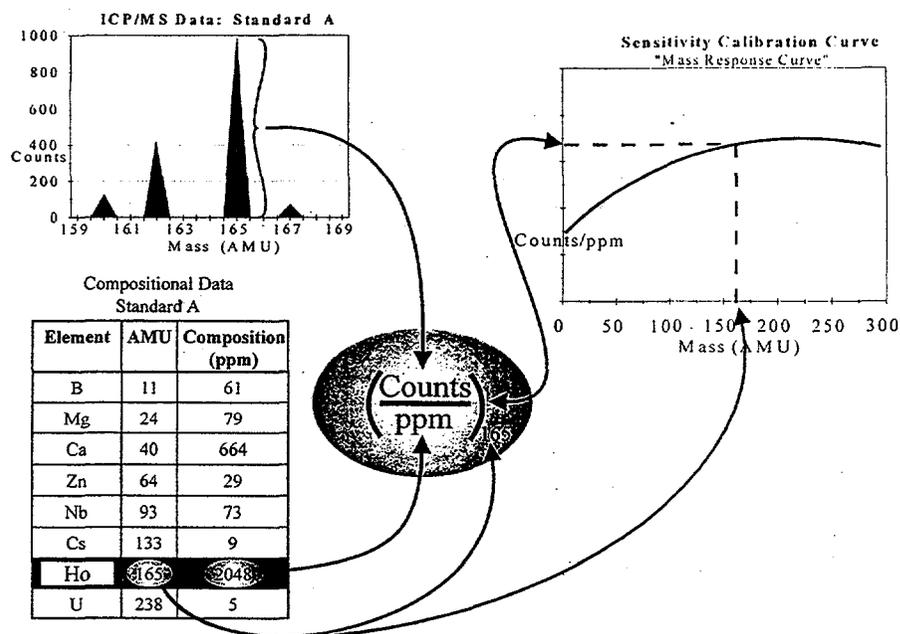


Figure 2.3. Method for calculating the Mass Response Curve using known sample composition data and corresponding mass spectrometer data.

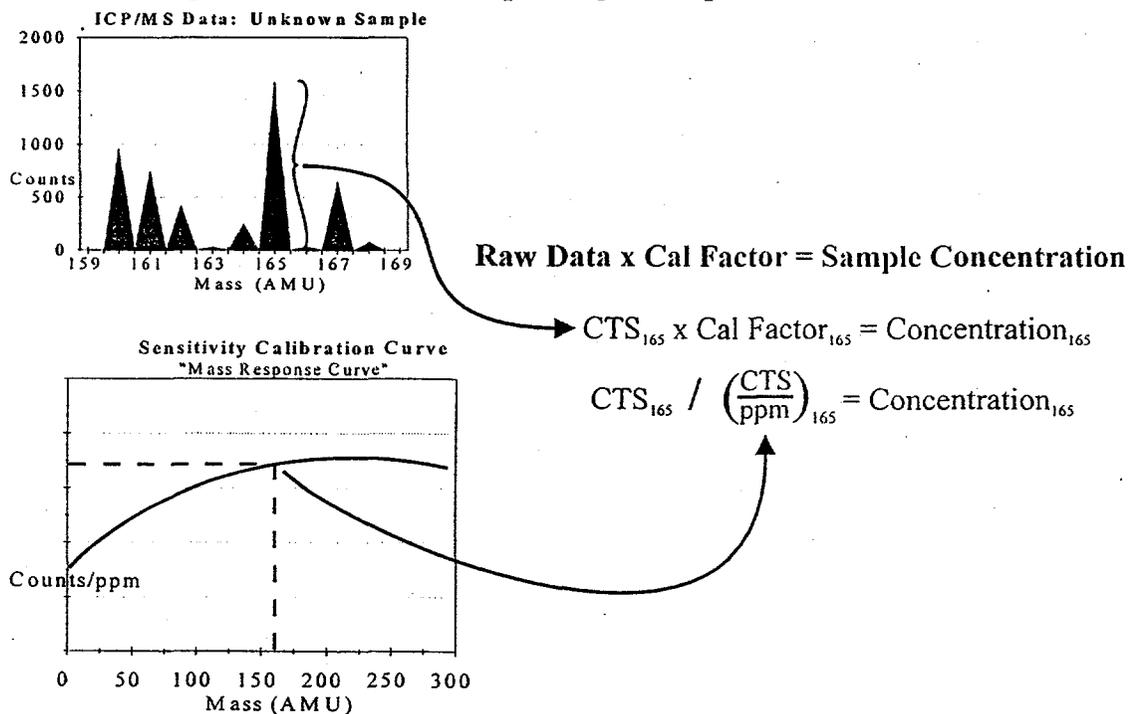


Figure 2.4. Method for calculating the concentration of an analyte in an unknown sample using the instrument Mass Response Curve and the mass spectrometer data recorded for the unknown sample.

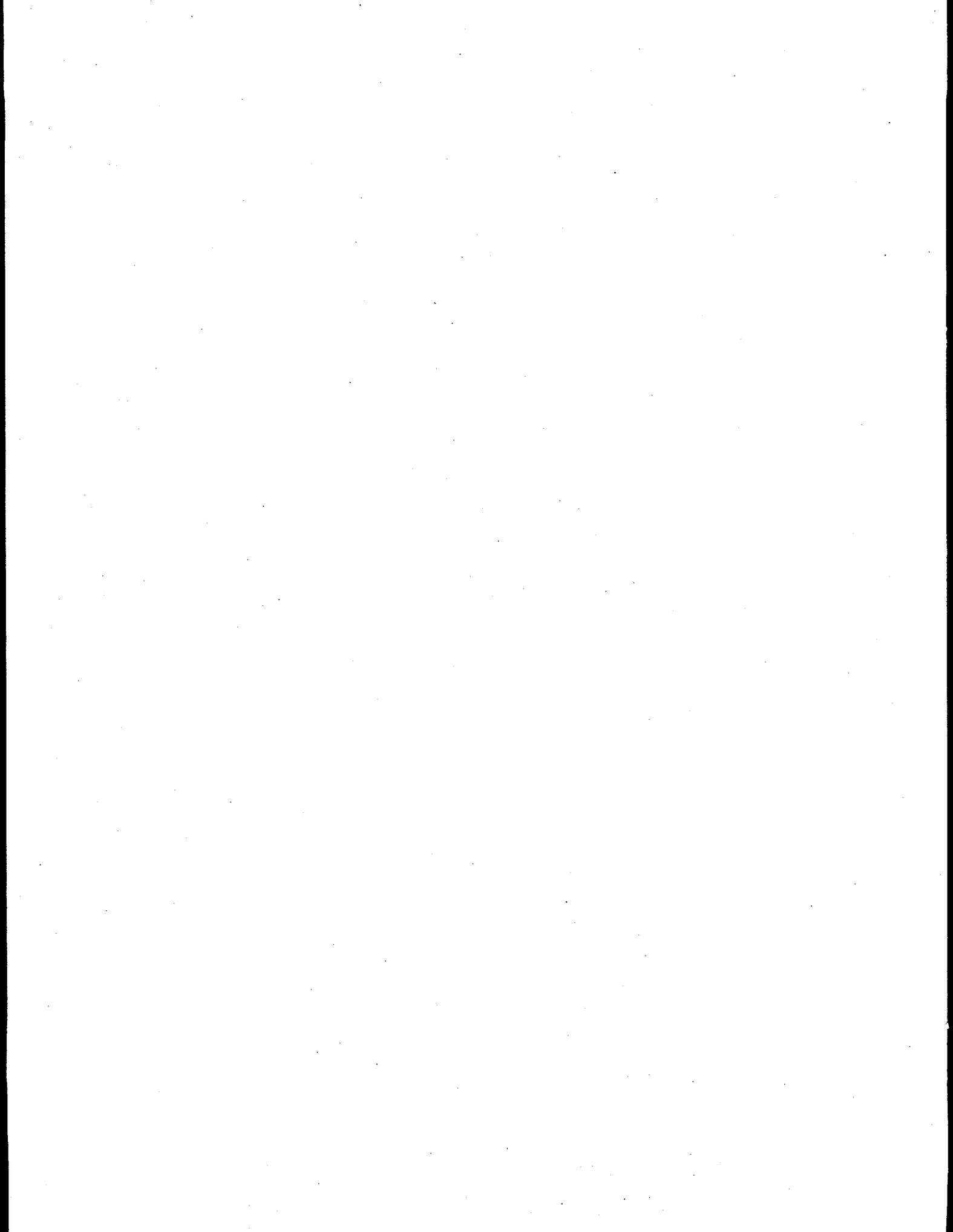
2.3 Summary of Factors Associated with the Application of LA/MS Methods for the Analysis of Solid Samples

A number of factors have been discussed which can affect the acquisition and interpretation of LA/MS data. While these factors may seem daunting to the reader, our experience has shown that:

- Effects of many of the factors can be minimized by the proper choice of operating conditions during data acquisition.
 - Previous results of laboratory testing on this project have provided a sound basis for the selection of robust laser ablation operating conditions for the analysis of Hanford tank waste samples. These laser ablation parameters provide for representative chemical sampling of the target material with minimal chemical fractionation.
 - Raster scanning of the laser beam across the sample's surface provides for area averaging of the sample's constituents which reduces sensitivity to spatial inhomogeneities in the sample. Repetitive rastering across the same region of the sample's surface can provide additional depth sampling of the material if this is desirable.
- A number of the other factors can be suitably compensated for during data reduction and analysis.
 - Several alternative methods have been identified and are under evaluation for establishing the ablation efficiency for different samples as required to allow quantitative data interpretation. Specific methods under evaluation include total ion current normalization and particle plume analysis (plume particle size distribution data).
 - Methods for the determination and use of the instrument mass response function are being refined to allow quantitative interpretation of the recorded mass spectra.
 - Elementally spiked waste simulant materials have been prepared which include a broad range of elemental spikes (broad mass range and concentration range) to allow better definition of the mass response function. The use of elemental spikes covering a broad mass spectrum will allow for significant improvements in establishing the mass response curve across the full mass spectrum anticipated for the tank waste samples. This will significantly reduce the uncertainty in the

use of the mass response function and will improve the analyte concentrations which are based on this function.

The waste analysis discussion which follows will build on these concepts for the ICP/MS mass response curve and provide additional information regarding detection of specific elements.



3.0 Experimental Description

3.1 Practical Deployment Configurations

The key LA/MS instrument system components were discussed in Section 2.1 and illustrated schematically in Figure 2.1. Practical LA/MS system implementation for analysis of radioactive samples is simplified by the fact that most LA/MS system components do not need to be located in high-radiation zones or enclosures.

Two LA/MS systems have been deployed at Hanford for the analysis of radioactive sample materials. A laboratory system is deployed to support research and development activities, and a hot cell system has been deployed to support routine analysis of tank waste samples. These systems have been configured to simplify system operation and maintenance. With this in mind, components located within radiation containment enclosures (e.g., hot cells, glove boxes, and radiation-qualified fume hoods) have been held to a minimum with the remainder of the system equipment located in adjacent work areas. Components located in the radiation enclosures are detailed in Table 3.1.

Table 3.1. LA/MS System Components Installed in Radiation Containment Enclosures

Type of Radiation Containment Enclosure	Laboratory LA/MS System	Hot Cell LA/MS System
Fume Hood	Sample & Sample Holder Beam Focussing Optics Sample Translation Stages	ICP/MS
Glove Box	ICP/MS	Not Applicable
Hot Cell	Not Applicable	Sample & Sample Holder Beam Focussing Optics Sample Translation Stages

3.2 Tank Waste Samples Analyzed with LA/MS Instrumentation

To date, the deployed Hanford LA/MS systems have been used to analyze a number of radioactive Hanford tank waste samples. Both raw waste samples (i.e., following extrusion and homogenization) and pretreated waste samples (i.e., following wash pretreatment to remove soluble components) have been examined. Table 3.2 provides a summary of the

analyses performed including identification of the LA/MS instrument system employed for the analysis.

Table 3.2. Hanford Tank Waste Samples Analyzed Using LA/MS Instrumentation Systems

Hanford Tank - Waste Condition	Laboratory LA/MS System	Hot Cell LA/MS System	Reference
Tank S-104 - Raw waste sludge - Washed waste sludge	X X		(Rapko 1995)
Tank T-104 - Raw waste sludge - Washed waste sludge	X X		(Rapko 1995)
Tank T-111 - Raw waste sludge - Washed waste sludge	X X		(Rapko 1995)
Tank U-105 - Raw waste sludge		X	(Fritts 1996)

These samples were chosen to provide representative sludge samples. Specifically, these samples were known to have a broad number of chemical constituents including heavy metals and radionuclides on the basis of prior independent analytical results (ICP/AES and radiochemistry analysis). Sample specifics include:

- S-104: Composite sample of segments 4 and 5 from Core 43 (222-S Jar Number 6588). The sample is described as a primary waste product from the reduction oxidation (REDOX) process high-level waste.
- T-104: Composite sample of segments 2, 3, and 4 from Core 46 (222-S Jar Number 6555). The sample is described as a first-cycle decontamination waste from the bismuth-phosphate process.
- T-111: Composite sample of segments 1 and 3 from Core 33 (222-S Jar Number 6591). The sample is described as a second-cycle decontamination waste from the bismuth-phosphate process.
- U-105: Tank: U-105 Core: 136 Segment: 9A (upper half)
 Sampled: 3/18/96 Extruded: 4/03/96
 Sample Description: Dark brown sludge
 Data package: WHC-SD-WM-DP-182, Rev. 1

3.3 Reference/Standard Samples Analyzed to Support Data Reduction

Several glass materials prepared by the Pacific Northwest Materials Characterization Center laboratory were chosen for use as reference materials during the LA/MS characterization of the tank waste samples. These glass materials previously had been analyzed extensively during inter-laboratory round robin testing conducted under the auspices of Pacific Northwest's Materials Characterization Center (MCC) (Smith 1992, Wyse 1993, and Pacific Northwest Laboratory 1988). Specific information on the reference materials utilized includes:

- CVS-19: CVS-19 is a glass composition prepared for the Composition Variability Study and designated as Formulation #19 in this study. CVS samples were obtained from the Materials Characterization Center (MCC) laboratory. Repetitive analyses of these samples by the HWVP LA/MS Project indicate that some compositional variability exists with respect to noble metals in CVS-19. CVS-19 is black in appearance with a high optical absorption coefficient.
- WV-205: WV-205 is designated as West Valley-205. This glass formulation is described in "Fabrication and Characterization of MCC Approved Testing Material ATM-WV/205 Glass" (Pacific Northwest Laboratory 1988). The ATM-WV/205 glass meets all specifications. Visually, the WV/205 glass bars appear uniformly glassy and generally without exterior features. Microscopic examination and x-ray diffraction revealed low (about 0.5 wt%) concentrations of 3- μ m iron chrome spinel crystals and 1- μ m ruthenium inclusions scattered randomly throughout the glassy matrix. The glass is black in appearance with a relatively high optical absorption coefficient.

While these glass reference materials have been used for the experiments described in this report, it is recognized that these materials have significant shortcomings for use as reference materials for LA/MS analysis of tank wastes. The elemental constituents in these glasses span only a portion of the mass range known to occur in the actual tank wastes. This means that the mass response function calculated using the glass compositional data covers only a portion of the mass range of the tank waste samples. Thus, actual waste sample data for high mass numbers must be interpreted using an extrapolation of the calculated mass response function.

As mentioned briefly in Section 2.3, elementally spiked waste simulant materials have been prepared which include a broad range of elemental spikes (broad mass range and concentration range) to allow better definition of the mass response function. The use of elemental spikes covering a broad mass spectrum will allow for significant improvements in establishing the mass response curve across the full tank waste mass spectrum. This will significantly reduce the uncertainty in the use of the mass response function and will improve the analyte concentrations which are based on this function.

Unfortunately, these new spiked simulant materials were not available for use at the time the tests described in this report were conducted. Additional testing with these new elementally spiked simulant materials is being performed to evaluate their usefulness for establishing improved mass response functions and interpreting LA/MS data recorded on unknown samples.

3.4 Experimental Conditions Employed for LA/MS Data Acquisition

3.4.1 Laser Ablation Conditions

Key test parameters employed for the laser ablation processes during these tests are shown in Table 3.3. These laser parameters were selected to provide the best sampling characteristics regarding the laser ablation process and the particulate plume created by the ablation process. The different values shown for the laser wavelength and pulse energy for the two cases above fall within the envelope of suitable operating parameters as determined during previous testing on this project and are not expected to result in significant performance differences.

Table 3.3. Laser Ablation Parameters Employed During the Analysis of Hanford Tank Waste Samples

Test Parameter	Laboratory LA/MS System	Hot Cell LA/MS System
Laser wavelength (nm)	266	355
Laser pulse energy (mJ) (energy/pulse at sample)	0.3	0.2
Laser pulse length (ns)	6	6
Laser pulse rate (Hz)	20	20
Focal length of final focusing lens (cm)	10	10
Beam diameter (μm) (at sample)	50	50

It should be noted that these laser parameters, which were selected for the TWRS sample analysis following significant project laboratory testing, differ very significantly from parameters that were commonly cited in the literature at the initiation of this project (infrared laser wavelengths [typically $\lambda = 1.06 \mu\text{m}$] and pulse energies of 100s of mJ). Project experimental results indicate that if literature recommendations for operational parameters had been utilized, the laser ablation sampling would have resulted in excessive quantities of material removed from the samples and entering the plume transfer system, a predominance of

large particles in the plume with associated plume transport problems, significant plume particle dropout in the transfer line, significant increases in the radioactive contamination of ICP/MS instrument "front-end" due to the increased plume material transport, and significant fractionation of analytes removed from the sample. The increased radioactive contamination of the ICP/MS entry stages would result in a direct increase the radiation exposure risk for the analytical staff operating the LA/MS system.

3.4.2 Sample Environment for Laser Ablation

Ablation of all samples was conducted with the sample placed in a closed sample holder with an argon cover gas. A low-level flow of argon gas was passed through the sample holder to entrain and carry the ablated plume material to the ICP/MS instrument for analysis. The sample holder included a quartz cover which provided high-quality transmission of the ablation laser beam to the sample.

In order to allow rapid sequential acquisition of reference and test sample data without requiring changes to the ablation cell/holder, the experiments were conducted with reference and test samples located at adjacent positions within the sample holder.

The ablation cell was placed on the computer-controlled x-y-z scanning stages to allow automated movement of the samples under the ablation beam to provide raster scanning over each sample/reference standard.

3.4.3 Plume Transfer Parameters

The carrier gas parameters employed to transfer the ablation plume material from the sample holder to the ICP/MS instrument are shown in Table 3.4. Identical conditions were utilized for both systems with the exception of the length of the transfer line. Both transfer lines were short compared to the line length where significant particulate deposits are expected.

3.4.4 ICP/MS Operating Parameters

The operating parameters utilized for the ICP/MS instrument are shown below. Nominally identical parameters were employed for data recorded on both the Laboratory and Hot Cell LA/MS systems.

ICP:	Cool gas:	12 l/m Ar
	Auxiliary gas:	0.5 l/m Ar
	Carrier (nebulizer) gas:	0.9 l/m Ar
	rf Power:	1250 Watts (<2 watts reflected)
MS:	Full Mass Scan (5 - 250 amu)	
	45-second acquisitions	

Table 3.4. Ablation Plume Transfer System Parameters Utilized for Actual Waste Sample Analyses

Ablation Plume Transfer System Parameters	Laboratory LA/MS System	Hot Cell LA/MS System
Transfer line interior diameter (cm)	0.46	0.46
Carrier gas	Argon	Argon
Carrier gas flow rate (l/min)	0.9	0.9
Carrier gas velocity (m/s)	~ 9	~ 9
Plume transfer line length (m)	~ 4	~ 2

3.5 Data Recorded

Integrated data sets were recorded for each unknown sample which included:

Mass Spectrometer Data

- Raw mass spectral data for the ablation plume from the unknown sample.

Test conditions: An ablation plume from the unknown sample is created by translating the unknown sample beneath the incident ablation laser beam. The ablation laser pulse rate (20 Hz) and the data integration time (typically 45 seconds) provide for the integration of an ablation plume created at a large number of sample positions by many individual ablation laser pulses. [The raster scanning combined with data integration provides for representative sampling of small-scale variations that may occur in the sample material composition (e.g., grain-to-grain variations)].

Data use:

- Provide raw MS spectra for calculation of the corrected MS spectra for the test sample.
 - The corrected mass spectra is used with the MS response function to determine the test sample composition.
- Raw mass spectral data for the ablation plume from the reference sample.

Test conditions: An ablation plume from the reference sample is created by translating the reference sample beneath the incident ablation laser beam. The ablation laser pulse rate (20 Hz) and the data integration time (typically 45 seconds) provide for the

integration of an ablation plume created by a large number of individual ablation laser pulses and sample positions.

Data use:

- Provide raw MS spectra for calculation of the corrected MS spectra for the reference sample.
 - The corrected mass spectra are utilized to determine the MS instrument response utilizing independent reference sample composition data.
- Raw background mass spectral data for the carrier gas collected during a period with no ablation of either the unknown or the reference sample.

Test conditions: These data are recorded during periods when the ablation laser beam is prevented from reaching either sample material. (The laser beam is mechanically blocked by a computer-controlled optical shutter in the optical source subsystem.) The data integration time is chosen to be the same as used for recording actual sample data (typically 45 seconds) to allow direct application of the data for calculating background corrections. Ideally only clean argon will enter the ICP/MS.

Data use:

- Provide instrument background data to allow the correction of raw MS data for both unknown and reference materials.

Sample Position Data

Sample position data (i.e., position of the sample x,y,z translation stages) are recorded during the tests and are linked with the corresponding test data. This provides a direct link to samples placed at different positions on the sample holder and also allows the interrogation of data anomalies that might be observed for highly inhomogeneous samples.

Ablation Laser Pulse Energy Data

Ablation laser pulse energy data are recorded during the tests and are linked with the corresponding test data.

Ablation Plume Particle Size Distribution Data

Ablation plume particle size distribution data were **not recorded** during these initial tests with radioactive tank waste samples.

- The laboratory LA/MS system for radioactive sample analysis does not include a particle size spectrometer at this time.

- The hot cell LA/MS system does include a particle size spectrometer, but it was not operational at the time the initial system demonstration was performed.

3.6 Test Sequence

A typical test sequence for the analysis of an unknown sample is outlined below. The different mass spectrometer data noted above are recorded at appropriate times in the sequence while sample position and laser pulse energy were recorded with all mass spectrometer data sets.

1) Reference sample sequence

- Replicate "BACKGROUND" data sets (typically 2 sets)
- Replicate "REFERENCE MATERIAL" data sets (typically 3 sets)
- Replicate "BACKGROUND" data sets (typically 2 sets)

2) Unknown sample sequence

- Replicate "BACKGROUND" data sets (typically 2 sets)
- Replicate "UNKNOWN SAMPLE MATERIAL" data sets (typically 3 - 5 sets)
- Replicate "BACKGROUND" data sets (typically 2 sets)

3) Reference sample sequence

- Replicate "BACKGROUND" data sets (typically 2 sets)
- Replicate "REFERENCE MATERIAL" data sets (typically 3 sets)
- Replicate "BACKGROUND" data sets (typically 2 sets)

Replicate data sets were recorded to allow an assessment of measurement stability and data scatter during the tests. Data scatter, when observed, may be due a number of possible factors including ICP/MS instrument system variations, laser pulse energy variations, and sample inhomogeneities. The reference data sets recorded prior to and following the unknown sample data sets allow for a) correction of instrumentation operating condition drift if it occurs and b) the use of reference sample composition information to aid in data reduction and interpretation.

4.0 Data Reduction Procedures

4.1 Individual Data Set Processing

The quadrupole mass spectrometers used in both the laboratory and hot cell LA/MS systems utilize a detector with a multi-channel analyzer (MCA), commonly using 4096 channels, to record signal contributions from individual ions. Raw data (mass spectra) as recorded by the MCA has the appearance of a fairly continuous function which includes sufficient detail to determine peak shape, peak resolution, etc.

During instrument set-up, the operator specifies how the MCA channels will be assigned to the programmed mass scan range (that is, how the MCA channels are assigned to corresponding element and isotope masses). Typically for the experiments described in this report, the MCA channels are assigned to cover the 0 - 250 amu mass range. Thus, roughly 16 - 20 channels correspond to each amu.

In routine operation, the ICP/MS instrument control computer software preprocesses the raw signal to determine the total number of counts received by all MCA channels assigned to individual mass numbers. (This corresponds to integrating the area under the raw signal curve for each of the assigned mass numbers.) The integrated value is then assigned to the corresponding mass number.

All subsequent data processing discussed below is performed on the "mass spectra" which result when the integrated peak area values are assigned to the corresponding mass numbers.

4.2 Background Corrections for MS Data

The raw MS data for both the reference and the unknown sample materials were corrected for signal contributions resulting from measurement background signals. The **background-subtracted MS** signals were determined by subtracting appropriate background signals from the corresponding raw MS signal at each mass number.

In practice, the raw MS spectra recorded for a sample (either reference or unknown) was corrected using the background spectra recorded immediately before and after the sample data sets.

- Background spectra examination and averaging
 - The replicate MS background data sets recorded before the sample data sets were analyzed to determine the corresponding average MS background spectra and the standard deviations of the background signal at each mass number.

- The same calculations were performed for the replicate MS background data sets recorded after the sample data sets.
- The average background spectra recorded before and after the sample data were compared.
 - If the "before" and "after" background spectra were comparable, then no significant system changes occurred during the sample analysis. The average of the "before" and "after" background spectra and the corresponding standard deviation values were then used for the background corrections. **(This is the typical outcome.)**
 - If the "before" and "after" background spectra exhibited significant differences, then significant system changes had occurred during the sample analysis. Since the time duration of the data acquisition sequence is rather short, the failure of this test would generally indicate that the system operation should be checked and the sample be re-analyzed. **(This is NOT typical for the LA/MS system operation.)**
- Background correction for raw MS spectra
 - The same procedure was performed for all raw MS data sets recorded for reference and unknown samples.
 - Background-corrected mass spectra were calculated by subtracting, for each mass number, the corresponding average background MS spectra from each of the replicate, raw MS spectra recorded for a given sample. The resulting spectra will be referred to as **background-corrected MS spectra**.

4.3 Replicate Data Set Processing

Replicate background-corrected MS spectra for each measurement were corrected to compensate for overall MS signal level shifts which may have occurred during the sample analysis (e.g., ablation efficiency as discussed at the end of Section 2.2.1). This was done for all data sets recorded for reference and unknown samples.

- 1) The total ion count for each individual data set was calculated from the background-corrected MS spectra by summing the detected ion count at each mass number specified in the mass spectrometer data acquisition menu.

Total Ion Count = $\Sigma(\text{ion count at mass } m_i)$ for all mass numbers scanned

(As discussed at the end of Section 2.2.1, several alternate normalization approaches are being evaluated by this project. The ion count method for data normalization was utilized for these data since no plume particle size distribution data was available to support the normalization.)

- 2) The average Total Ion Count for the group of replicates is calculated.

$$\text{Average Total Ion Count} = (\sum \text{Total Ion Count})_i / N$$

where i , the number of an individual replicate data set, is summed over all replicate data sets for the specific sample and N is the total number of replicates recorded for the specific data.

- 3) Each replicate background-corrected MS spectra was normalized by multiplying the count at each mass number in the MS spectra by the ratio of the Average Total Ion Count for the group of replicates divided by the Total Ion Count for that individual replicate data set. This compensated for differences in ablation efficiency and put all replicate data sets on a common basis.
- 4) The normalized, background-corrected MS spectra replicates for each sample were analyzed to determine a) an average MS signal curve and b) the Relative Standard Deviation (RSD) of the MS signals for each mass number in the mass spectra. For each mass number, the normalized replicate data set count rates were used to calculate an average count rate and a standard deviation.

An average, normalized background-corrected mass spectra resulted by plotting the average count value at each mass number (for the replicate spectra) versus the mass number.

The effective RSD value of the average, normalized background-corrected mass spectra for each mass number was calculated as the square root of the sum of the squares of the RSD values for both the average, normalized background-corrected mass spectra and the corresponding background spectra.

For data recorded on homogeneous samples and under highly stable test conditions, the RSD values for mass numbers with good counting statistics can be indicative of the practical data precision limits for the LA/MS measurement capability with the system equipment. Increases in RSD values, above the optimal values, may be observed for mass numbers with low signal levels (i.e., poor counting statistics), samples with significant spatial inhomogeneities (i.e., inhomogeneities which occur over large distances relative to the raster scan dimensions), and when equipment operating conditions vary.

These normalization and RSD calculations were performed for all data sets including those for unknown samples and reference samples.

4.4 MS Instrument Mass Response Function Calculation

Background-corrected, normalized MS data recorded for reference materials are used with independently obtained reference sample composition data to calculate the instrument Mass Response Function following the procedure illustrated in Figure 2.3. As discussed in Sections 2.2.2 - 2.2.4, not all elements will fall on the Mass Response Curve seen in Figure 2.3 following the simple calculation in the figure.

After calculation, the mass response curve fulfills two significant functions.

- First, the calculated curve is used as an aid in confirming the ICP/MS instrument is properly adjusted and is operating suitably. If the mass response curve does not fall within an acceptable range for the instrument, the operator immediately knows the instrument must be checked for operational problems including control parameter settings.
- Second, the calculated curve establishes the conversion factors which allow MS data for unknown samples to be used to calculate elemental concentrations in the unknown sample materials.

Background-corrected MS signal levels are used for elements in the reference material for which analyte concentration levels are known from independent sample analyses. At each mass number, the value of the mass response function is calculated by dividing the MS signal level (i.e., counts or counts/sec) by the corresponding analyte concentration (i.e., parts per million, ppm). The value of the calculated mass response function for each element (counts/ppm or counts/sec/ppm) establishes the instrument measurement sensitivity for each mass number.

Data for a number of elements can be used immediately to determine the general shape of the Mass Response Curve. In general, these elements have ionization potentials below 7 eV and their masses fall in regions of the mass spectrum where molecular ions and isobaric interferences are of minimal importance. Elements commonly in this group include Li, Mg, Ti, Cr, Fe, Ni, Y, Sr, Ba, rare earth elements (REEs), Pb, Th, and U). When these elements are present in the sample in sufficient quantities, the resulting MS data exhibit low RSDs and the elements are very useful for the mass response curve calculation. Data for these elements will establish a smooth mass response curve. (Elements exhibiting this type of performance are illustrated conceptually in Figure 4.1 by the circle symbols labeled A_1 , A_2 , and A_3 .)

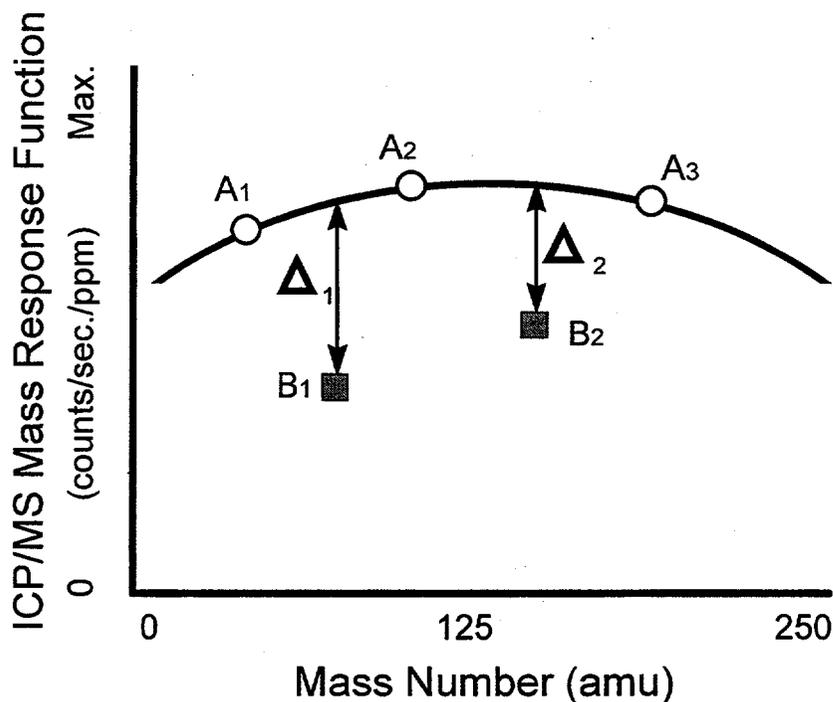


Figure 4.1. Conceptual illustration of calculated mass response function showing examples of elements which are readily ionized by the ICP (e.g., A_1 , A_2 , and A_3) and elements which are ineffectively ionized by the ICP (e.g., B_1 and B_2)

A second group of elements provide a very predictable MS response but their raw MS signal levels will not result in points that fall on the smooth mass response curve calculated with the elements discussed above. Again, these elements have masses which fall in regions of the mass spectrum where molecular ions and isobaric interferences are generally not a problem. However, these elements have relatively high ionization potentials which reduce the percentage of these atoms which are ionized by the ICP. Thus, the mass response function value calculated for these elements will fall below the smooth curve calculated above. (Elements exhibiting this type of performance are illustrated conceptually in Figure 4.1 by the square symbols labeled B_1 and B_2 .) Empirical correction factors for this reduction in ionization efficiency can be determined for these elements which account for the elemental deviation from the smooth mass response curve. (In the figure, Δ_1 and Δ_2 correspond to the reduced response due to the ionization efficiency effects.) The ionization efficiency correction factors for individual elements in this group are relatively insensitive to sample matrix effects. Elements

in this group (and their rough empirical ionization efficiency correction factors) are B (25%), Si (25%), and Cd (50%).

Finally, there are some elements that are problematic for measurement with ICP/MS-based methods including the LA/MS method. The elements may be difficult to measure because their mass peaks fall in complicated regions of the mass spectrum (e.g., significant, common interferences) or their ionization potentials may be very high which results in the MS seeing a very small percentage of the atoms that enter the ICP. Elements in this group include P, S, As, Se, Cl, and Br.

4.5 Calculation of Semi-Quantitative Sample Composition Results

The calculation of sample composition from recorded MS spectra utilizes the instrument response knowledge built into the mass response curve and follows the concept shown schematically in Figure 2.4. As stated above, the mass response function value for a given mass number corresponds to the conversion factor which relates the MS signal level for each element in the unknown sample to the corresponding elemental concentration.

Elemental concentration levels in the unknown sample can be calculated by dividing the MS signal level at each mass number (i.e., either counts or counts/sec) by the corresponding mass response function value (i.e., either counts/ppm or counts/sec/ppm).

Until a method can be established to reliably and accurately determine the laser ablation efficiency, the calculated results will remain semi-quantitative. As discussed in Section 2.2.1, several candidate methods to meet this requirement have been identified and are being evaluated within this project in FY 1997. (The detected ion count method will be used for the data discussion that follows.) Another alternative is available if the analytical chemist has some prior knowledge about the concentration of some elements in the sample (e.g. in effect the existence of internal standards). This has been employed for soils analysis with the LA/MS method (Anderson and Brayman 1994; Anderson, Brayman, McIntosh et al. 1994). If an internal standard is available, the semi-quantitative values calculated using the mass response function can be normalized using the known internal standard values and most elemental concentrations can be calculated. Elements which are not as predictable (i.e., last group discussed in Section 4.4) may not be quantitative without determining ionization efficiencies and matrix effects.

5.0 Data Interpretation for Hanford Tank Waste Samples

The analysis of Hanford tank waste materials using ICP/MS methods offers significant advantages beyond the obvious ability to determine a broad range of elemental constituents with high-detection sensitivity and measurement dynamic range. Due to the presence of nuclear materials and the irradiation history of the wastes, the detailed waste chemical constituent inventory in the tanks is a product of both conventional and radiologically driven chemical processes, nuclear fission processes, and radioactive capture and decay processes. ICP/MS-based methods, which provide isotopic measurement capability, offer additional advantages since they can provide definitive knowledge of both a) the non-radioactive and non-radiogenic and b) the radioactive and radiogenic constituents.

- a) The use of mass spectroscopy for the determination of **non-radioactive and non-radiogenic constituents** (i.e., general elemental constituents) in the waste materials is comparable to the analysis of conventional, non-radioactive samples. The ability to gain broad analyte characterization of these general constituents from a single analysis can provide very time- and cost-effective data. The methods discussed in previous sections for the analysis of reference and waste simulant samples applies to the analysis of these general elemental constituents. The discussion of actual waste sample data analysis which follows will include comments on general chemical constituents in the waste samples.
- b) The use of mass spectroscopy provides data sets which include elemental and isotopic information on **radioactive and radiogenic constituents**. The nuclear-related sample constituents have significant importance for the tank waste cleanup programs and present unique data interpretation issues that do not occur in non-radioactive samples.

Specifically, the Hanford tank waste samples include radioactive and radiogenic constituents which are present at levels determined by:

- Specialized materials irradiated in the Hanford reactors (i.e., nuclear fuel, cladding, materials with unnatural/enriched isotopic ratios, etc.)
- Chemicals used in and chemical by-products of the separation processes used after fuel irradiation to obtain special nuclear materials
- Chemicals used in and chemical by-products of processing steps employed in subsequent years to reduce waste volumes and manage the waste storage inventory

- Fission products resulting from fuel fission during reactor operation and spontaneous fission during storage in the tanks
- Radionuclides created by neutron activation (i.e., n- γ reactions).

Present practices used to determine these nuclear-related elemental and isotopic constituents in waste materials require sample dissolutions, lengthy radiochemical separations, and significant laboratory facilities to accomplish. The LA/MS method discussed here can determine much of the tank waste's bulk elemental composition and radionuclide content.

When combined with laser ablation, the ICP/MS methods can be used to obtain data to meet both the conventional and nuclear-related elemental and isotopic analysis requirements in a timely and cost-effective manner. (Rough time and cost advantages were noted in the Preface.) When properly interpreted, the isotopic concentration data in the mass spectral regions corresponding to the fission products (both non-radioactive and radioactive isotopes) can provide major insights that will be of value for the tank waste program operation and information to support the long-term remediation of the waste materials. However, correct data interpretation requires deconvolution of isobaric interferences (i.e., isotopes of different elements with the same masses). Key complementary data which enhances the analyst's ability to usefully interpret the mass spectral data includes knowledge of:

- Fission processes including fission paths, probabilities, and decay process time constants (i.e., half-life times)
- Nuclear capture and decay processes, decay half-life values, and capture and decay path probabilities (i.e., neutron capture cross sections)
- Natural abundance ratios for different isotopes of individual elements.

An experienced radio-chemist can reach significant conclusions pertaining to the tank waste materials using the waste isotopic constituent data available from LA/MS analysis, the independent data detailed above, and information about the waste material's history (e.g., nuclear fuel employed, cladding material, date of fuel irradiation, separation process chemistry, etc.), if available. In addition to using historical records, full use of the data available from LA/MS analysis of these waste materials can provide significant insights into the waste material's history and support the confirmation/validation of historical process records [i.e., Historical DQO (McCain 1996), finger printing tank waste materials, tank processing history, estimates of fuel burn-up, etc.], and the LA/MS isotopic data can allow better prediction of future issues that are likely to be of importance for estimating long-term stability of the waste material in different remediation approaches (radioactive constituents that will govern future radioactive decay paths, products, half lives, estimated time dependent nuclear decay profiles for the future).

The discussion of sample analysis results in the next chapter will include complementary discussions of the general chemical constituents and the radioactive and radiogenic constituents.

5.1 Supplementary Information for Analysis of Samples with Radiogenic Constituents (Fission and Activation Products)

The analysis of mass spectrometric data to determine bulk element concentrations (i.e., the total concentration of all isotopes for an individual element) in natural (i.e., non-nuclear history) samples often utilizes known natural isotope population ratios for specific elements. For example, silicon's natural isotopes and their relative concentrations are known to be ^{28}Si (92.18%), ^{29}Si (4.17%), and ^{30}Si (3.12%). Thus, from a definitive measurement of the concentration of one of these isotopes, the total concentration of silicon can be calculated. The ability to utilize known isotopic concentration ratios allows the analyst to choose mass numbers with minimal isobaric interferences (i.e., isotopes of different elements at the same mass number, for example ^{138}Ba and ^{138}La) and molecular ion interferences (e.g., ^{106}ZrO and ^{106}Pd) as the basis for calculating the bulk element concentration for specific elements. Concentration calculations for some elements are more complex as isobaric interferences cannot easily be avoided. However, many of these can be resolved by evaluating isotopes detected at several adjacent mass numbers and using the isotopic ratio knowledge of elements represented in the specific mass range to sort out the relative concentrations.

The analysis of samples with unnatural isotopic ratios (i.e., containing materials resulting engineered isotopic enrichment processes) and/or having a unnatural nuclear irradiation history (i.e., recent compared to the geologic formation period) presents a unique problem to the analyst. In these materials, many elements still will exhibit the known isotopic ratios as they have not been enriched and they are largely unaffected by the nuclear environment to which they have been exposed. However, many other elements will have altered isotopic ratios due to enrichment and/or radiogenic process effects. This added complication requires the analyst to utilize additional caution in selecting isotopes (mass numbers) for elemental characterization. The effects of these considerations on several mass ranges will be discussed in general terms below. Discussions of specific sample data in Section 6 will build on these concepts.

Fortunately, essentially all low mass elements (i.e., elements with isotopes below mass 80) in the Hanford tank wastes will exhibit the natural isotopic ratios (i.e., they have not been significantly altered isotopically). This is for one two reasons:

- Many of these elements were not contained in materials which were integral component materials within the confines of the nuclear reactor.
- If these elements were contained in materials used as fuel cladding, reactor core construction materials or neutron moderators, they were there by design due to their

low neutron capture cross-sections which minimized their alteration by the reactor neutron exposure.

Consequently, the analysis of these low mass elements (below 80 amu) have been determined conventionally in this report.

Other elements which can be conventionally calculated are elements which have masses in the range from 160 to 210. Although the majority of the elements in this mass range are insignificant matrix components, Tl, Hg, Pb, and Bi are the exceptions. Bismuth can be a predominate matrix component (i.e., bismuth phosphate process) and Tl, Hg, and Pb can be important from the standpoint of toxicity and/or waste processing.

The elements which have masses in the range between mass 80 and 160 and masses greater than 210 have the greatest potential of having altered isotopic abundances. The mass range between 80 and 160 amu is the most complex for the analyst seeking to assign signals at individual mass numbers to a specific element or elements (isobars). (This region will be discussed below in more detail.) Masses above 210, in most cases, can be assumed to be the element which has the longest half-life. For example the dominant elements at specific masses include Th for masses 230 and 232; U at masses 233,234,235,236, and 238; Np at mass 237; Pu at masses 239, 240, 242 and 244; and Am at masses 241 and 243.

In fact, the production rate of fission products far outweighs the production of plutonium by many orders of magnitude. The relative production of these fission products can be estimated using known fission yields and are plotted in Figure 5.1. As one can see, the primary isotopes produced by U and Pu fission correspond to two separate mass regions (80 to 110 and 130 to 150 amu), with virtually no production of isotopes between these regions. The profiles represented by these fission yield curves are representative for conventional types of nuclear reactors. The processes which produce these fission products initially produce very unstable radioisotopes which are predominately neutron rich. Subsequent decay via negatively charged beta (β^-) particles eventually produced the present-day fission products found in the Hanford tank waste today.

Given that conventional reactors were used to produce plutonium and the wastes generated from these processes were quantitatively collected and stored in the Hanford tanks, the mass spectra of this region should produce isotopic signatures which conform relatively to the fission yield curves shown in Figure 5.1.

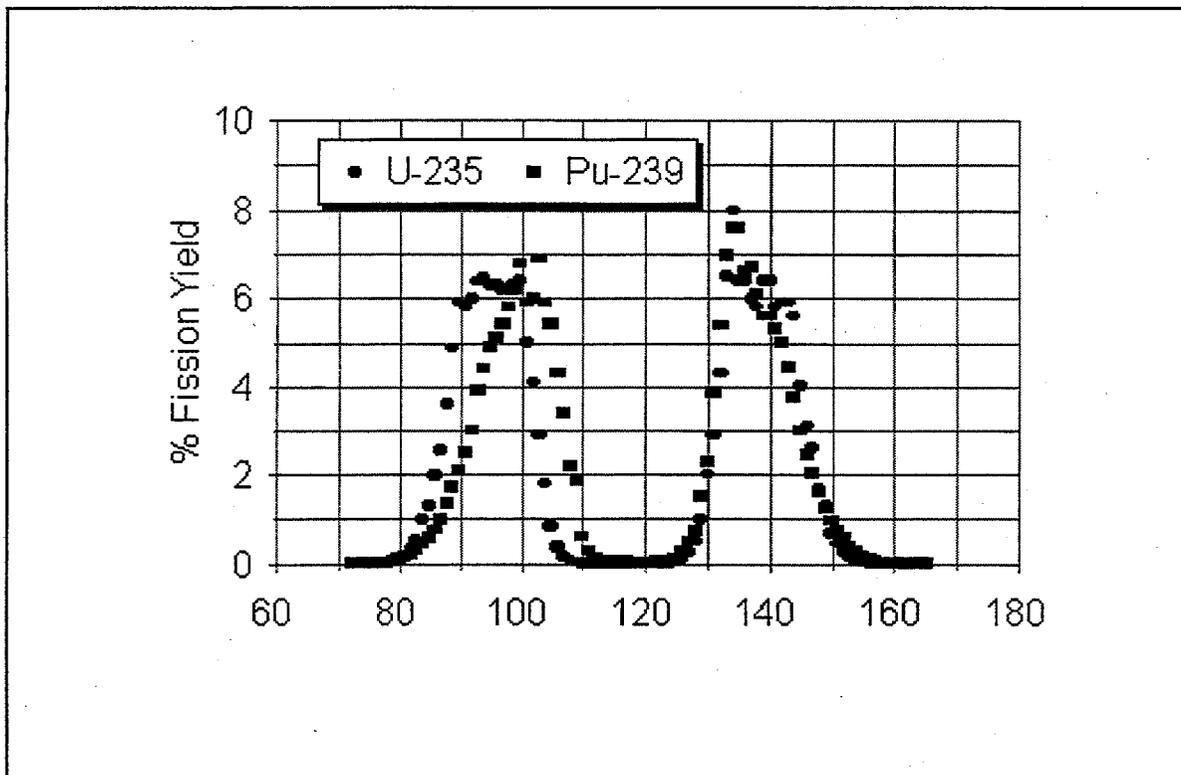


Figure 5.1 Typical fission yields of isotopes produced from the fission of ^{235}U and ^{239}Pu via conventional (moderated neutron) reactors

6.0 Experimental Results and Discussion

Seven radioactive Hanford tank waste samples have been analyzed using LA/MS methods. Six of the samples were evaluated with a laboratory LA/MS system while the last sample was analyzed using the recently installed hot cell LA/MS system. Complementary discussions will be given for the laboratory and hot cell system analyses.

6.1 Sample Analyses Conducted with Laboratory LA/MS System for Radioactive Samples

As shown in Table 3.2, six radioactive tank waste samples have been analyzed using the laboratory LA/MS instrument system which is available for radioactive sample analysis. The samples, from three Hanford waste tanks (S-104, T-104, and T-111), were obtained from the TWRS Pretreatment program for analysis using the LA/MS method. Samples received from each tank included a "raw" sample (i.e., no treatment beyond core extrusion, subsampling, and homogenization) and a "pretreated" sample. The pretreated samples had been "washed" in an effort to remove soluble analytes which were left in the waste following removal from the tanks and extrusion in the hot cell. The sample materials had been previously analyzed using independent methods for the TWRS Pretreatment Program and those data were made available to aid in evaluating these preliminary LA/MS results for actual waste samples (Rapko 1993). Sample specifics were detailed in Section 3.2 of this report.

6.1.1 Measurement Precision (Relative Standard Deviations)

As discussed in Section 4.3, the Relative Standard Deviation values (RSDs) calculated from the LA/MS data from different runs (using the same sample) provide a direct indication of the data reproducibility or precision. For data recorded on homogeneous samples and under highly stable test conditions, the RSD values for mass numbers with good counting statistics can be indicative of the practical data precision limits for the LA/MS measurement capability with the system equipment. RSD values can be readily increased above the optimal values for mass numbers with low signal levels, samples with spatial inhomogeneities, and when equipment operating conditions vary.

Figures 6.1 through 6.3 show the calculated RSD values for various elements in the untreated S-104, T-104, and T-111 samples, respectively. Since mass numbers with very low signal levels frequently exhibit relatively high RSD values due to poor counting statistics, the elements for each sample are plotted in the order of increasing analyte concentration (i.e., low concentration at the left with high concentration on the right). This will help in distinguishing between the effects on RSD values of low signal levels, sample inhomogeneities, and other reasons for increased data scatter. Specific elements are labeled along the x-axis. It should be noted that since the element concentrations were different for each of these samples, the order

of the elements is different on each plot. The concentrations of the elements present in the samples range from a few ppm to a few 10's of percent. Generally, concentrations of > 10 ppm have sufficient counting rates to provide good counting statistics. Consequently, poor precision (i.e., high RSD values) for elements above this concentration are generally attributable to other factors (e.g., instrument sensitivity, sample heterogeneity, etc.).

a) General observations

The observed precision is 5 - 15% for most elements at higher analyte concentrations (i.e., on the right-hand side of the plots). Overall, there is a strong correlation between very low analyte concentration and higher standard deviation (lower precision) due to the increasing importance of data scatter at low signal levels. The estimated locations of the 10 ppm concentration level are shown on the plots.

The highest standard deviation values result from elements with concentrations less than 10 ppm. This certainly should not inhibit use of LA/MS analysis to support TWRS Characterization as the TWRS program is generally not focused on the presence of elements and isotopes which are present at trace levels. Also, it does not pose a fundamental problem for measuring the lower concentration constituents by this method if necessary. The data shown here were the result of averaging at least 3 repeat analyses. Should more sensitivity be required for specific radionuclides, longer MS signal integration times or higher ablation laser pulse energies can be used.

In addition, it is noted that some specific analytes tend to exhibit consistently high data scatter when analyzed with ICP/MS methods (e.g., either solution-based ICP/MS analysis or LA/MS analysis). Very similar results are seen for both the glass and tank waste samples. Two exceptions to the general trend of lower RSDs at higher concentrations are P and S. These elements are traditionally problematic for solution-based ICP/MS analysis, so their behavior in LA/MS is not surprising.

The possible contribution of ablation laser pulse energy variations (i.e., pulse-to-pulse and short-term drift) to the data scatter was not taken into account for these three samples.

b) Sample specific observations

The data recorded for the S-104 and T-111 tank samples clearly exhibited lower RSD values for non-trace constituents (Figures 6.1 and 6.3) than observed for the T-104 tank sample (Figure 6.2). Non-trace elements in samples S-104 and T-111 exhibited RSD values in the range of 4 - 12%. These RSD values are comparable to the corresponding values recorded previously for glass reference materials (CVS-19 and WV-205) where sample homogeneity issues are expected to be minimal.

The consistency of the RSD values observed for untreated waste samples and homogeneous glass samples is significant as it indicates that the raster scanning of the ablation laser across the sample surface and the 45-second data integration period are providing effective area averaging of the sample's constituents.

The corresponding data for the T-104 sample exhibited values in the range of 6 - 17%. Detailed reasons for the higher RSD values observed for the T-104 sample have not been established at this time.

6.1.2 General/Non-Radiogenic Chemical Analysis Results

Estimated elemental concentrations for raw (untreated) tank sludge and pretreated (washed) sludge for Hanford Tank samples from S-104, T-104, and T-111 are shown in Tables 6.1 through 6.3. The LA/MS data can be compared with previously reported data obtained from other laboratories using conventional dissolution and analysis (ICP/AES) techniques. Generally good agreement between the LA/MS data and data obtained from the two independent analytical facilities is seen in Figures 6.4 through 6.6. For illustrative purposes the elements are shown in the order of increasing concentration (i.e., least populous elements at the left and most populous at the right in the figures) relative to the untreated sample. Comparison of data for the same element in the pretreated and untreated waste provides a direct indication of the effectiveness of the pretreatment wash for removal of specific analytes.

Examination of the figures indicates that in most cases, the LA/MS data agree reasonably well within the range of previously reported values (from Pacific Northwest and Los Alamos National Laboratory). In addition, these figures also illustrate that the LA/MS method readily provides data across a very large range of elemental concentrations, ranging from ppm to high weight percent levels. In general, the data comparison does not indicate any severe instrumental bias for any particular element, indicating, at least for these data, glass standards are useful as standards to calibrate instrumental response and bias corrections for sludge samples.

6.1.3 Radiogenic Analysis (Fission and Activation Products)

In Figure 6.7, mass spectra between mass regions 80 and 110 are shown for S-104 sludge. Symbols represent the relative yields expected from the fission of ^{235}U and ^{239}Pu . For this figure and figures showing mass spectra for T-104 and T-111 samples, approximate concentrations can be estimated by multiplying the peak heights by 5 to correspond to peak integrated counts per second (cps). For example, the peak height at mass 90 is about 5 cps which calculates to about 25 ppm.

Focusing on the mass range between 90 and 96, it can be seen that the fission yield curve follows reasonably well with peaks observed for the tank sample. These masses generally can be interpreted to represent most of the Zr isotopes in non-radiogenic Zr. However, natural Zr

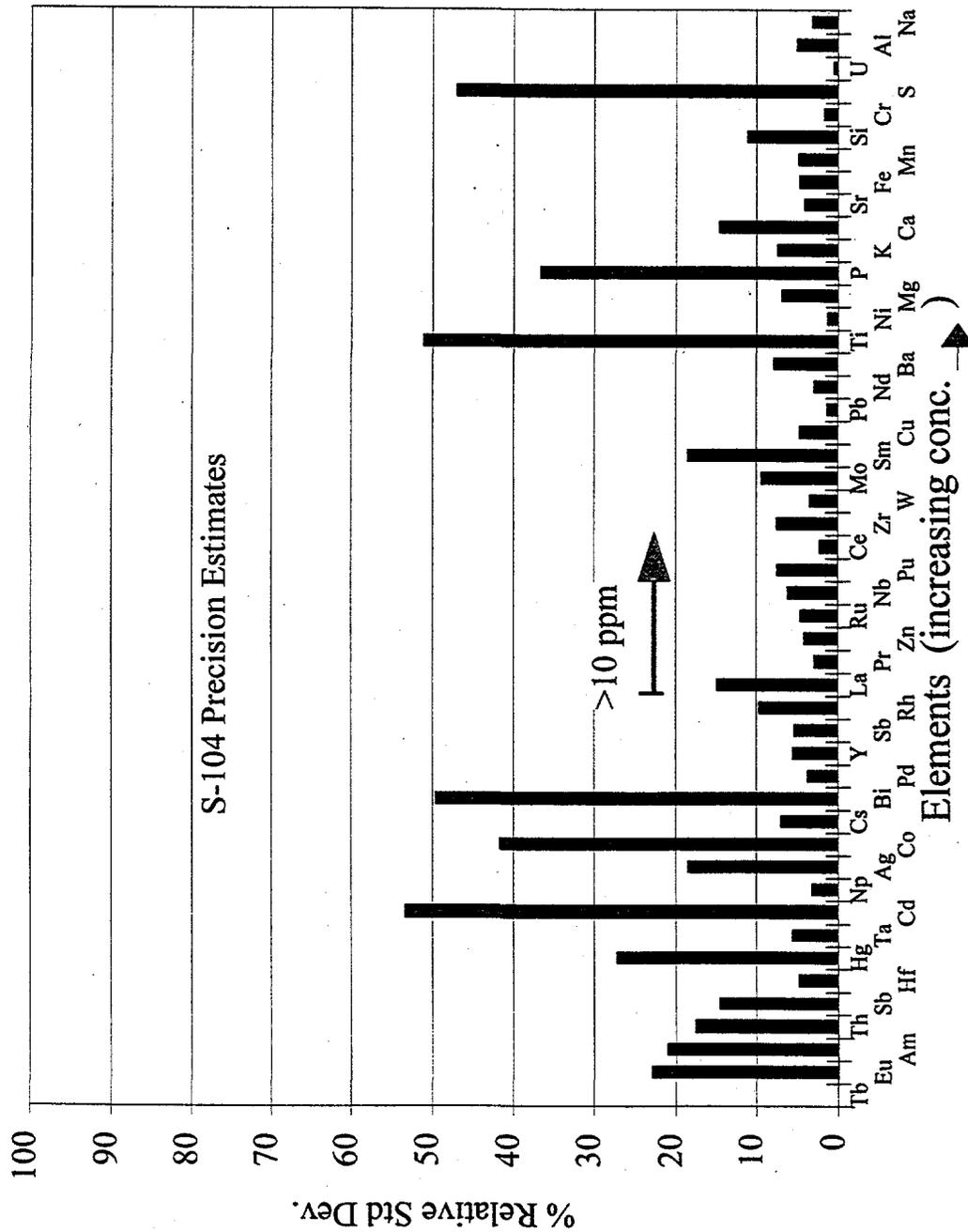


Figure 6.1 Plot of LA/MS Relative Standard Deviation values versus elements for constituents of an untreated S-104 tank waste sample. Elements are plotted in the order of increasing concentration

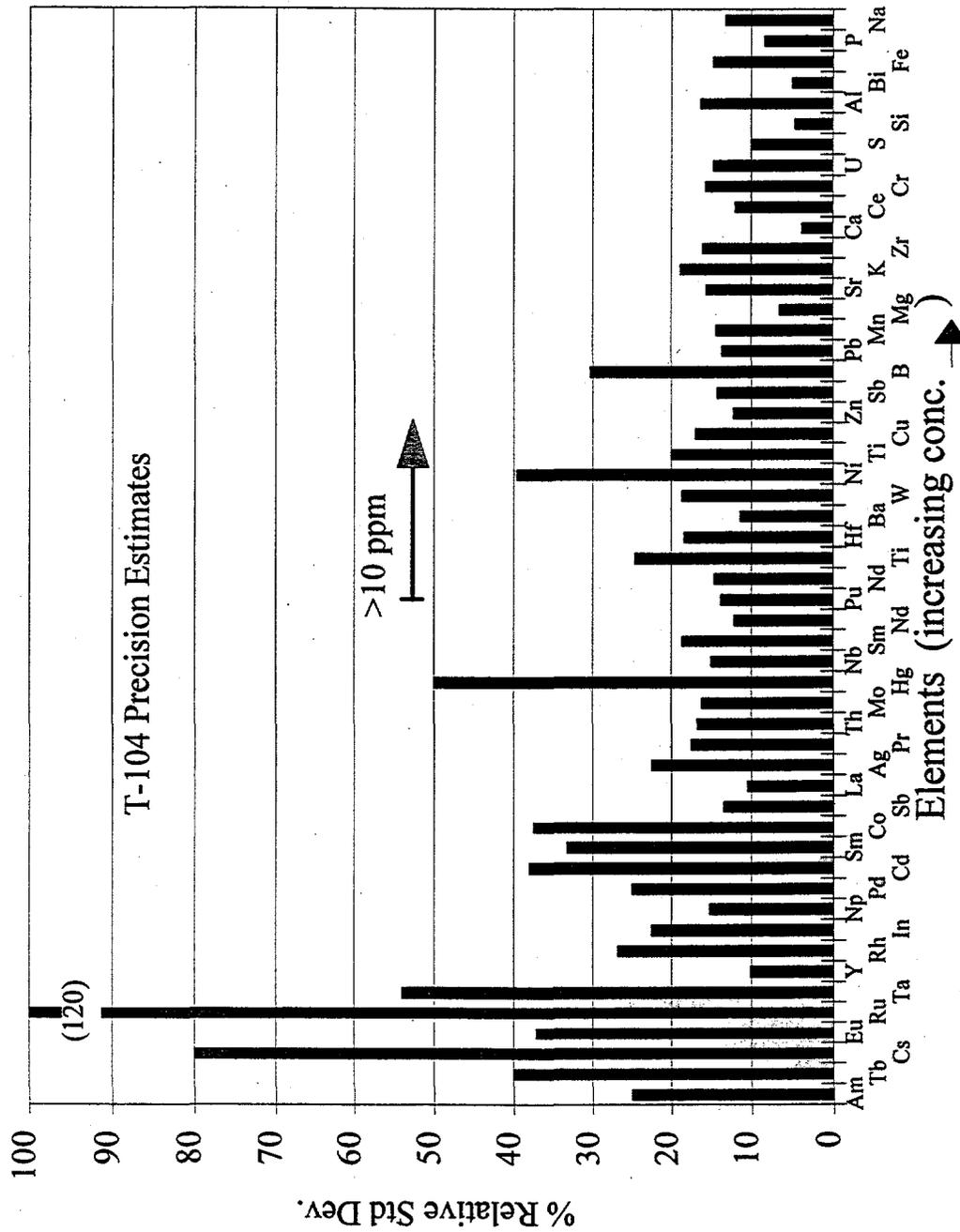


Figure 6.2 Plot of L.A/MS Relative Standard Deviation values versus elements for constituents of an untreated T-104 tank waste sample. Elements are plotted in the order of increasing concentration

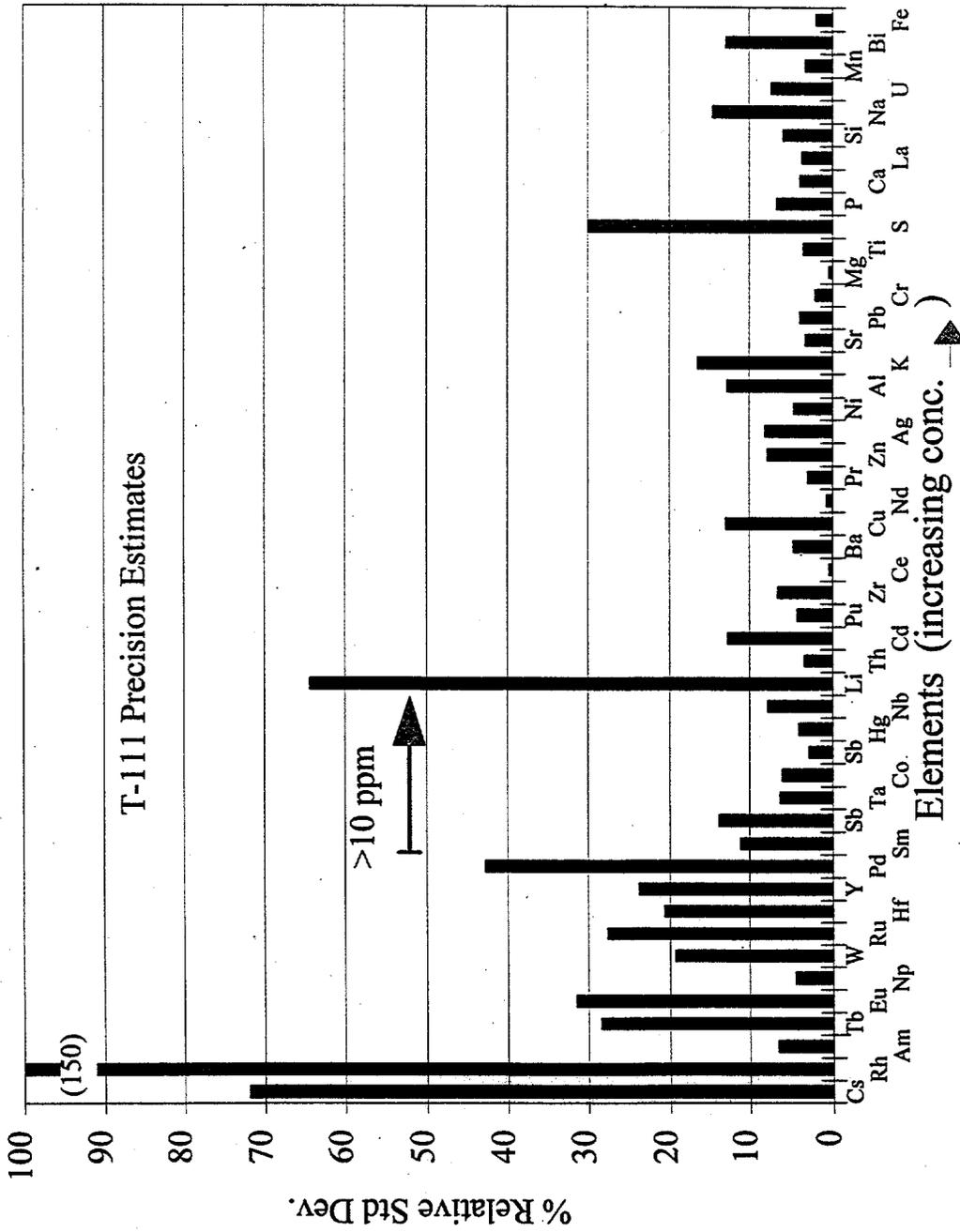


Figure 6.3 Plot of LA/MS Relative Standard Deviation values versus elements for constituents of an untreated T-111 tank waste sample. Elements are plotted in the order of increasing concentration.

Table 6.1. Tank S-104 Sludge Component Analysis Showing LA/MS Results with Independent Analysis Results Where Available (ppm per Dry Weight)

ELE SYM	MASS	S104(raw sludge)					S104(pretreated sludge)				
		AVG	Std Dev	LAMS	ICP PNNL	ICP LANL	AVG	Std Dev	LAMS	ICP PNNL	ICP LANL
		cps	cps	ppm	ppm	ppm	cps	cps	ppm	ppm	ppm
Li	7	-125	8			3	-95	10	0		6
B	11	-2	1		200		-8	1	0	1000	
Na	23	287136	9005	202202	200000	172000	60984	2517	42945	50000	45547
Mg	24	129	9	143		122	393	14	437	400	264
Al	27	235500	11785	178228	150000	167000	313230	4118	237056	330000	328947
Si	28	1681	201	4349	6800	1820	3043	371	7870	5100	4670
Si	29	90	10	4308	6800	1820	204	16	9765	5100	4670
P	31	8	3	152		<85	7	2	145		80
S	34	17	8	6693			14	8	5512		
K	39	1260	94	379		49200	245	44	74		44112
Ca	44	50	7	485	2200	311	88	16	855	1800	1037
Ti	48	201	103	60	90	17	164	21	49	65	54
Ti	49	19	12	73			17	3	65		
Cr	52	27963	473	6047	4700	3100	1547	47	334	370	301
Mn	55	24287	1165	3830		1830	70531	2338	11121	7200	4514
Fe	57	486	23	3277		3950	1613	95	10880	12000	10177
Co	59	12	5	2			56	5	7		
Ni	60	175	2	141		130	727	37	584		420
Cu	63	125	6	41	210	72	257	4	84	240	115
Zn	64	30	1	13	100	47	85	4	38	100	43
Zn	66	13	3	9			38	10	27		
Sr	88	16058	661	572	610	640	49899	1384	1777	2200	1367
Y	89	180	10	5			366	5	11	20	17
Zr	90	342	26	20			963	46	57	160	57
Zr	91	349	17	96			836	11	230		
Nb	93	542	33	17			1551	14	49		
Mo	95	175	16	35			151	18	30		17
Ru	101	86	4	15			429	82	77		51
Rh	103	300	29	9			1081	87	32		16
Pd	105	27	1	3			11	5	1		
Ag	107	27	5	1			96	16	5		
Cd	111	3	2	1			9	4	4		3
In	115	3	2	0			2	3	0		
Sb	120	113	6	6			170	89	9		
Sb	121	7	1	0			33	5	1		2
Cs	133	193	13	2			22	7	0		
Ba	137	576	45	52	60	40	1913	99	173	180	151
La	139	1055	157	10		31	2449	111	23	60	64
Ce	140	1924	44	20		16	7523	279	78	90	56
Pr	141	1148	33	10			3768	247	33		
Nd	144	1390	40	47		43	3969	349	134	100	142
Nd	146	721	93	32			1892	205	84		
Sm	147	813	151	40			1607	181	79		
Sm	149	24	6	1			53	4	3		
Eu	151	2	0				13	3	0		
Tb	159	2	0				13	3	0		
Hf	178	23	1	0			67	10	1		
Ta	181	163	9	1			614	13	3		
W	184	1818	62	32			712	70	12		
Hg	200	11	3	1			19	4	1		
Pb	208	5369	69	41		53	22644	2179	173		122
Bi	209	680	338	3			2326	209	9		67
Th	232	58	10	0			175	8	0		1
U	235	26285	140	7491	9000	6540	124951	91	35610	32000	22646
Np	237	715	23	1			3674	51	7		
U	238	4867578	25898	9058	9000	6540	23139043	16814	43059	32000	22646
Pu	239	9445	704	17			23779	898	43		
Am	241	19	4				76	13	0		

Table 6.2. Tank T-104 Sludge Component Analysis Showing LA/MS Results with Independent Analysis Results Where Available (ppm per Dry Weight)

ELE SYM	MASS	T104(Raw Sludge)					T104(pretreated sludge)				
		AVG	Std Dev	LAMS	ICP PNNL	ICP LANL	AVG	Std Dev	LAMS	ICP PNNL	ICP LANL
		cps	cps	ppm	ppm	ppm	cps	cps	ppm	ppm	ppm
Li	7	-7	16	0		<4	-40	30	0		<4
B	11	9	3	69	2200	<13	4	6	116	1100	<120
Na	23	108110	14298	108759	190000	200000	141927	18610	499727	230000	75721
Mg	24	121	8	192	300	267	111	25	616	500	1202
Al	27	33458	5461	36173	47000	53500	16279	1699	61600	33000	78125
Si	28	7079	743	26160	23000	16000	6974	838	90200	38000	16346
Si	29	410	19	28037	23000	16000	425	71	101720	38000	16346
P	31	2166	182	61674	69000	66800	2054	169	204711	62000	7692
S	34	10	1	5625			3	1	5906		
K	39	1075	202	462			1867	562	2809		
Ca	44	47	2	660	1300	400	23	2	1117	1800	1803
Ti	48	32	8	14	40		190	90	284	94	66
Ti	49	5	1	27			29	25	554		
Cr	52	10611	1665	3278	3100	2140	5904	585	6384	4600	4928
Mn	55	784	113	177	360	90	442	57	348	440	385
Fe	57	4077	599	39277	28000	28100	2291	60	77243	59000	118990
Co	59	8	3	2			2	1	1		
Ni	60	21	8	24		25	14	5	58		118
Cu	63	61	10	28	70	54	24	5	39	460	204
Zn	64	85	10	54	100		40	12	88	270	144
Zn	66	55	21	57			24	4	87		
Sr	88	7667	1195	390	330	267	4242	381	756	670	1106
Y	89	7	1	0			5	2	1		<1
Zr	90	7436	1191	628	240	521	4263	413	1260	250	1923
Zr	91	1957	336	768			1004	116	1379		
Nb	93	160	24	7			94	9	15		
Mo	95	21	3	6		7	8	2	8		3
Ru	101	1	1	0			2	1	1		1
Rh	103	8	2	0			1	1	0		
Pd	105	4	1	1			2	1	1		
Ag	107	40	9	3			2	1	1		
Cd	111	1	1	1		1	-1	0	0		4
In	115	13	3	0			1	1	0		
Sb	120	707	101	56			45	9	13		
Sb	121	56	8	2		1	31	8	5		4
Cs	133	3	2	0			2	3	0		
Ba	137	183	21	24	40	29	130	19	59	70	113
La	139	183	19	2		2	93	18	4		9
Ce	140	59488	7129	881	400	535	29609	2756	1535	1400	2163
Pr	141	269	47	3			165	17	7		
Nd	144	274	40	13			157	6	26		
Nd	146	157	19	10			104	17	23		
Sm	147	104	19	7			55	1	14		
Sm	149	18	6	1			6	3	2		
Eu	151	5	2	0			4	1	0		
Tb	159	5	2	0			4	1	0		
Hf	178	764	140	21			410	55	39		
Ta	181	37	20	0			7	6	0		
W	184	980	183	24			109	18	9		
Hg	200	94	47	7			5	1	1		
Pb	208	10726	1461	117		147	6864	700	263		637
Bi	209	6721500	334744	37631	52000	40900	4470000	11295	87590	110000	203846
Th	232	1457	244	4			727	68	8		15
U	235	10756	1583	4379	4000	3070	3656	307	5210	5000	9615
Np	237	250	38	1			135	5	1		
U	238	1887247	277664	5017	4000	3070	641611	53841	5970	5000	9615
Pu	239	5106	706	13			2403	84	22		
Am	241	8	2	0			4	2	0		

Table 6.3. Tank T-111 Sludge Component Analysis Showing LA/MS Results with Independent Analysis Results Where Available (ppm per Dry Weight)

ELE SYM	MASS	T-111 A (Raw Sludge)				T111(pretreated sludge)					
		AVE	LA/MS	ICP PNLL	ICP LANL	AVG	Std Dev	LA/MS Anal 1	LA/MS Anal 2	ICP PNLL	ICP LANL
=====	=====	cps	ppm	ppm	ppm	cps	cps	ppm	ppm	ppm	ppm
Li	7	151	9	0	0	25	16	42	65	0	0
B	11					-2	2			1100	
Na	23					35797	5205	84028		56000	
Mg	24	41678	2557	1570	2000	1090	6	4039	3000	2430	4200
Al	27	47948	2941	2375	4900	335	43	845	600	3640	5700
Si	29	578737	35504	23625	47000	167	10	26647	9200	33000	34000
P	31	521812	32012	56869	26000	259	18	17182	18400	14000	13000
S	34	227117	13933	5125	3333	10	3	13124		300	3333
K	39					886	146	888			
Ca	44	418574	25678	10083	16000	630	25	20522	23100	15300	22000
Ti	48	4614	283	0	360	5857	210	5853	8810		1100
Ti	49					547	15	6961			1100
Cr	52	124486	7637	8210	4500	5152	110	3714	3200	2850	3200
Mn	55	951081	58346	26375	53000	175801	5808	92400	55900	41000	96000
Fe	57	1549533	95059	77080	60000	5910	119	132844	103585	120000	130000
Co	59	356	22	48	100	49	3	22		70	60
Ni	60					309	15	828			
Cu	63	7	0	140	3300	205	27	223		220	240
Zn	64	10268	630	440	1300	270	21	398	540	690	820
Zn	66					169	21	407			
Sr	88	20627	1265	1241	680	13188	437	1566	1140	1920	1300
Y	89	41	2	0	0	25	6	3			
Zr	90					417	28	82		120	
Zr	91					123	6	113			
Nb	93					293	23	31			
Mo	95	52	3	0	0	-0	1				40
Ru	101	25	2	0	0	3	1	2			
Rh	103	4	0	0	0	1	1				100
Pd	105	43	3	0	0	7	3	3			
Ag	107	14106	865	533	200	4618	377	813		830	420
Cd	111	770	47	0	50	35	4	45	85		60
In	115					9	3				
Sb	121	209	13	0	0	235	7	24	40		
Cs	133					1	0				
Ba	137	3749	230	287	200	722	34	217	240	440	330
La	139	163692	10042	17583	9200	748115	27981	23652		27400	20000
Ce	140	2361	145	0	0	5142	24	178	140		200
Pr	141					10917	329	323			
Nd	144	3105	190	0	300	2273	18	256	180		300
Nd	146					1704	64	251			
Sm	147					98	11	16			
Sm	149					18	2	3			
Eu	151	6	0	0	0	7	2				10
Tb	159					7	2				
Hf	178					33	7	2			
Ta	181					309	20	5			
W	184					16	3	1			
Hg	200					147	6	25			
Pb	208	44851	2751	1520	2000	91941	3642	2346	3450	2300	3500
Bi	209	2270683	139300	108125	63000	8067310	1039481	105386	136700	167500	110000
Th	232					6172	214	44			
U	235					87891	6530	83494	50000	18210	39600
Np	237					88	4				
U	238	945721	58017	11670	22600	14408717	1070464	89375	50000	18210	39600
Pu	239					13463	576	81			
Am	241					15	1				

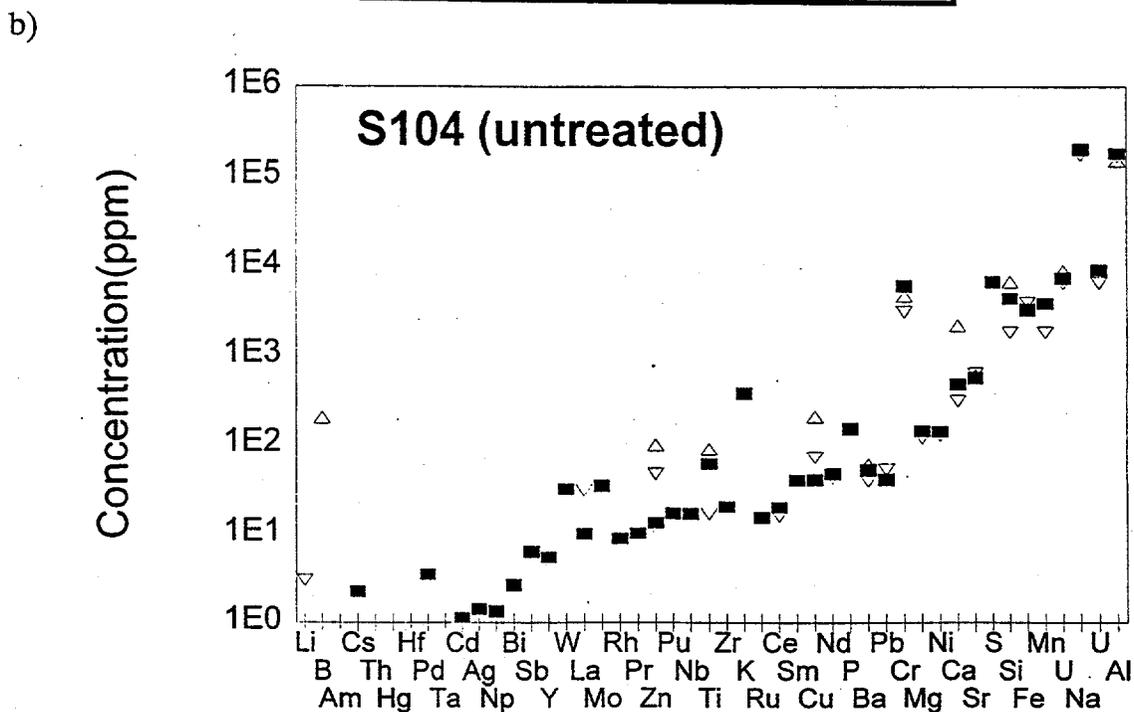
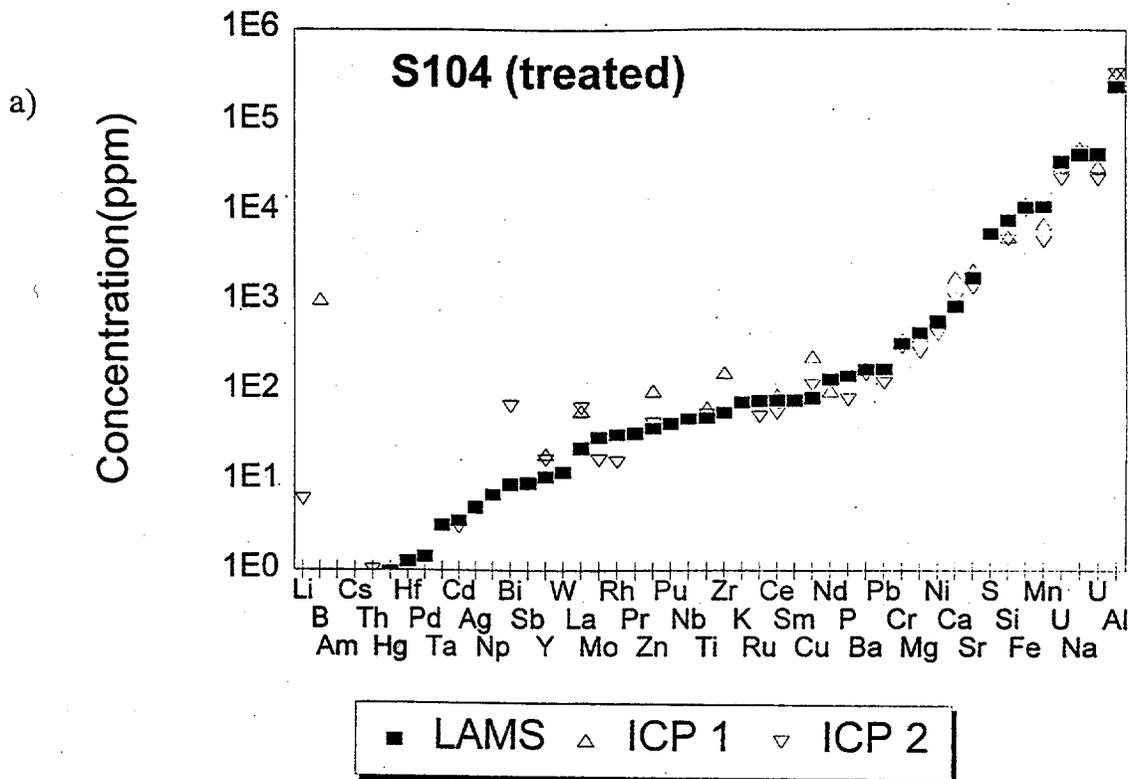


Figure 6.4 Logarithmic plot of elemental concentrations in S-104 tank waste samples as determined by independent analysis (ICP/AES analysis of solution based samples) and preliminary LA/MS analysis. Elements are shown in order of increasing concentration in the pretreated sample.
 a) Pretreated/washed waste and b) Raw/untreated waste

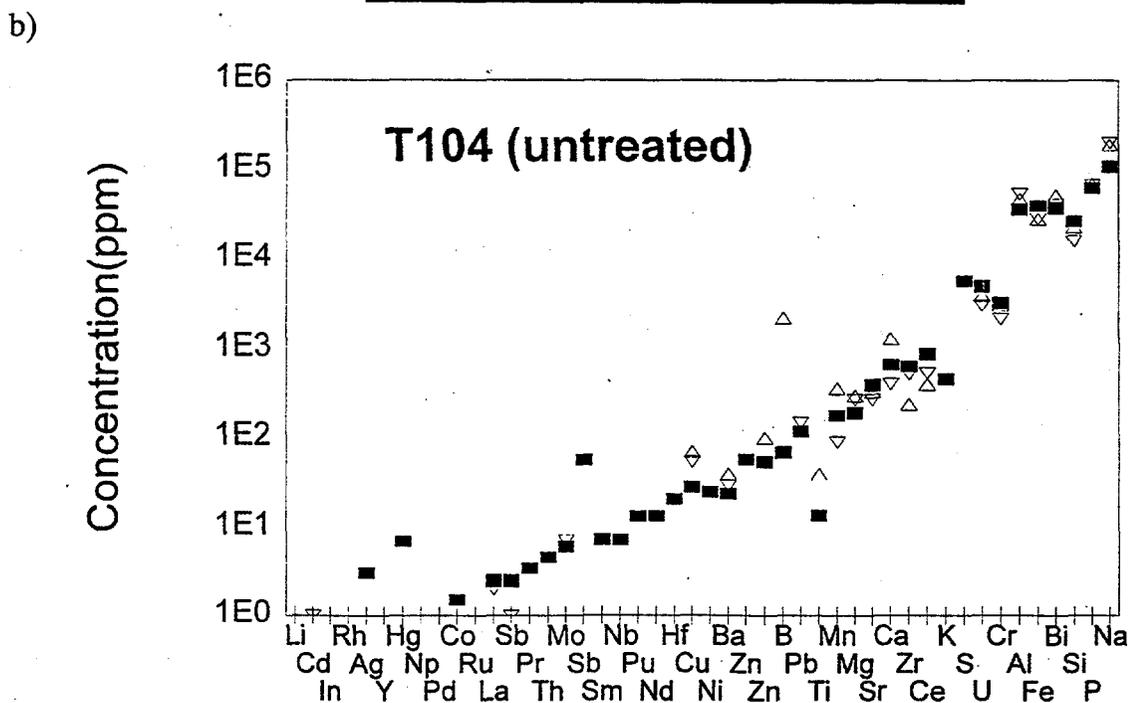
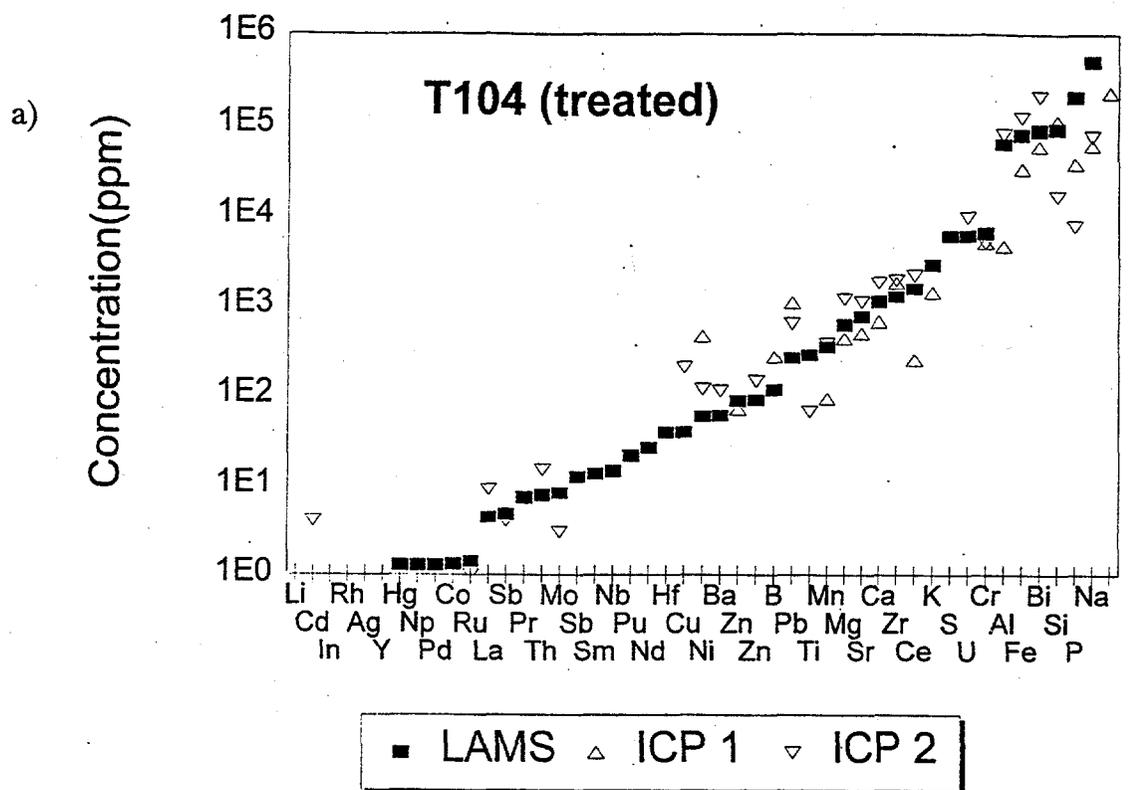


Figure 6.5 Logarithmic plot of elemental concentrations in T-104 tank waste samples as determined by independent analysis (ICP/AES analysis of solution-based samples) and preliminary LA/MS analysis. Elements are shown in order of increasing concentration in the pretreated sample.
 a) Pretreated/washed waste and b) Raw/untreated waste

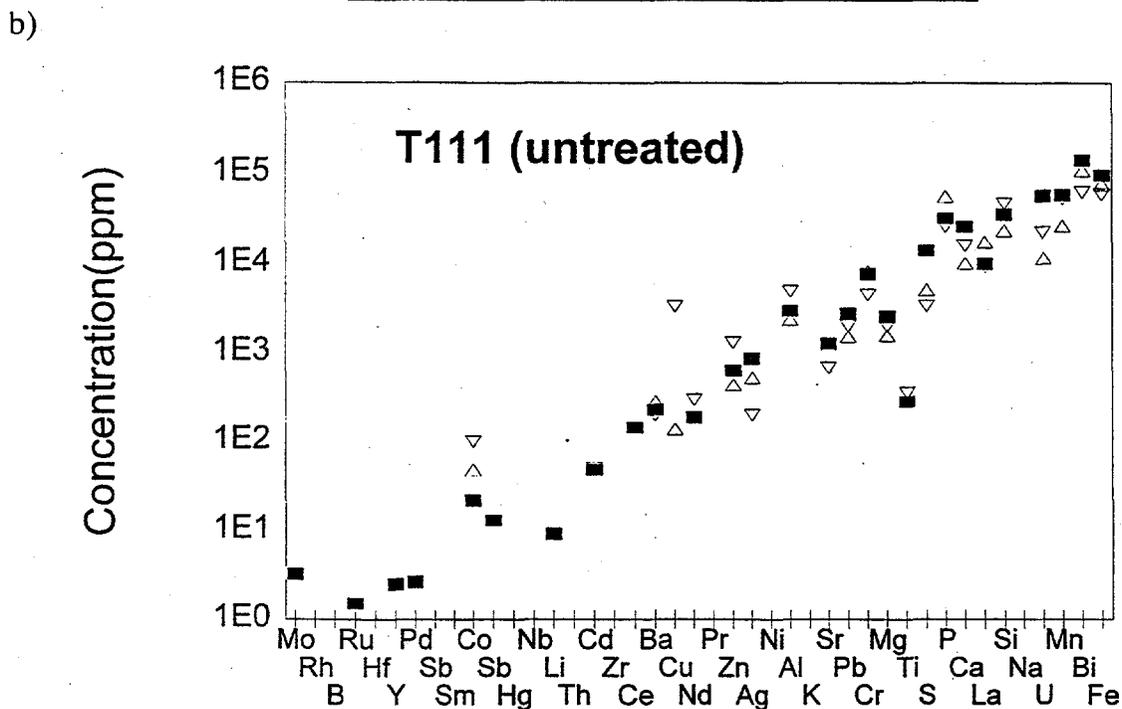
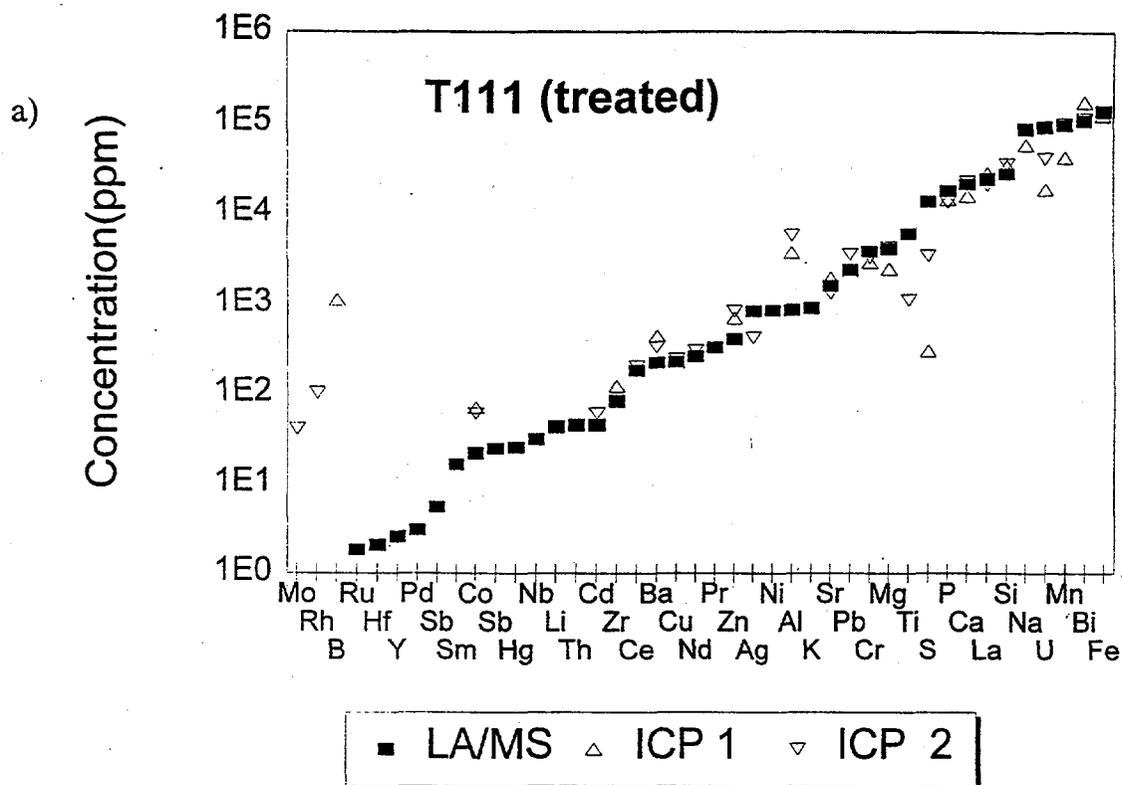


Figure 6.6 Logarithmic plot of elemental concentrations in T-111 tank waste samples as determined by independent analysis (ICP/AES analysis of solution based samples) and preliminary LA/MS analysis. Elements are shown in order of **increasing** concentration in the pretreated sample.
 a) Pretreated/washed waste and b) Raw/untreated waste

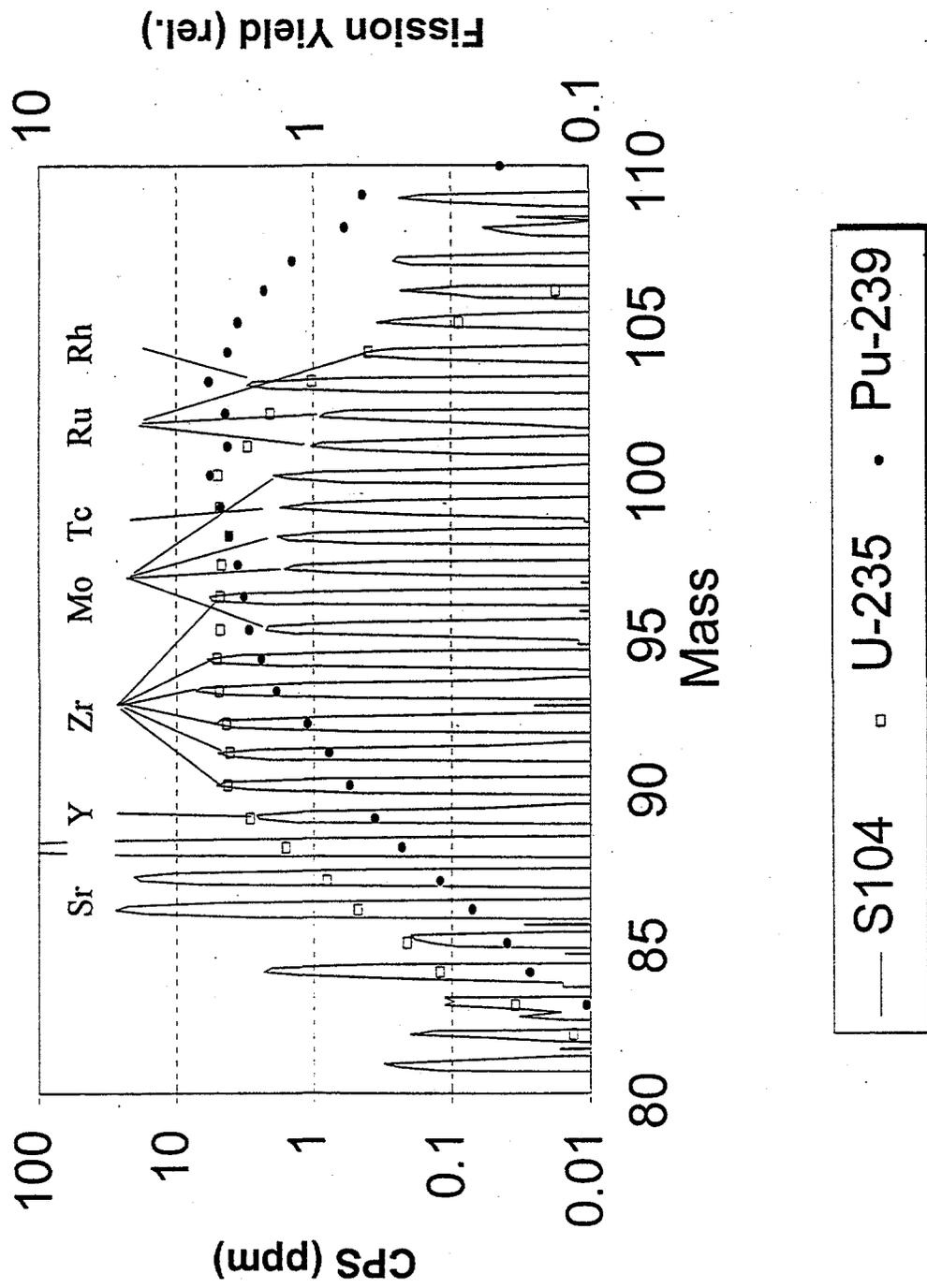


Figure 6.7 Logarithmic plot of mass spectrometer signal levels for isotopes in the lower fission product mass spectral region (80 - 110 amu) from LA/MS analysis of a tank S-104 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions

does not contain ^{93}Zr as it has long since decayed to insignificant levels. This mass would normally be reserved for the only natural isotope of Nb. In this tank sludge, the mass at 93 is primarily the radionuclide, ^{93}Zr ($t_{1/2} = 1.5$ million years). From this mass region, one can also observe predominant peaks at masses 84, 86, 87 and 88. These peaks are attributed to non-radiogenic Sr isotopes since their relative peak heights are consistent with natural isotopic abundances. One can only assume that non-radiogenic Sr was added to the tank waste, presumably for assisting with a separation process. Although most of the Sr in this sample is non-radiogenic, some ^{90}Sr must be present as well and can be estimated from these data. Since the masses representing Zr isotopes do not seem to be related in any way to natural Zr isotopic abundances, the peak at 90 must subsequently be derived from fission and consequently represent ^{90}Sr and its decay product, ^{90}Zr . Roughly estimating the age of the tank waste to be about one half-life of ^{90}Sr (i.e., 29 years), the contribution of ^{90}Sr to the peak at mass 90 is calculated to be about 50% or about 10 ppm.

The peaks corresponding to masses ranging from 95 to 105 can be used to infer the distribution of soluble compounds in tank sludge. This mass region contains isotopes of Mo, Tc, and the noble metal, Ru. All of these elements are known to predominately form soluble complexes. Relative to the predicted fission products, estimated by fission product Zr, these data suggests a significant loss of these soluble fission products. Since the peaks at masses 103 and 105 (corresponding to Rh and Pd, respectively) are not abnormally low, we must assume that the relative fission yield curve should accurately represent the radiogenic products produced. Although these data indicates a loss of soluble components, this conclusion may be misleading since it is possible that the solutions contained in the sludge samples were not sampled representatively.

Similar types of information about the fission product content in tank sludge can be gained by studying the concentrations found at the high mass range of the fission product spectrum (i.e., 130 - 150 amu) as shown in Figure 6.8. Like the low mass region, this region contains elements which exist as soluble and insoluble complexes. Cesium is generally thought to be present in the aqueous portions of Hanford tank sludge. In this figure the peaks which correspond to fission produced Cs isotopes (i.e., masses from 133 to 137) are significantly smaller than expected almost by an order of magnitude, again suggesting a loss of soluble fission products. The insoluble fission products in this heavy mass region are predominated by rare earth elements. The figure also shows that the predicted fission product levels follow well with corresponding Rare Earth Element (REE) peaks. A number of difficult-to-measure radionuclides are present in this mass region (e.g. ^{151}Sm and $^{152,154,155}\text{Eu}$). Using the fission yield curves fitted to more easily determined isotopes of La, Ce, Nd and Sm, one can estimate the concentrations of these radionuclides.

As with the two above figures, Figures 6.9 through 6.12 show similar spectra for tank samples T-104 and T-111. Relative to S-104, the figures indicate that these samples contain much smaller amounts of fission products. In fact, the data for T-111 (Figures 6.9 and 6.10)

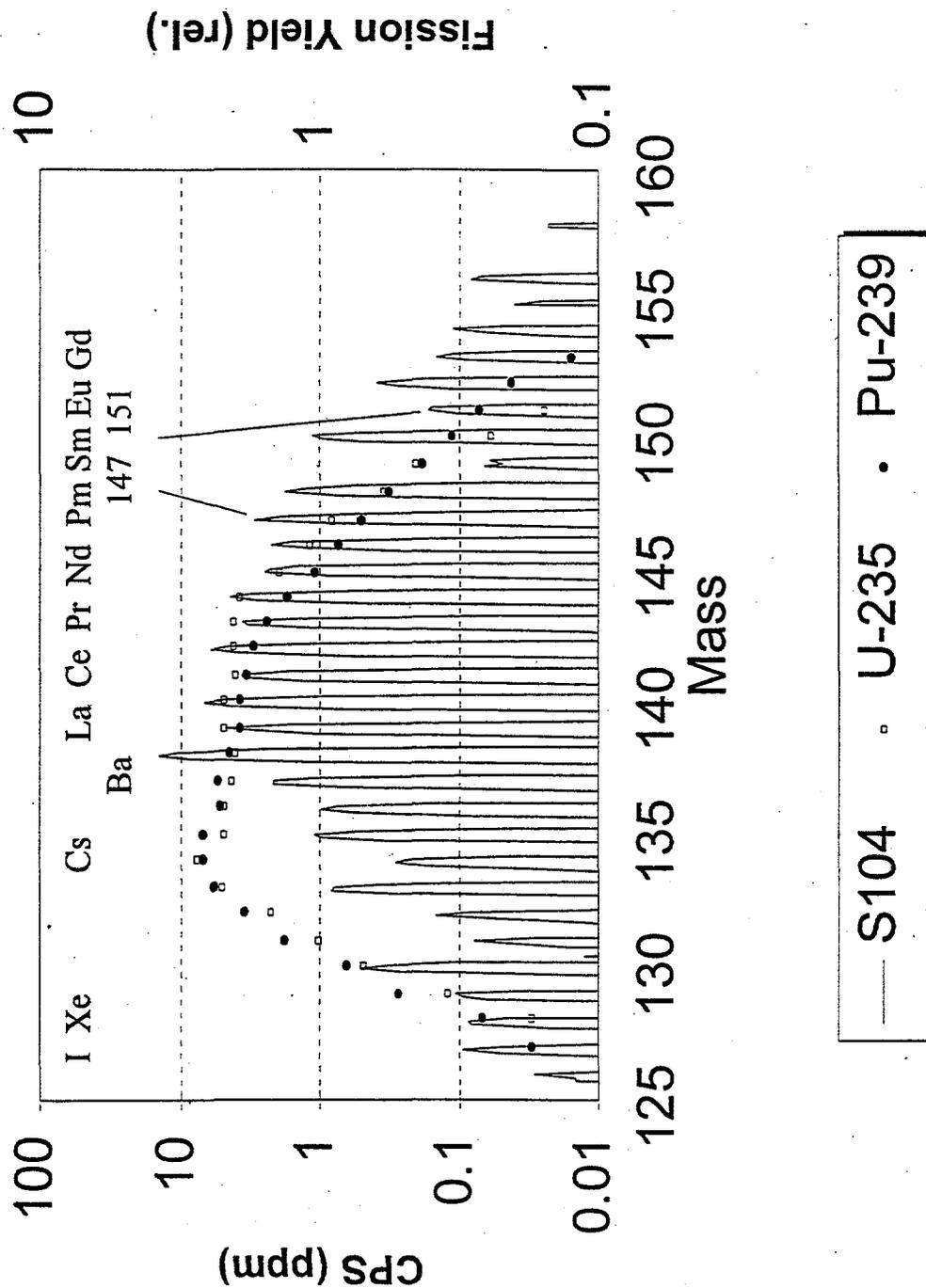


Figure 6.8 Logarithmic plot of mass spectrometer signal levels for isotopes in the upper fission product mass spectral region (125 - 160 amu) from LA/MS analysis of a tank S-104 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions

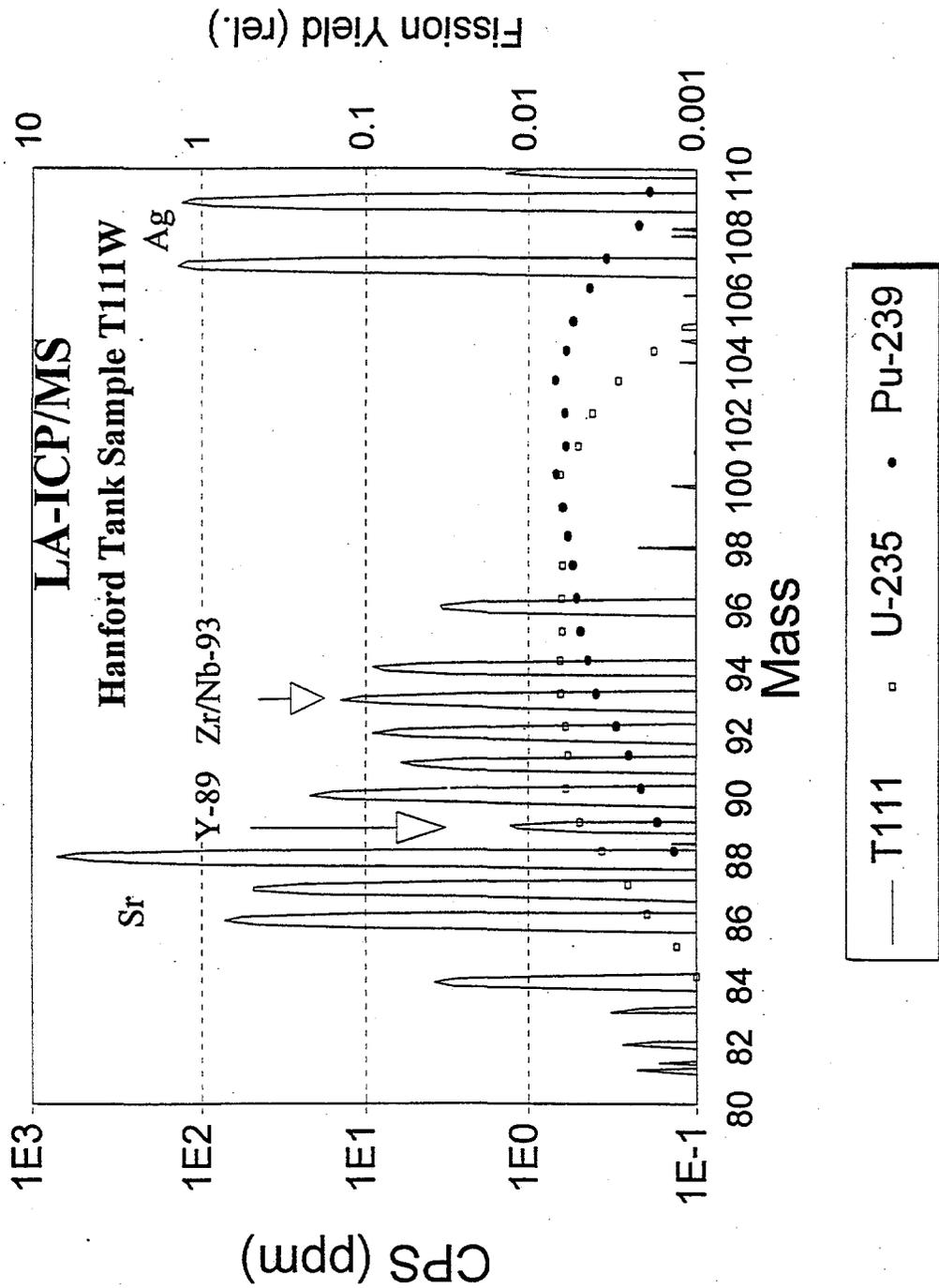


Figure 6.9 Logarithmic plot of mass spectrometer signal levels for isotopes in the lower fission product mass spectral region (80 - 110 amu) from LA/MS analysis of a washed (i.e., pretreated) tank T-111 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions

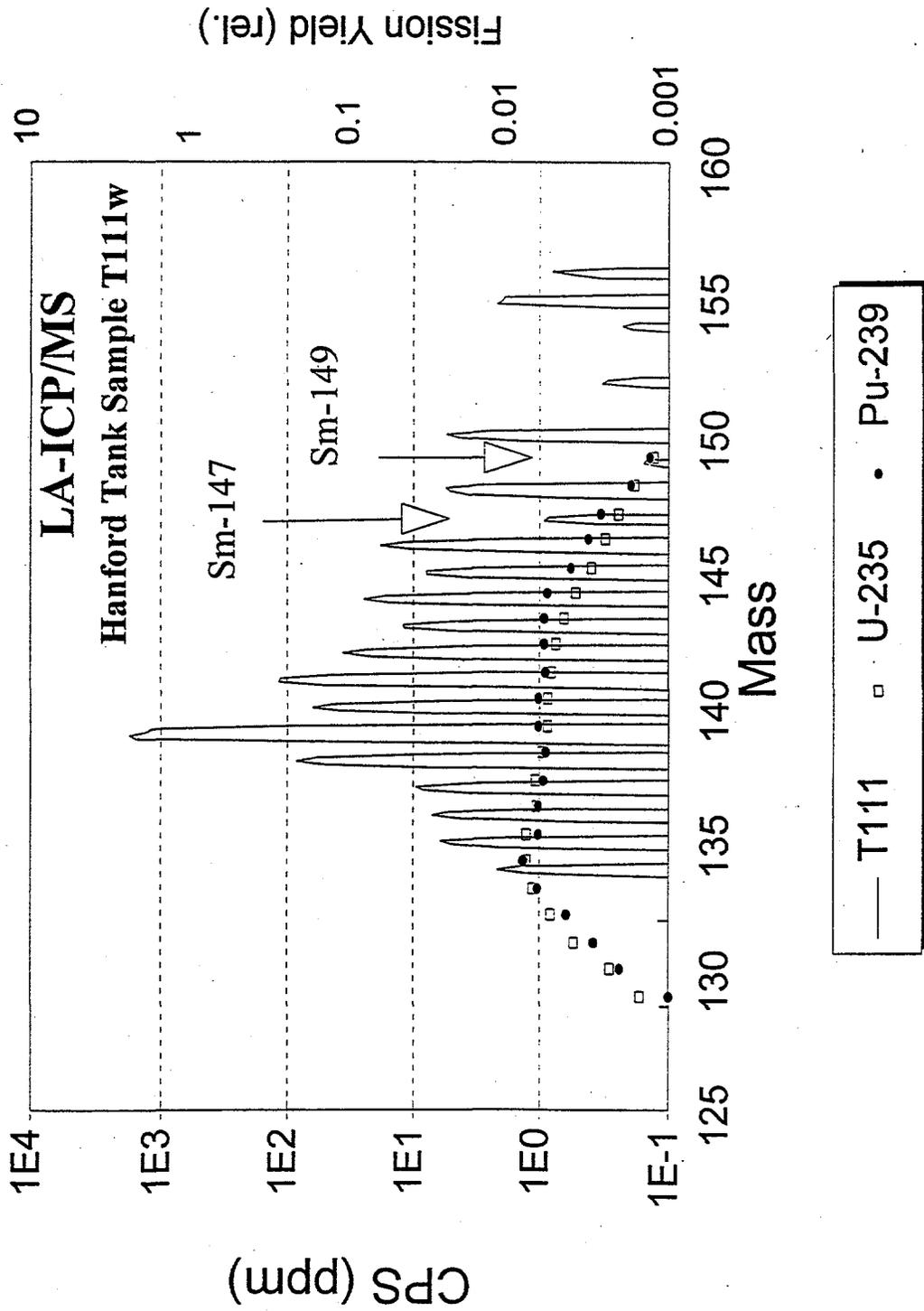


Figure 6.10 Logarithmic plot of mass spectrometer signal levels for isotopes in the upper fission product mass spectral region (125 - 160 amu) from LA/MS analysis of a washed (i.e., pretreated) tank T-111 sample. Fission yield curves are shown for U^{235} and Pu^{239} decay to facilitate comparison of observed signal strengths with primary simple fission product distributions

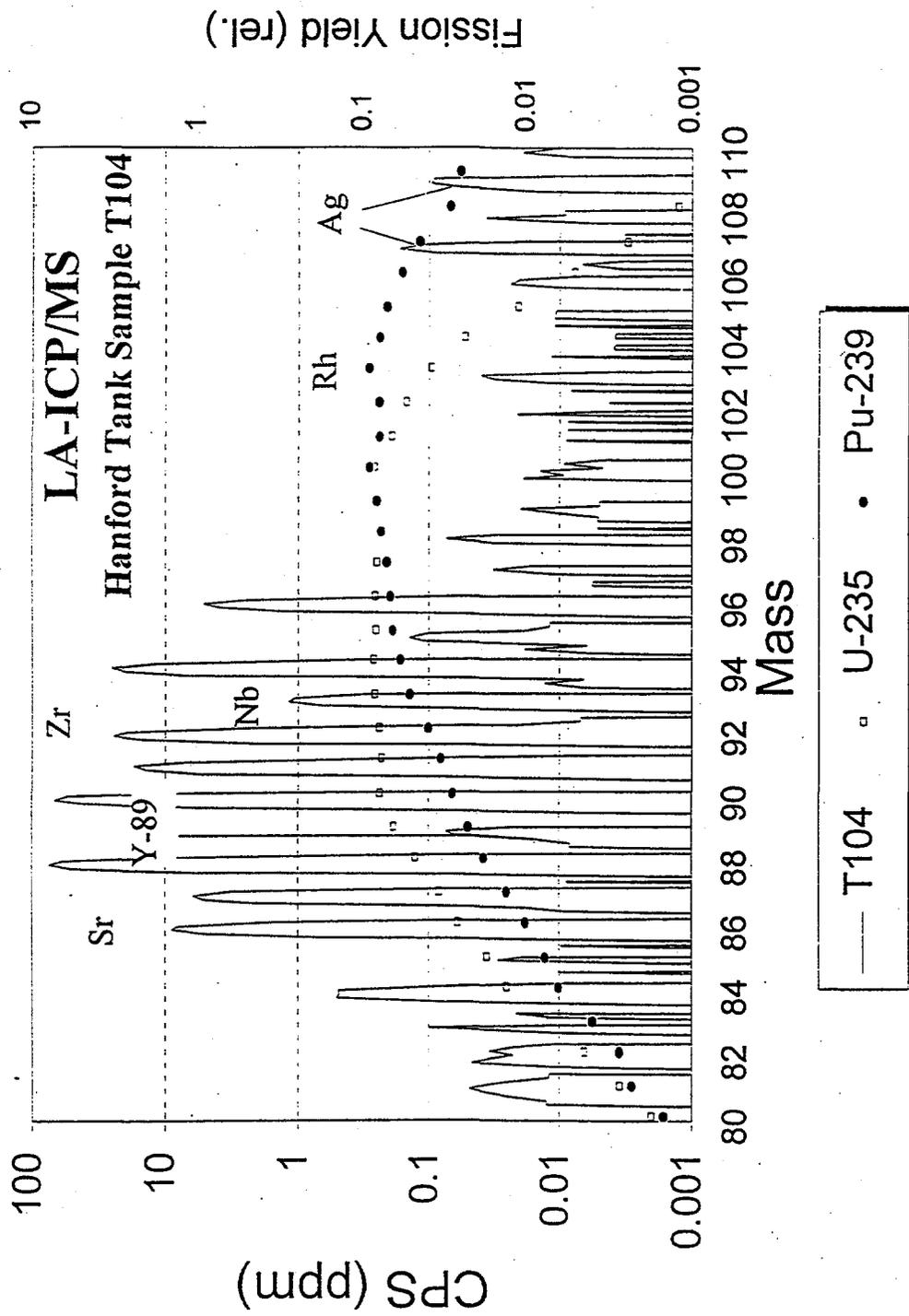


Figure 6.11 Logarithmic plot of mass spectrometer signal levels for isotopes in the lower fission product mass spectral region (80 - 110 amu) from LA/MS analysis of a tank T-104 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions

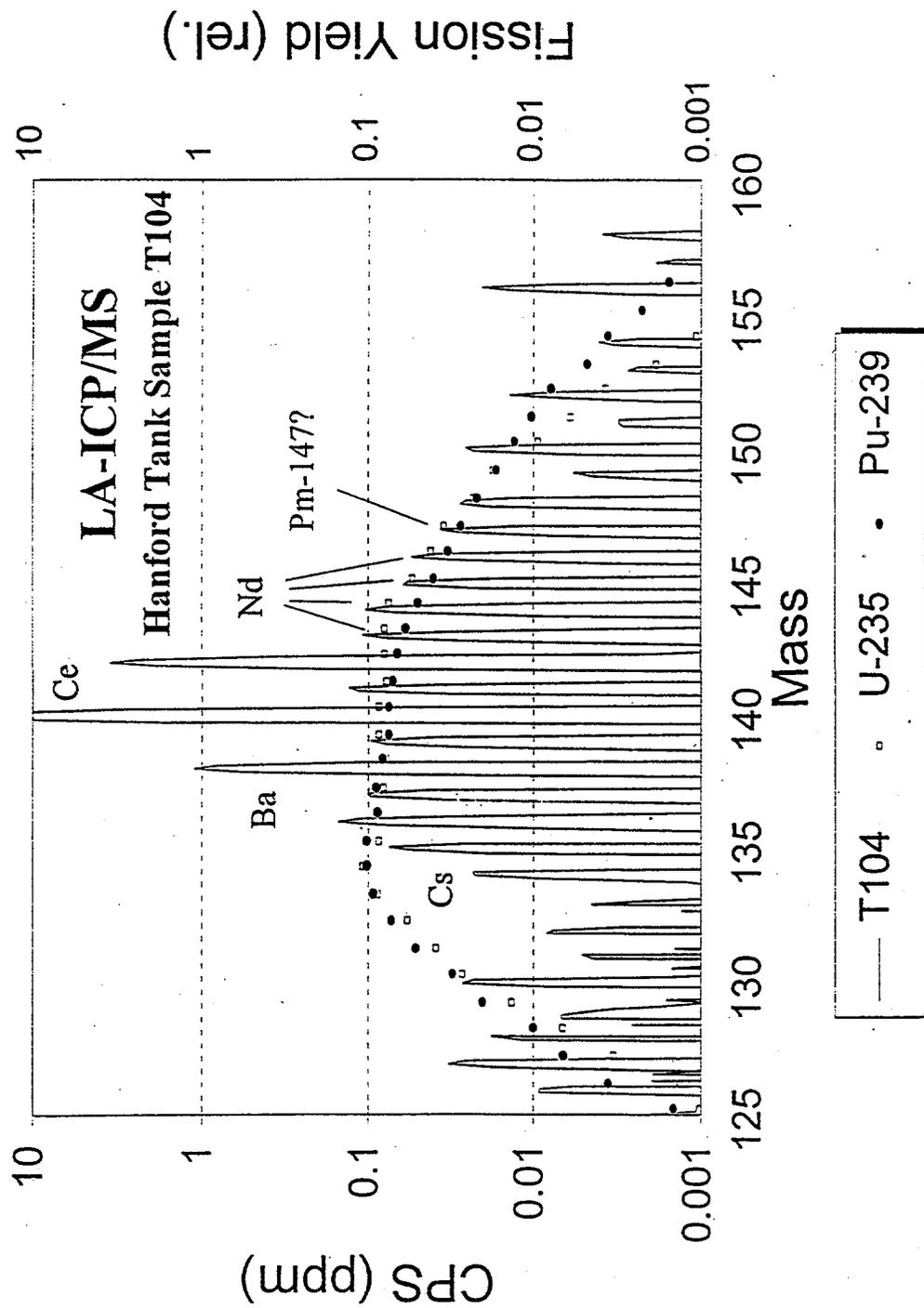


Figure 6.12 Logarithmic plot of mass spectrometer signal levels for isotopes in the upper fission product mass spectral region (125 - 160 amu) from LA/MS analysis of a tank T-104 sample. Fission yield curves are shown for ^{235}U and ^{239}Pu decay to facilitate comparison of observed signal strengths with primary simple fission product distributions

indicates essentially non-measurable fission product content. The data does, however, indicate that a number of elements are present which are not derived from radiogenic processes. High concentrations of Sr, Zr, Ag, Ba, La, and Nd are observed. Fission product spectra for the Tank T-104 sample falls in between the two previous samples with respect to its radio- and nonradiogenic content. In Figure 6.11, we see non-radiogenic Sr and Zr and potentially radiogenic ^{89}Y , ^{93}Zr and Ag. Since a number of non-radiogenic elements are present in this region of the fission mass spectra, this data cannot unequivocally be used to ascertain the fission product levels in this tank sample. However, from Figure 6.12, the Nd isotopic abundances can be used to establish the insoluble fission product contents. This high-mass fission product spectrum indicates that non-radiogenic Ce was used for post-irradiation separation processes contrary to T-111 which indicates use of a number of REE, in particular light rare earth elements, La, Ce, Pr, and Nd.

Summarizing the above interpretations, each of the tank samples investigated by LA/MS have fission product spectra which allow the analysis to determine bulk radiological contents introduced by fission. Using stable isotopes and by determining the isotopic abundances of the various elements produced by fission, radioactive isotopes can be calculated, thus avoiding the need to perform tedious and time-consuming radiochemical separations. One major caveat to this conclusion requires that the radionuclides must all be proportionally represented in the ablated plume, including those which exist primarily in the soluble components of the sludge.

- Example of Radionuclide Determinations

An example analysis of the Tank S-104 sample data will be described to provide more insight into the analysis procedures and the type of results that can be obtained. As described above, determining radiogenic constituents in samples which are composed of elements with radio and non-radiogenic origins cannot be performed without assumptions. This analysis has been performed under the assumption that the radiogenic components were produced by conventional fission of ^{235}U or ^{239}Pu . In addition, it was assumed that ions detected at actinide masses are due to isotopes which have substantial half-lives (i.e., > 50 years).

Table 6.4 summarizes the results of an analysis to assign radiogenic and non-radiogenic constituents found in sample S-104 based on these assumptions. Graphically, Figures 6.13 through 6.15 illustrate how the fission product assignments were derived.

Figure 6.13 shows the estimated isotope concentration (ppm) as determined from the integrated count signals for the fission product mass region. Again, one can see that the S-104 spectrum suggests a characteristic fission product distribution with two exceptions. High concentrations are observed for masses 86, 87 and 88 (representing Sr isotopes) and significant peaks at masses 116, 117, 118, 119, and 120 (representing Sn isotopes). The Sn peaks occur in a mass region where fission yields are essentially nonexistent. (Although relatively small, an interfering doubly charged ^{238}U peak is

Table 6.4 Estimated radiogenic and non-radiogenic isotopes/elements in the fission product mass spectral region in the raw tank S-104 waste.

MASS	S-104 LA/MS Conc. (ppm)	Predicted Fission Products (ppm)	Assignments	S-104 Process Chemicals (ppm)	Assignm
84	3.0	2.2		0.8	
85	0.4	2.9		0.0	
86	47.5	4.3		43.2	Sr
87	37.9	5.6		32.3	
88	472.4	7.9		464.5	
89	5.4	10.7	Y-89	0.0	
90	10.4	13.0	Sr-90, Zr	0.0	
91	10.7	12.8	Zr	0.0	
92	12.2	13.2	Zr	0.0	
93	17.0	14.0	Zr-93	3.0	
94	14.2	14.2	Zr	0.1	
95	5.5	13.8	Mo	0.0	
96	15.2	13.9	Zr	1.4	
97	3.8	13.6	Mo	0.0	
98	4.4	12.8	Mo	0.0	
99	3.8	13.9	Tc-99	0.0	
100	4.7	14.1	Mo	0.0	
101	2.6	11.0	Ru	0.0	
102	2.6	9.0	Ru	0.0	
103	8.9	6.4	Rh	2.5	
104	1.3	4.0	Ru	0.0	
105	0.8	1.9	Pd	0.0	
106	0.4	0.8	Pd	0.0	
107	0.7	0.4	Pd-107	0.4	Ag
108	0.1	0.2	Pd	0.0	
109	0.6	0.1	Ag	0.5	Ag
110	nd+	0.05	Ag-110	0.0	
111	0.1	0.03		0.1	Cd
112	0.3	0.03		0.3	Cd
116	9.4	0.02		9.4	Sn
117	5.2	0.02		5.2	Sn
118	16.2	0.02		16.2	Sn
119	7.4	0.02		7.4	Sn +U++
120	20.6	0.02		20.6	Sn
121	1.2	0.03		1.2	Sb
125	0.1	0.1	Sb-125 + Te	0.0	
126	0.1	0.2	Sn-126	0.0	
127	0.2	0.6	I	0.0	
128	0.2	1.1	Xe	0.0	
129	0.1	2.2	I-129	0.0	
130	1.2	4.4	Xe	0.0	
131	0.1	6.4	Xe	0.0	
132	0.2	9.5	Xe	0.0	
133	2.2	14.3	Cs	0.0	
134	0.7	17.6	Xe	0.0	
135	2.9	14.1	Cs-135	0.0	
136	2.4	14.1	Xe	0.0	
137	5.8	13.2	Cs-137	0.0	
138	18.5	12.8	Ba	5.7	
139	10.0	14.1	La	0.0	
140	17.7	14.1	Ce	3.6	
141	10.2	12.8	Pr	0.0	*
142	15.7	13.0	Ce	2.7	
143	9.6	13.0	Nd	0.0	*
144	11.2	12.3	Nd	0.0	*
145	7.0	8.8	Nd	0.0	*
146	5.5	6.8	Nd	0.0	*
147	6.0	5.7	Pm-147 + Sm	0.3	
148	4.5	3.7	Sm	0.8	
149	0.2	2.9	Sm	0.0	
150	3.1	1.5	Nd + Sm	1.5	
151	0.5	1.0	Sm-151	0.0	*
152	1.0	0.6	Sm	0.4	*
153	0.4	0.3	Eu	0.1	*
154	0.3	0.2	Eu-154 + Gd	0.1	
155	0.1	0.1	Eu-155 +Gd	0.0	
156	0.2	0.03	Gd	0.2	
Actinides					
232	0.1		Th-232		
233	nd				
234	0.4		U-234		
235	52.4		U-235		
236	1.0		U-236		
237	1.4		Np-237		
238	8988.2		U-238		
239	17.0		Pu-239		
240	0.3		Pu-240		
241	0.03		Am-241		

+ nd = not detected
* excess produced by n-capture

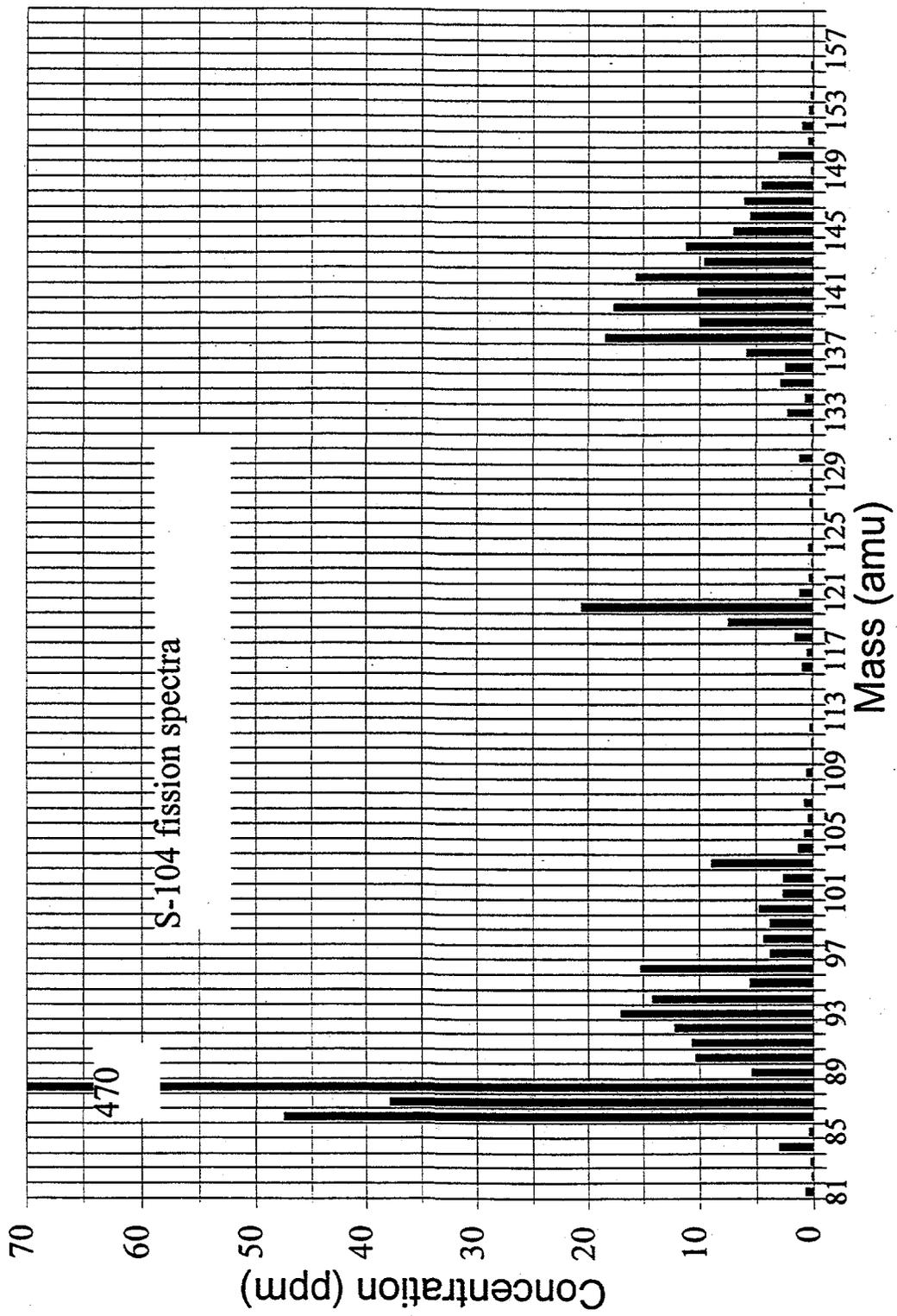


Figure 6.13 Mass concentration spectrum determined from LA/MS data for raw waste sample from tank S-104

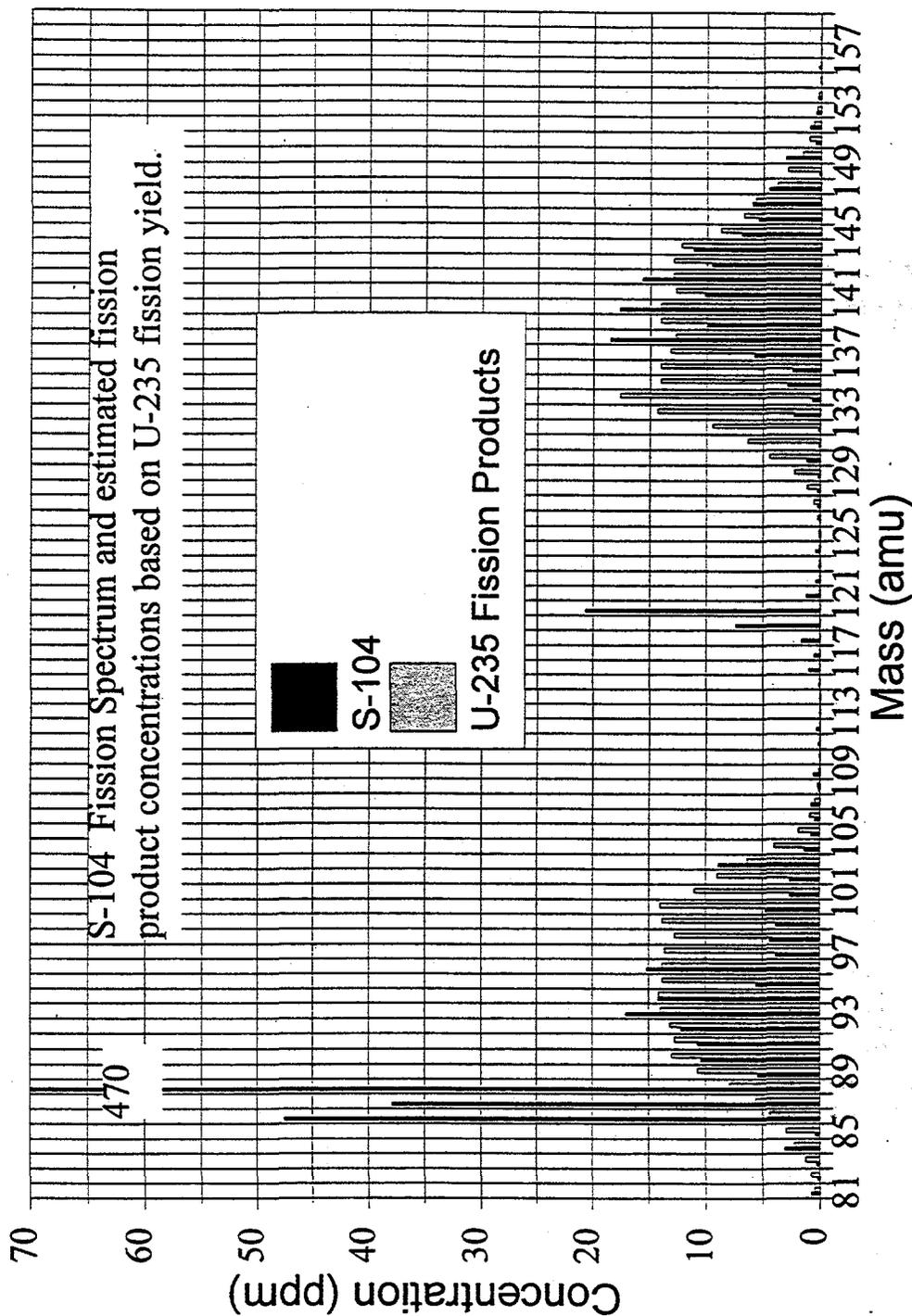


Figure 6.14 Tank S-104 mass concentration spectrum (solid black bars) with amplitude adjusted fission yield data (grey bars)

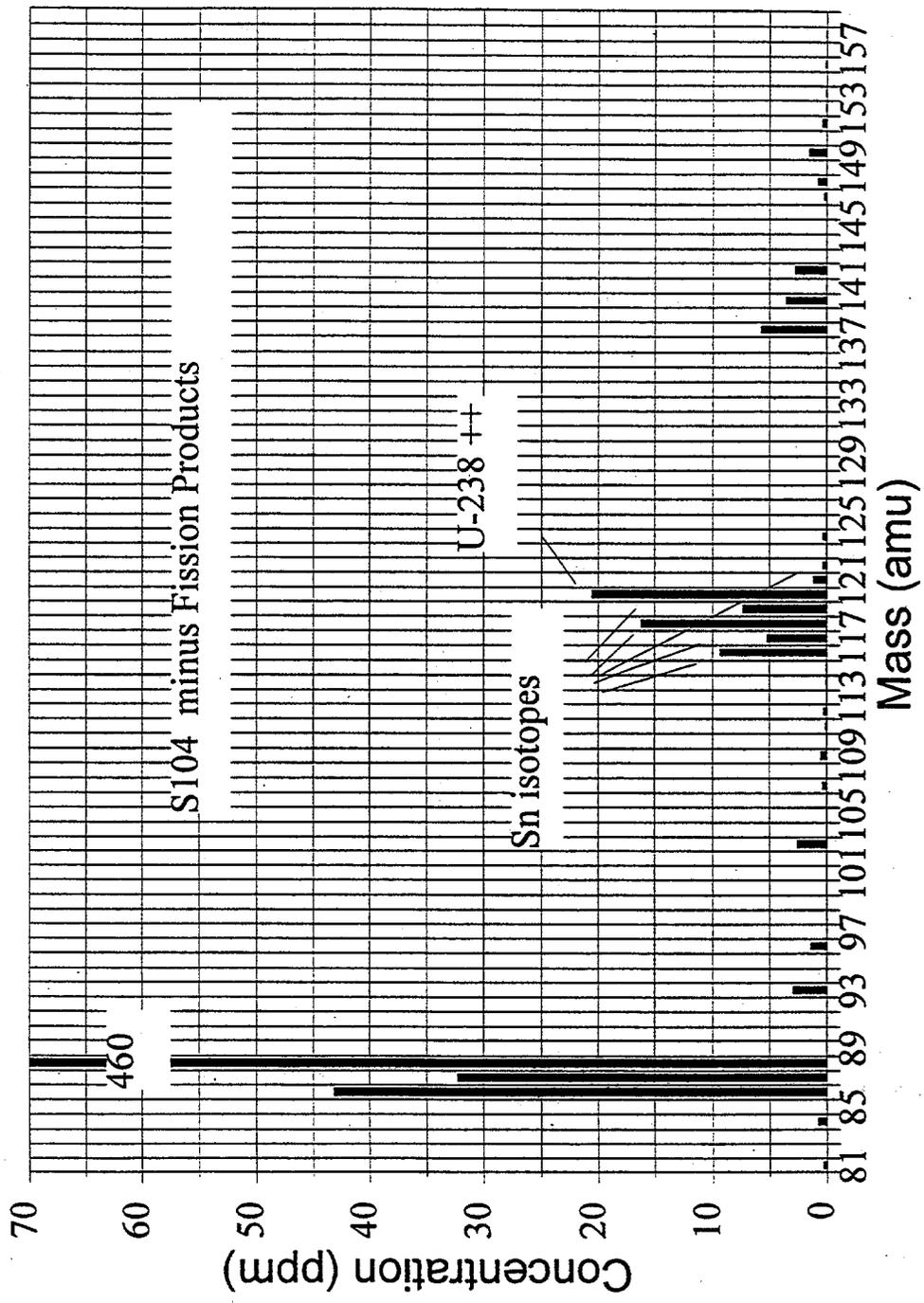


Figure 6.15 Plot of difference values between S-104 peak amplitudes and amplitude adjusted fission yield values from Figure 6.14. (Negative values are not shown.)

present at mass 119. This interference often occurs when very high concentrations of Uranium exist in the sample and represents about 0.1% of the peak height at mass 238.) Uncharacteristic of natural isotopic abundances, the isotopes of Zr and REE suggest that these components must be derived primarily by fission processes. Using an iterative approach, these indicators of fission product concentrations were used to derive the fission product concentrations expected from the fission of ^{235}U .

Figure 6.14 shows the S-104 concentration levels at each mass adjacent to the corresponding fission curve peak. The fission curve peaks have been amplitude adjusted to provide good amplitude agreement with the S-104 data at both the low and high ends of the fission spectra region. From the figure, one can see that the Zr and REEs present in the S-104 have very similar abundances to what would be expected from the fission of ^{235}U . However, other fission product elements (Mo, Ru, Xe, I, and Cs) are not equally represented in the S-104 sample, having noticeably lower than expected concentrations. We suspect that because these elements are generally soluble, they have either been removed during previous waste reduction campaigns, left in the tank with the waste supernate during core sampling, or were not representatively sampled.

Finally in Figure 6.15, the peaks shown resulted from the subtraction of the corresponding peaks at each mass shown in Figure 6.14 (i.e., observed concentrations minus the fission curve values). The resulting spectrum indicates that Sr and Sn are the only non-radiogenic components found in S-104. Residual amounts of isotopes are also shown. These isotopes are those which were produced by n-capture processes not accounted for in the ^{235}U fission yields. Since fission yields only estimate the production of isotopes as they are created, subsequent bombardment of these products by high neutron fluences results in another transformation. This transformation, in simplistic terms, results in an increase of 1 amu to the observed isotope.

From Table 6.4, a number of radionuclides concentrations can be estimated. The concentration of isotopes corresponding to masses 90, 93, 99, 107, 129, 135, 137, 147, 151, 154 and 155 can be assigned to radioactive constituents. Depending on how old the tank wastes are, the proportions of certain shorted-lived radioactive isotopes will be reduced by simple decay.

- a) For example, the mass at 90 initially represented essentially all ^{90}Sr . However, with approximately 30 years of storage, about half of this ^{90}Sr has decayed to the stable isotope Zr.
- b) The concentration at mass 93 is estimated to be about 17 ppm. We believe this mass can be assigned to the radionuclide ^{93}Zr ($t_{1/2} = 1.5\text{M}$ years). However, since the fission yield estimates 14 ppm, some contribution of the 93 peak could be due to Nb.

- c) Mass 99 has been assigned to ^{99}Tc ($t_{1/2} = 0.21\text{M}$ years). The LA/MS data indicated about 4 ppm, where, as the fission yield estimates based on Zr and REE suggest, 14 ppm should be present.
- d) The mass at 107 could represent some ^{107}Pd ($t_{1/2} = 6.5\text{M}$ years); however, the sensitivity of this particular analysis limits us from determining the concentration for this radionuclide in S-104 except to base its concentration solely on the concentration estimated from fission yields.
- e) The mass at 129 could represent some ^{129}I ($t_{1/2} = 16\text{M}$ years). Again, the large discrepancy between the measured concentration at 129 and that which is predicted by fission yields suggests this radionuclide was not sampled.
- f) Similar conclusions can be made for the Cs radionuclides falling on masses 135 and 137.
- g) The mass at 147 has been assigned to ^{147}Pm ($T_{1/2} = 2.62$ years) and its stable daughter ^{147}Sm . Again most of this short-lived radionuclide has decayed and now is represented by ^{147}Sm .
- h) The mass at 151 has been assigned to ^{151}Sm ($t_{1/2} = 93$ years). The LA/MS data suggest about 0.5 ppm is present. Although the fission yield calculations indicate about 1 ppm, this radionuclide would likely have undergone a transformation by n-capture since it has a very large neutron cross section (i.e., 1000's of barns).
- i) The two masses at 154 and 155 have been assigned to Eu radionuclides and their corresponding Gd daughters. As with iodine, estimating the concentrations of these low-yield radioisotopes can not be performed due to the lack of sensitivity for this particular experiment.

Another major contribution to the radioactivity of tank wastes are represented by the actinides. Figure 6.16 shows the mass spectral region defining the actinides present in the three tank samples investigated. Cross-hatched boxes represent the isotopic ratio for natural uranium. Interestingly, the relative actinide abundances of each of the three samples investigated does not correlate with their fission product concentrations. Although there is no *a priori* reason why uranium content should correlate to fission product concentrations, one would expect that activation products Np, Pu and Am should be similar at least relatively. Nevertheless, this figure shows that the concentrations of the major actinide elements can be determined using LA/MS.

6.2 Sample Analyses Conducted with Hot Cell LA/MS System for Radioactive Samples

An initial demonstration of the hot cell LA/MS instrumentation system was completed in late September 1996 to meet an FY 1996 LA/MS Project milestone. The objective of this demonstration, which fulfilled a major FY 1996 project milestone, was to acquire initial data on a single tank waste sample with the hot cell LA/MS system and rapidly identify major and minor constituents in the sample. The demonstration was completed with the analysis of a

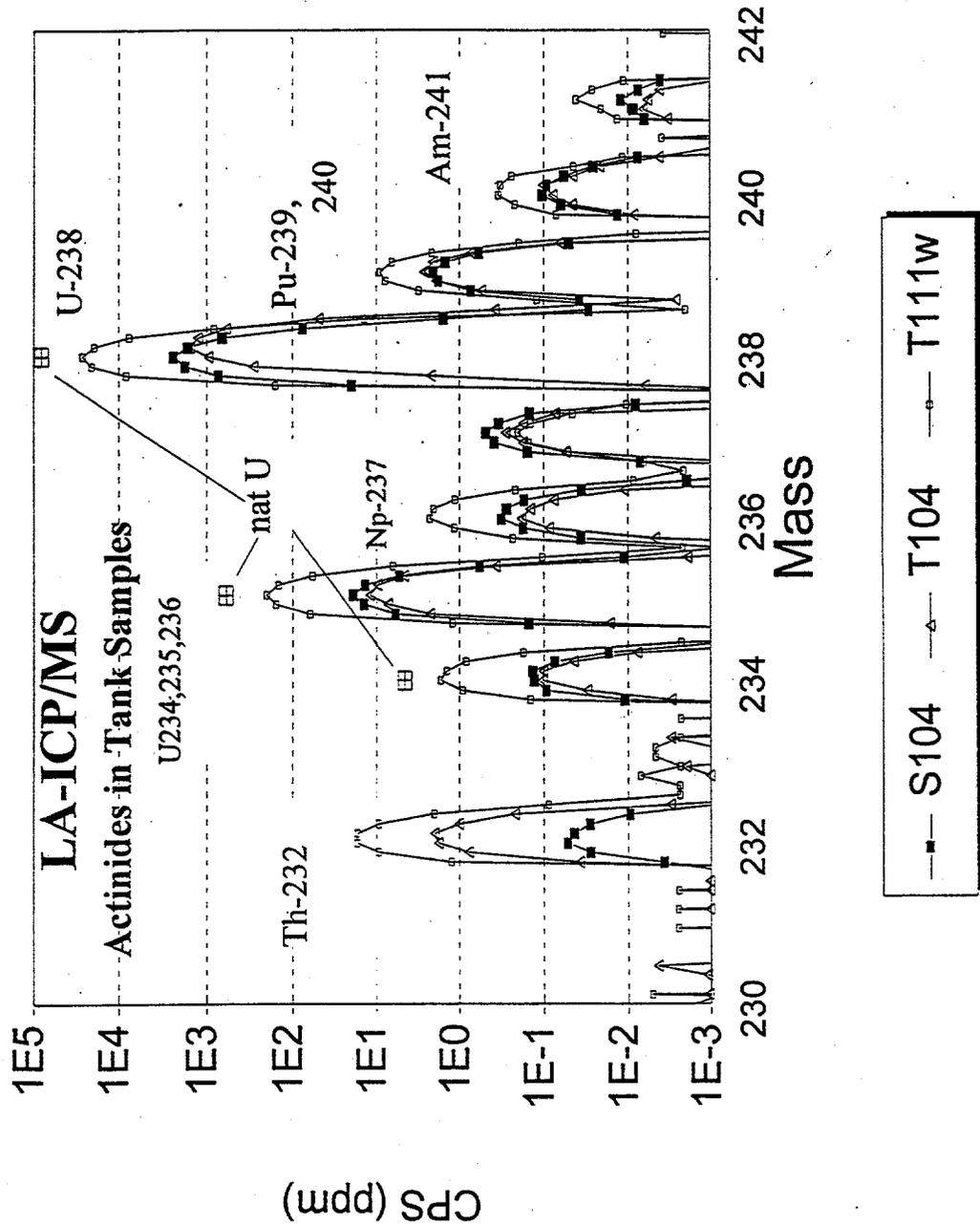


Figure 6.16 Logarithmic plot of mass spectrometer signal levels for isotopes in the actinide mass spectral region (230 - 242 amu) from LA/MS analysis of three tank samples (S-104, T-104, and T-111)

U-105 TWRS tank waste sample on September 24 and 26, 1996. These initial data were qualitative and no attempt was made to perform quantitative interpretation or to conform to the Hanford Analytical Services Quality Assurance Plan (Rev 2) standards (DOE/RL 1996). This was fully consistent with the FY 1996 project objectives. Since that time, the data recorded during the demonstration test have been analyzed further and the results will be discussed below.

The waste sample, from tank U-105, was selected to provide a sludge sample which was known to contain a broad range of chemical constituents including heavy metals and radionuclides. Sample specifics were detailed in Section 3.2 of this report. Independent analytical results (e.g., ICP/AES and radiochemistry analysis, Fritts 1996) for the sample were available to allow a comparison with the initial LA/MS data recorded with the hot cell system. The independent analysis results are summarized in Tables 6.5 and 6.6.

6.2.1 Results of Rapid Determination of Major and Minor Waste Constituents

Figure 6.17 shows the background-corrected mass spectra (i.e., counts detected during the 45-second data integration period).

The data are shown on a logarithmic plot to allow the simultaneous presentation of the signal level data for both high- and low-concentration analytes in the waste sample. As discussed above (Sections 2.2.2 through 2.2.4), the ICP/MS instrument detection sensitivity is a function of the detected mass number. Thus, the instrument sensitivity effects must be taken into account before any quantitative interpretation of the data can be made.

Using the independent analysis results for this sample (shown in Table 6.5), it can be seen that this single mass spectrometer data set covers analyte concentrations ranging from 20% (sodium) to less than 10 parts-per-million. Several general mass ranges are labeled including the low mass constituents that contribute heavily to the general waste form matrix, the mass ranges of 80 - 110 amu and 130 - 150 amu where fission products occur (in addition to natural constituents), the Pb - Bi region at about 200 - 210 amu, and the actinide region from about 230 - 250 amu.

Figure 6.18 shows an expanded view of the low mass region (0 - 80 amu) of the spectrum with a number of individual analyte peaks labeled. The sodium peak (23 amu) clearly exhibits the highest mass spectrometer signal level in this data set which correlates well with the independent analysis results shown in Table 6.5. Other elements with high-mass spectrometer signal levels in this portion of the mass spectrum include K, Fe, Al, Mn, Cr, P, Ni, and Cu. Examination of the independent analysis results for the elements reveals that these elements generally were found in the upper portion of the sample composition list. It is also clear from a comparison of independent analysis results and the LA/MS signal strength for these analytes that a strong but imperfect correlation exists between the two data sets. This is not surprising

Table 6.5 Independent Elemental Analysis Results for U-105 Tank Waste Sample (Fritts 1996). Elements Are Shown in the Order of Descending Concentration

Element	Symbol	Al. Number	Al. Weight	Anal Method	Modifier	Conc (ppm)	Anal Method	Modifier	Conc (ppm)
Sodium	Na	11	22.99	ICP-Acid Dig		200000	ICP - Fusion		202000
Phosphorus	P	15	30.97	ICP-Acid Dig		18700	ICP - Fusion		18200
Aluminum	Al	13	28.98	ICP-Acid Dig		9800	ICP - Fusion		9770
Iron	Fe	26	55.85	ICP-Acid Dig		5710	ICP - Fusion		6220
Chromium	Cr	24	51.99	ICP-Acid Dig		2650			
Manganese	Mn	25	54.94	ICP-Acid Dig		2520			
Uranium	U	92	238.03	ICP-Acid Dig		2330	Phosphor.		3070
Sulfur	S	16	32.08	ICP-Acid Dig		1800			
Potassium	K	19	39.09	ICP-Acid Dig		786			
Silicon	Si	14	28.08	ICP-Acid Dig		578	ICP - Fusion	<	1010
Lead	Pb	82	207.21	ICP-Acid Dig		333			
Calcium	Ca	20	40.08	ICP-Acid Dig		203			
Thallium	Tl	81	204.38	ICP-Acid Dig	<	195			
Nickel	Ni	28	58.69	ICP-Acid Dig		152			
Boron	B	5	10.81	ICP-Acid Dig		139			
Magnesium	Mg	12	24.31	ICP-Acid Dig		132			
Zirconium	Zr	40	91.22	ICP-Acid Dig		130			
Cerium	Ce	58	140.12	ICP-Acid Dig		110			
Neodymium	Ne	60	144.24	ICP-Acid Dig		110			
Arsenic	As	33	74.92	ICP-Acid Dig	<	97.5			
Bismuth	Bi	83	208.98	ICP-Acid Dig	<	97.5	ICP - Fusion	<	2010
Samarium	Sm	62	150.36	ICP-Acid Dig	<	97.5			
Selenium	Se	34	78.96	ICP-Acid Dig	<	97.5			
Antimony	Sb	51	121.75	ICP-Acid Dig	<	77.6			
Barium	Ba	56	137.33	ICP-Acid Dig	<	48.8			
Lanthanum	La	57	138.91	ICP-Acid Dig	<	48.8			
Molybdenum	Mo	42	95.94	ICP-Acid Dig	<	48.8			
Vanadium	V	23	50.94	ICP-Acid Dig	<	48.8			
Zinc	Zn	30	65.38	ICP-Acid Dig	<	44.3			
Silver	Ag	47	107.87	ICP-Acid Dig		34.7			
Cadmium	Cd	48	112.41	ICP-Acid Dig		28.8			
Cobalt	Co	27	58.93	ICP-Acid Dig	<	19.5			
Copper	Cu	29	63.55	ICP-Acid Dig		14.9			
Lithium	Li	3	6.94	ICP-Acid Dig	<	9.75	ICP - Fusion	<	201
Strontium	Sr	38	87.62	ICP-Acid Dig	<	9.75			
Titanium	Ti	22	47.88	ICP-Acid Dig	<	9.75			
Beryllium	Be	4	9.01	ICP-Acid Dig	<	4.88			

Table 6.6 Independent Radiochemical Analysis Results for U-105 Tank Waste Sample (Fritts 1996)

U-105 Core Sample Data from 222-S				
Radiochem analysis results				
Element	Isotope	Analysis Method	Conc (uCi/g)	Rel % Ct Error
Cobalt	60	GEA	0.0958	29.2
Cesium	137	GEA	87.46	0.54
Europium	154	GEA	1.204	7.91
Europium	155	GEA	0.7469	24.9
Americium	241	GEA	1.449	30.9

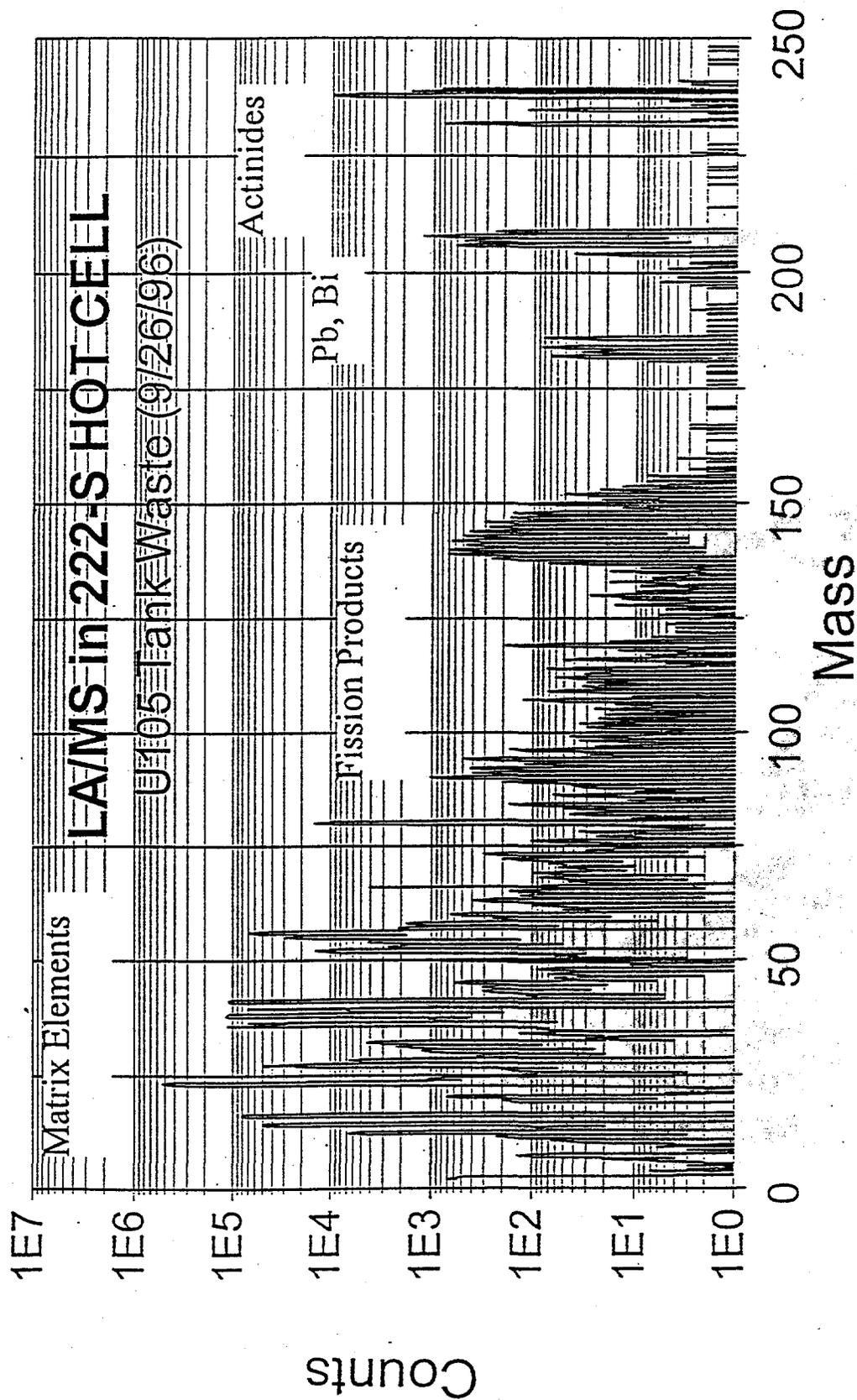


Figure 6.17 Logarithmic plot of mass spectrometer signal level versus mass number for the mass range of 0 - 250 amu for U-105 tank waste sample. Data recorded using hot cell LA/MS instrument system

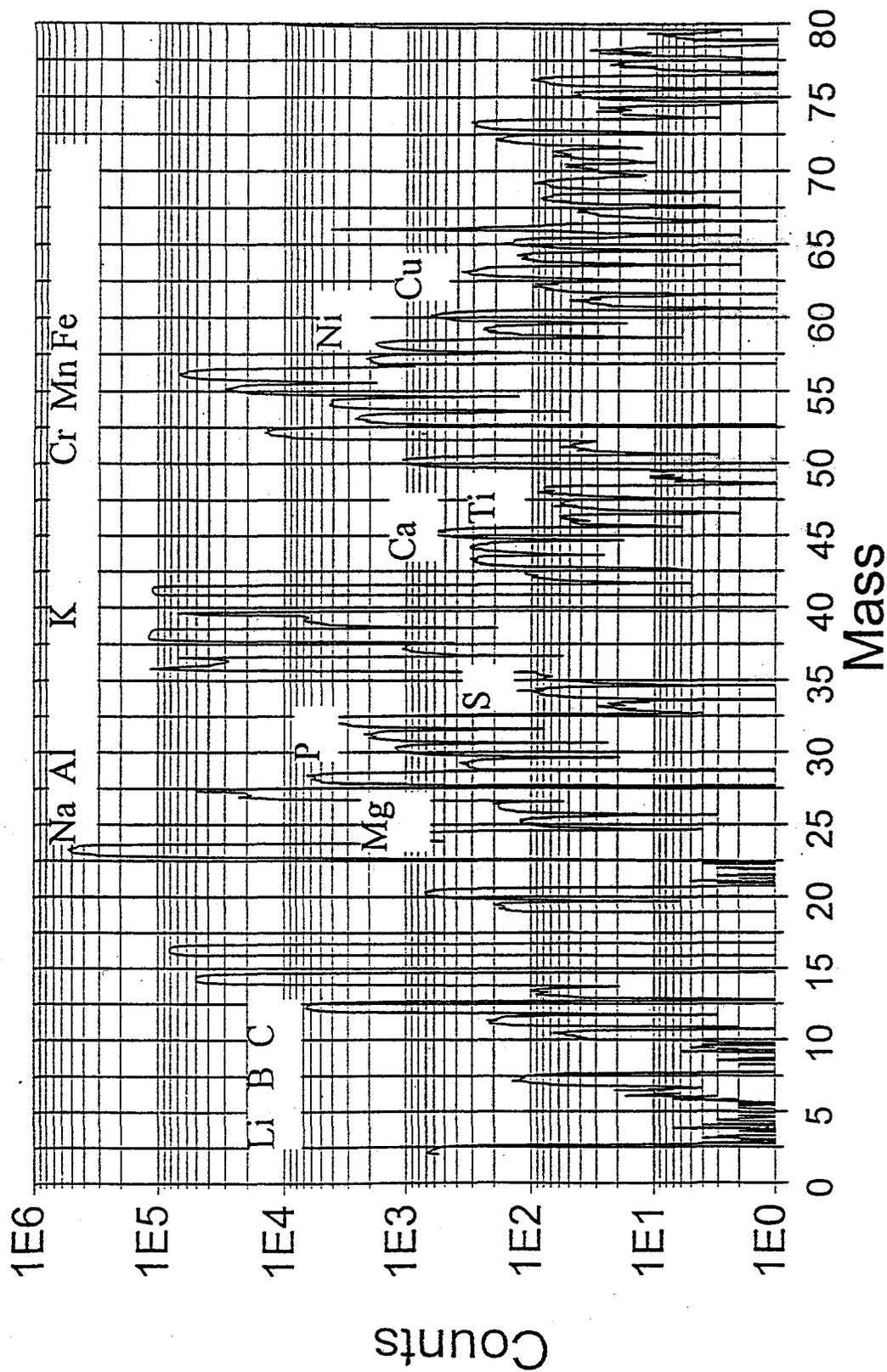


Figure 6.18 Logarithmic plot of mass spectrometer signal level versus mass number for the mass range of 0 - 80 amu for U-105 tank waste sample. Selected sample constituent peaks are identified. Data recorded using hot cell LA/MS instrument system

as the LA/MS data presented in this figure represents the raw signal strength and have not been processed in any way to compensate for instrument response factors including element-to-element response variations.

Figure 6.19 shows an expanded view of the middle mass region (75 - 160 amu) of the spectrum with a number of individual analyte peaks labeled. In addition, a number of signal peaks which are attributed to fission products are labeled in both the lower (80 - 110 amu) and upper (130 - 150 amu) fission product spectral regions. The peak at 119 amu is attributed to a doubly charged ^{238}U ion.

Figure 6.20 shows an expanded view of the upper mass region (150 - 250 amu) of the spectrum with a number of individual analyte peaks labeled. A number of Pb isotopes and a Bi peak are seen at the low end of this plot. Actinide peaks are seen for Th, U (several isotopes), Pu, and possibly Am. The signal levels seen for most of these peaks are still strong even though they are orders of magnitude weaker than for the principal analytes in the waste material.

6.2.2 Measurement Precision (Relative Standard Deviations)

The Relative Standard Deviation values for the U-105 tank waste sample data are shown in Figure 6.21. The observed RSD values generally fall in the range of 4 - 10% which is consistent with the previously discussed results for the S-104, T-104, and T-111 samples. Several elements at relatively high concentrations again exhibit fairly high RSD values. However, in contrast to the previously discussed data, the U-105 data do not include many elements at low concentrations with high RSD values. This results primarily from the fact that the hot cell system mass spectrometer provides greater detection sensitivity (about 1 order of magnitude) than the mass spectrometer used in the laboratory system. (This is due to instrument design differences associated with the relative ages of the two instruments.)

6.2.3 General/Non-Radiogenic Chemical Analysis Results

Reduction of the tank U-105 LA/MS data to obtain elemental concentration estimates was performed following a method which deviated from that discussed in Sections 4.4 and 4.5. The change in procedure was a result of issues which arose with the reference sample employed during the hot cell system demonstration. The mass spectra recorded for the reference material did not fully match the spectra for the intended reference material. The major constituents matched but the minor constituents differed significantly. Thus it appears that another reference material (i.e., a close derivative of the intended reference material) was inadvertently utilized during the hot cell system demonstration. While the major constituents could be used to calculate the general shape of the mass response function, the disagreement on the minor constituents prevented the calculation of the full mass response function. The general shape of the mass response function determined from the major constituents was

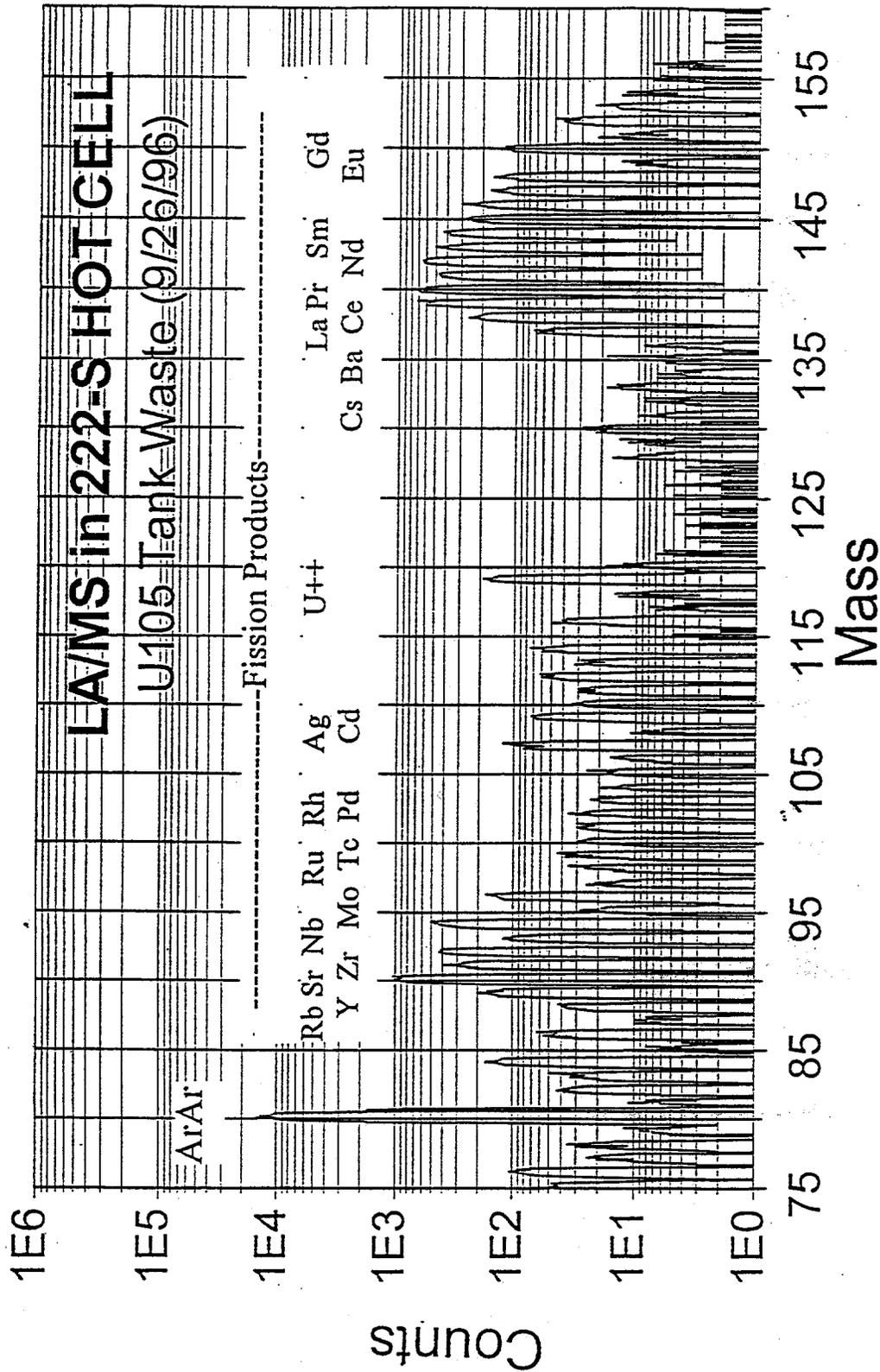


Figure 6.19 Logarithmic plot of mass spectrometer signal level versus mass number for the mass range of 75 - 160 amu for U-105 tank waste sample. Selected sample constituent peaks are identified. Data recorded using hot cell LA/MS instrument system

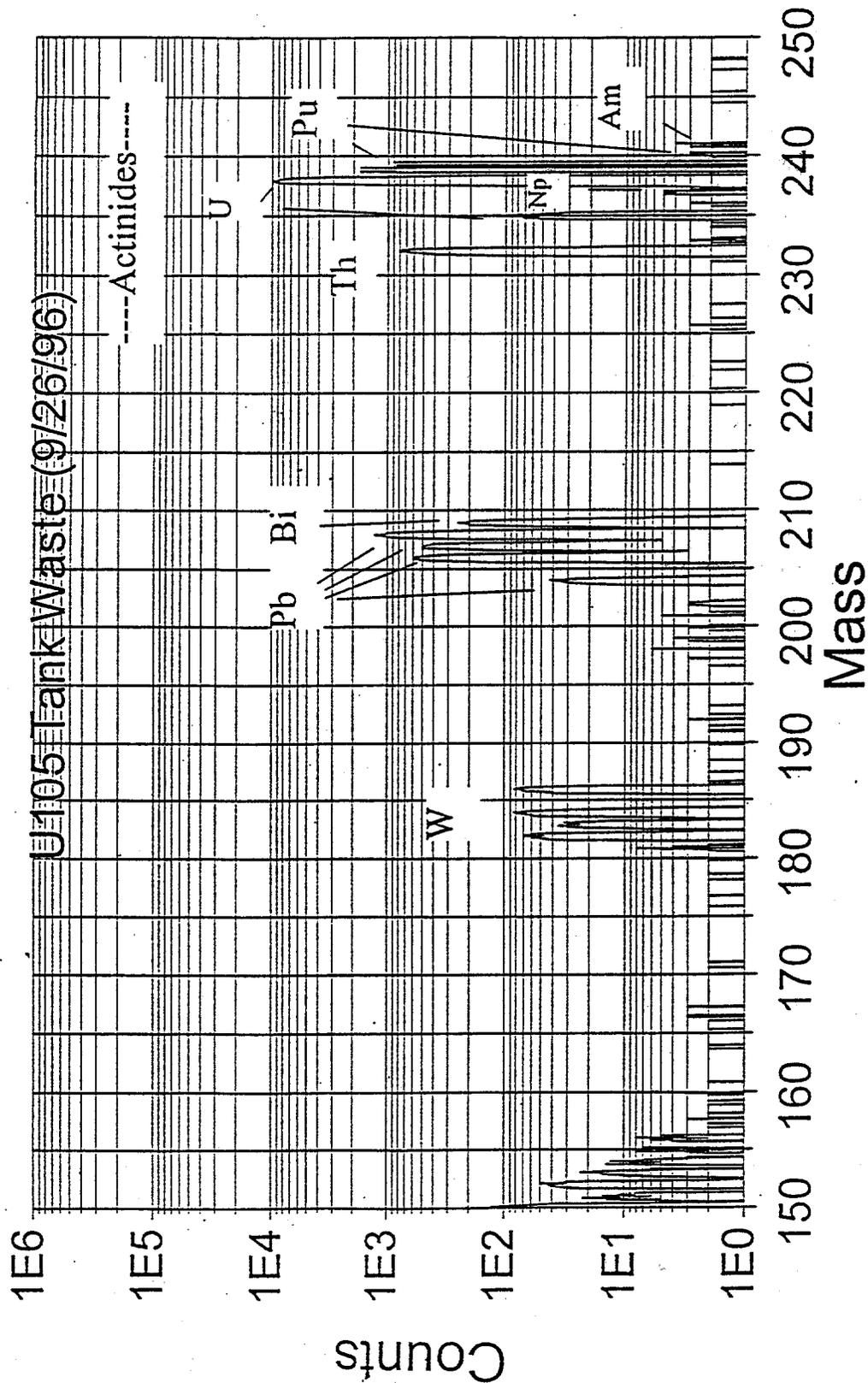


Figure 6.20 Logarithmic plot of mass spectrometer signal level versus mass number for the mass range of 150 - 250 amu for U-105 tank waste sample. Selected sample constituent peaks are identified. Data recorded using hot cell LA/MS instrument system

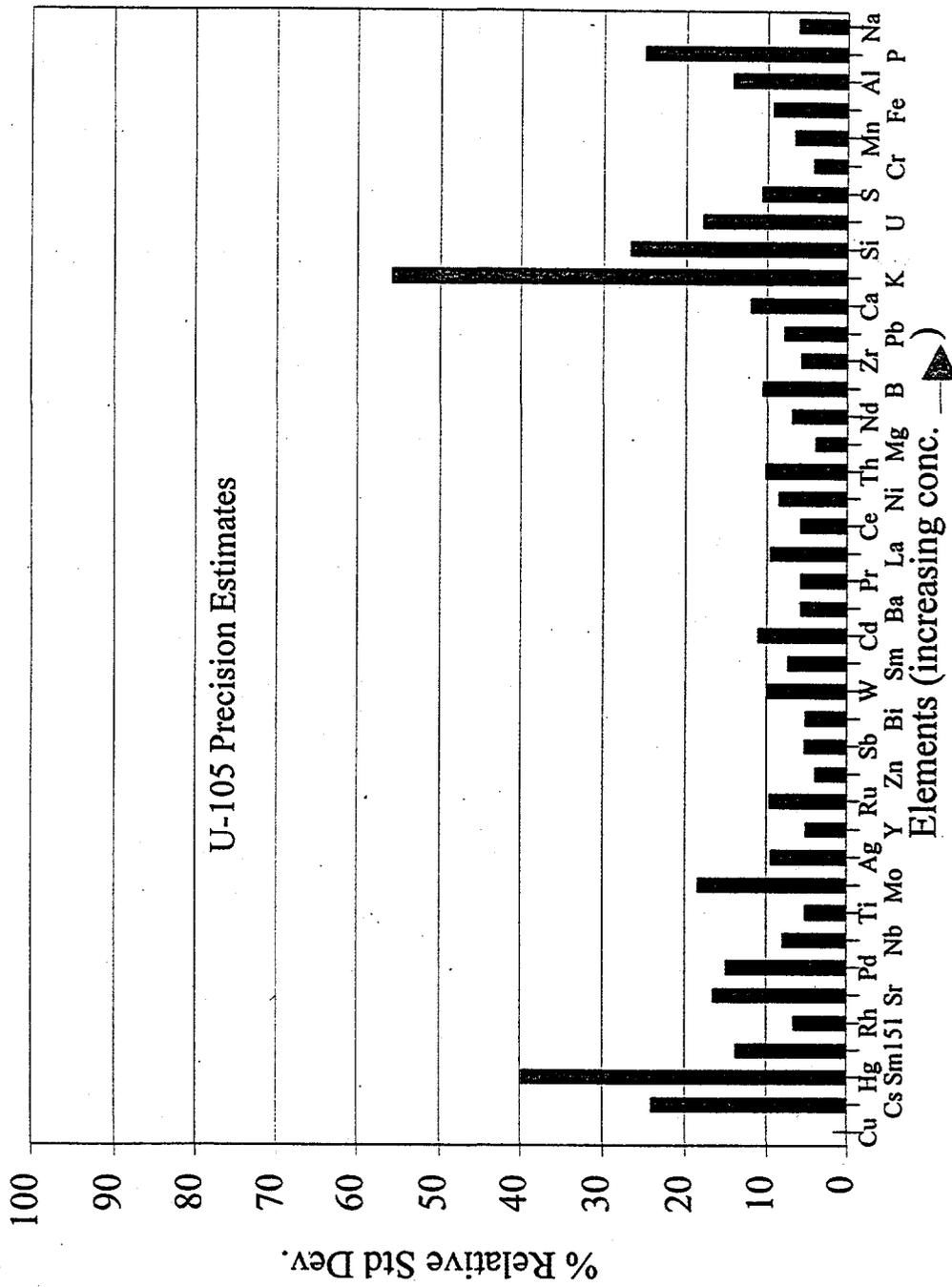


Figure 6.21 Plot of LA/MS Relative Standard Deviation values versus elements for constituents of an untreated U-105 tank waste sample. Elements are plotted in the order of increasing concentration

comparable to the mass response function observed for an ICP/MS instrument (same model and vintage) used on a non-radioactive laboratory LA/MS system.

The general shape of the mass response function was utilized to correct the raw LA/MS signal strength values for instrument sensitivity differences. The corrected LA/MS signal strength data were scaled to the independent analysis results by setting the LA/MS data value for Si, Mg and U equal to the value determined by ICP/AES. All other LA/MS concentration values were then determined by mass response function-corrected LA/MS signal strength values for each mass number. [This procedure is analogous to utilizing a known, internal standard to scale all data as a means of obtaining quantitative data. This was previously employed for soils analysis using LA-based methods (Anderson 1 & 2).]

Estimated elemental concentrations for the U-105 tank waste are shown in Table 6.7. The LA/MS data can be compared with previously reported data obtained from the Hanford TWRS Analytical Laboratory using conventional dissolution and analysis (ICP/AES) techniques. Generally good agreement between the LA/MS data and the independent analysis results is seen in Figure 6.22. Again, the elements are shown in the order of increasing concentration (i.e., least populous elements at the left and most populous at the right in the figures) as determined from the LA/MS data. Note that the results are identical for (Si, Mg and U) as required by the internal scaling method employed for this data set.

Examination of the figure indicates that in most cases, the LA/MS data agree reasonably well with the previously reported values. In addition, these figures also illustrate that the LA/MS method readily provides data across a very large range of elemental concentrations, ranging from ppm to high weight percent levels. In general, the data comparison does not indicate any severe instrumental bias for any particular element, indicating, at least for these data, glass standards were useful as standards to calibrate instrumental response and bias corrections specific to certain elements.

6.2.4 Radiogenic Analysis (Fission and Activation Products)

Fission product spectral region data (80 - 160 amu) for the Tank U-105 sample is shown Figure 6.23. In general, the data exhibit spectral patterns that are very similar to those discussed above for samples from Tanks S-104, T-104, and T-111. Similar relationships are noted for both non-radiogenic components (major, minor, and trace) and radiogenic contributions from fission products and actinides.

Data analysis procedures employed followed those discussed in Section 6.1.3. Low mass and non-radiogenic elements were determined conventionally. Again, concentrations for constituents in the fission product and actinide mass regions were determined by assigning each mass to individual isotopes and summing their concentrations to obtain the bulk element concentration. As previously discussed, good agreement with prior analyses was obtained (see

Table 6.5). In this section we focus on the LA/MS results which allow semi-quantitative information to be obtained for radiogenic components found in the U-105 sample.

Figure 6.23 also shows that the U-105 sample contains significant number of fission products. As with previous samples, the fission yield proportions are plotted which best correspond to isotopes which represent fission products. For this sample, the fission yield curve was scaled using the Nd isotopes. Note that the low mass fission products suggest that the scaled fission yield curve should be reduced by a factor of two if the recorded data resulted from fission of ^{235}U . However, the data correspond well to the scaled fission yield curve expected for fission products of ^{239}Pu .

As with the other waste samples analyzed, soluble components (Mo, Tc, Ru, I, and Cs) are significantly depleted relative to Sr, Zr, and REE elements. Unlike the other samples discussed previously, the U-105 data indicates that Rh and Pd also fall significantly below the scaled fission yield curve. At the same time, the Zr and Cd peaks fall conspicuously above the fission product curves. The spectra also indicate the presence of interfering doubly charged ^{238}U ions and possibly trace amounts of Ce and Ag. Once the ^{235}U fission proportions are subtracted, these elements (Zr, Cd, Ce, and Ag) were found, within counting statistics, to have normal-nonradiogenic isotopic abundances. This indicates these constituents resulted from chemical processing or, in the case of Zr, represent fuel cladding material. Roughly, the concentrations measured by the LA/MS for notable radionuclides, ^{93}Zr , ^{99}Tc , and ^{151}Sm , are 16, 4 and 1 ppm respectively. The peak at 137 may represent ^{137}Cs ; however, we believe this is unlikely since sub-ppm concentrations are found for other Cs isotopes (ie. 133 and 135).

6.3 Summary of Initial LA/MS Analyses Conducted on Hanford Tank Waste Samples

Seven solid-form, radioactive tank waste samples have been analyzed using LA/MS instrument systems deployed at Hanford. Analysis of the resulting LA/MS data allowed the determination of both a) general/non-radiogenic and b) radiogenic constituents in the waste samples. The ability to determine isotopic constituents using the LA/MS method yielded significant advantages over ICP/AES analysis by providing valuable information on fission products and radioactive constituents.

These initial waste sample analyses have demonstrated that LA/MS data provide the basis for rapid identification of major and minor components in solid (sludge) samples. Although the current data reduction methods are limited to providing semi-quantitative results, the results obtained from these LA/MS data are consistent with previously reported values determined by current laboratory analytical methods for most sample constituent concentrations

Table 6.7 Tank U-105 Sludge Component Analysis Showing LA/MS Analysis Results with Independent Analysis Results (Fritts 1996) Where Available (ppm per Dry Weight)

Element	LA/MS (Hot Cell)		ICP-OES
	Concentration	%RSD	Concentration
Li	nd*		<5
B	186	10	139
Na	207027	6	200000
Mg	147	4	132
Al	7885	14	9690
Si	896	27	1010
P	16973	25	18700
S	3298	11	(1800)
K	603	56	786
Ca	450	12	203
Ti	13	5	<10
Cr	3424	4	2650
Mn	6264	7	2520
Fe	7477	9	6220
Ni	122	8	152
Zn	28	4	44
Cu	1	262	15
Sr	10	17	<10
Y	19	5	
Zr	276	6	130
Nb (Zr-93)	11	8	
Mo	9	18	<50
Ru	8	10	
Rh	2	7	
Pd	5	15	
Ag	17	9	35
Cd	46	11	29
Sn	31	5	78
Cs	1	24	
Ba	33	6	<50
La	69	10	<50
Ce	155	6	110
Pr	55	6	
Nd	180	7	110
Sm	20	7	<100
Eu (Sm151)	2	14	
W	35	10	
Hg	2	40	
Pb	367	8	333
Bi	34	5	<100
Th	130	10	
U	2120	18	2200

* Not detected

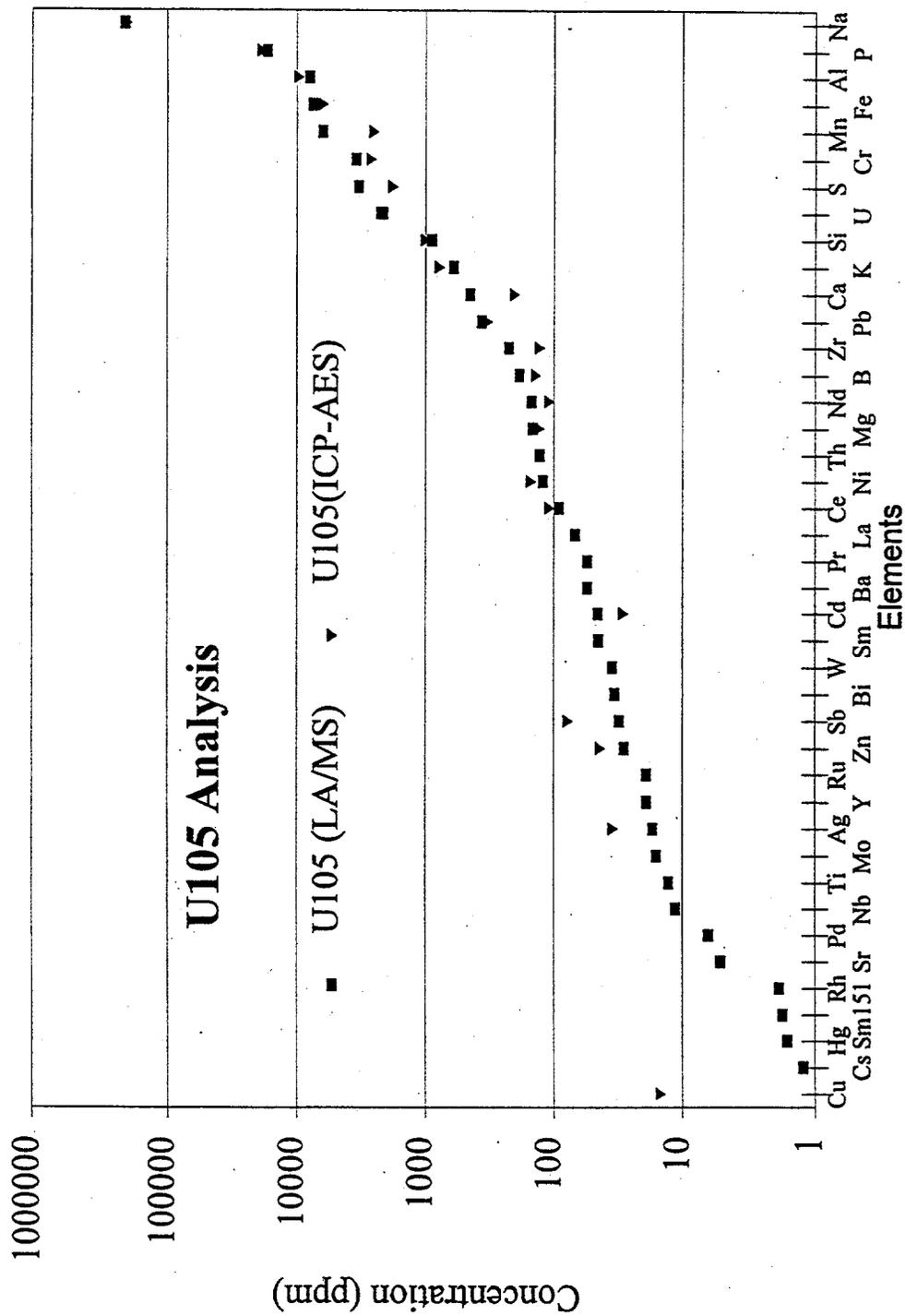


Figure 6.22 Logarithmic plot of elemental concentrations in U-105 tank waste samples as determined by independent analysis (ICP/AES analysis of solution based samples) and preliminary LA/MS analysis. Elements are shown in order of increasing concentration as determined from the LA/MS data

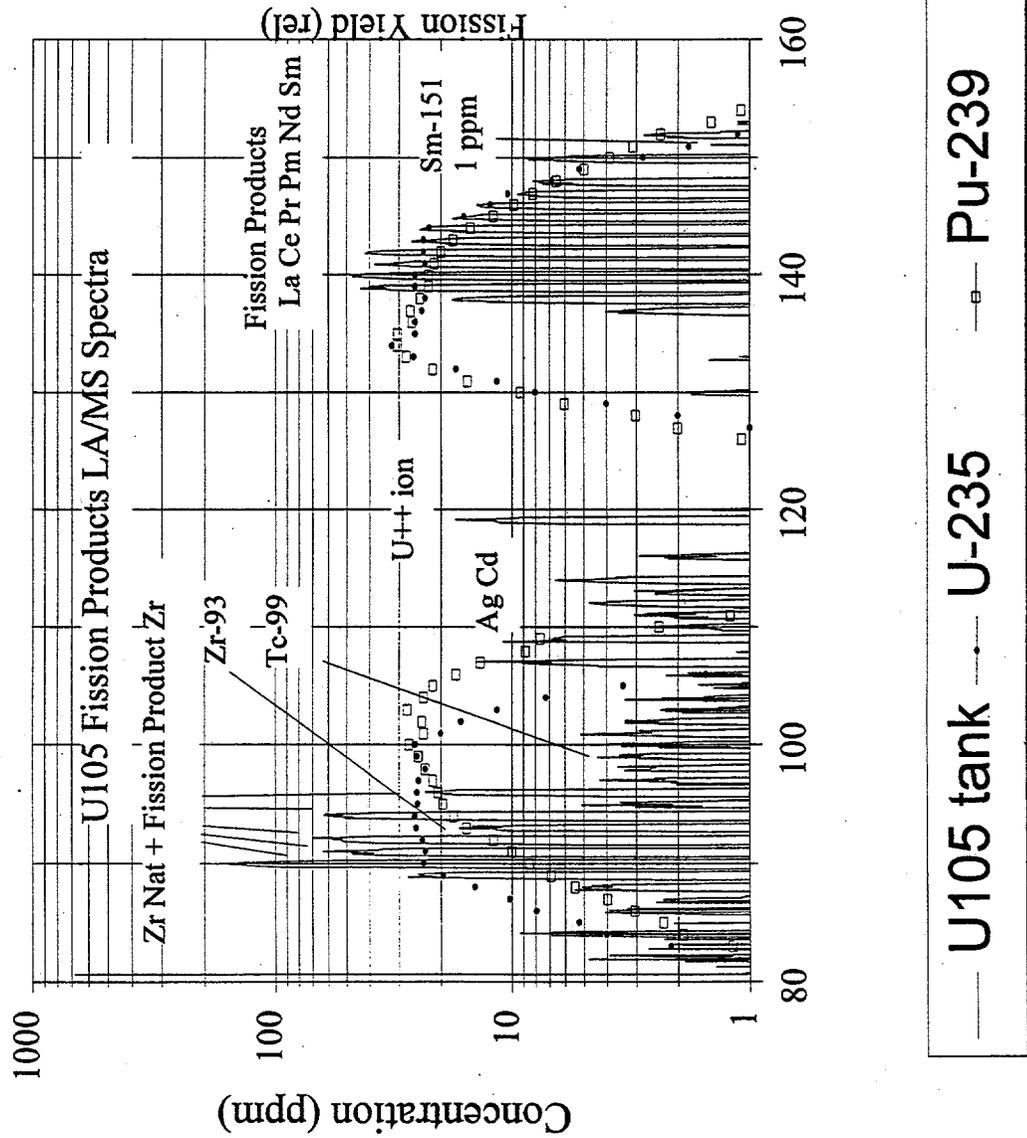


Figure 6.23 Logarithmic plot of estimated isotopic concentration levels versus mass number for the range of 80 - 160 amu's for the U-105 waste sample. Fission yield curves for ^{235}U and ^{239}Pu are shown with selected peaks identified

Looking forward, the accurate measurement of bulk sludge constituent concentrations will require a knowledge of the liquid-to-solid ratios in the sample. This is true for LA/MS and all other analytical methods.

The LA/MS analysis mass spectra allowed rapid determination of the fission products present in each sample. The recorded LA/MS data exhibited both natural components (non-radiogenic, presumably materials used for processing the nuclear fuels) and radiogenic products (due to the nuclear fuel composition and irradiation history). The radioactivity levels due to the fission products can be estimated directly using known fission yields and the LA/MS mass spectral data. Each of the tank waste samples analyzed have fission product spectra which allow an analyst to determine bulk radiological contents introduced by fission. Using a knowledge of stable isotopes and by determining the isotopic abundances of the various elements produced by fission, radioactive isotopes can be identified and their abundances calculated. This avoids the need to perform tedious and time-consuming radiochemical separations. For accurate quantification, it is necessary that the radionuclides must be sampled equally, including those which exist primarily in the soluble components of the sludge.

In addition, the LA/MS data provided direct information on actinide isotopes present in the samples. These isotopes make another major contribution to the radioactivity of tank wastes. This was illustrated in Figure 6.13 which shows the mass spectral region containing signal peaks due to actinide constituents present in the three tank samples investigated. Cross-hatched boxes represent the isotopic ratio for natural uranium. The relative actinide abundances for each of the three samples investigated do not correlate with their fission product concentrations. Although there is no *a priori* reason why uranium content should correlate to fission product concentrations, one would expect that activation products Np, Pu and Am should be similar, at least relatively. Nevertheless, this illustrates that the major actinide element concentrations can be determined using the LA/MS method.

The LA/MS data provided direct indication of the actinide element concentration in each of the tank wastes. The recorded mass spectra in the actinide mass range included numerous isotopes of Th, U, Np, Pu and Am. These data, even if qualitative, can be used with known relative isotopic abundance information to provide an estimate of the bulk fissile material in the tank wastes. Relative abundances of the actinides can be determined which may be used to evaluate sample composition relative to tank safety criteria. In addition, these data can be used to project long-term radioactive constituents and levels in both low-level and high-level waste forms.

7.0 Conclusions

Initial LA/MS analyses of Hanford tank waste samples have been performed successfully using laboratory and hot cell LA/MS instrumentation systems. The experiments described in this report have demonstrated that the LA/MS data can be used to provide rapid analysis of solid, radioactive Hanford tank waste samples to identify:

- Major, minor, and trace constituents (elemental and isotopic) and
- Fission products and radioactive isotopes.

The ability to determine isotopic constituents using the LA/MS method yielded significant advantages over ICP/AES analysis by providing valuable information on fission products and radioactive constituents.

The LA/MS method capability for rapid identification of major and minor components in solid (sludge) samples has been demonstrated successfully for radioactive waste samples. The LA/MS data contains both natural components (non-radiogenic, presumably materials used for processing the nuclear fuels) and radiogenic products (due to the nuclear fuel composition and irradiation history). Although the current data reduction methods are limited to providing semi-quantitative results, the results obtained from these LA/MS analyses reported are consistent with previously reported values determined by current laboratory analytical methods for most sample constituent concentrations.

Data precision (i.e., relative standard deviations) for the LA/MS data for the majority of these initial waste samples was in the range of 4 - 12% for most sample constituents (with sufficient count rates for good data statistics). This is comparable to results obtained for homogeneous glass reference materials and indicates that the LA/MS raster scanning and data integration periods employed for these initial tests were sufficient to provide useful averaging of sample constituents exposed on the sample's surface.

These initial analyses of radioactive tank waste samples using the LA/MS method has also demonstrated the ability for rapid determination of the fission products present in samples. The radioactivity levels due to the fission products can be estimated directly using known fission yields and the LA/MS mass spectral data. An analyst can determine a sample's bulk radiological contents introduced by fission based on the sample's LA/MS fission product spectra. Using a knowledge of stable isotopes and by determining the isotopic abundances of the various elements produced by fission, radioactive isotopes can be identified and their abundances calculated. This avoids the need to perform tedious and time-consuming radiochemical separations. For accurate quantification, it is necessary that the radionuclides

must be sampled equally, including those which exist primarily in the soluble components of the sludge.

The LA/MS data for tank waste samples has provided direct information on the sample's actinide. The actinides make another major contribution to the radioactivity of tank wastes. The initial results of tank waste analyses using LA/MS exhibited numerous isotopes of Th, U, Np, Pu and Am. These data, even if qualitative, can be used with known relative isotopic abundance information to provide an estimate of the bulk fissile material in the tank wastes. Relative abundances of the actinides can be determined which may be used to evaluate sample composition relative to tank safety criteria. In addition, these data can be used to project long-term radioactive constituents and levels in both low-level and high-level waste forms.

8.0 Future Task Activities

LA/MS method and technology development activities are continuing with the objective of advancing the capability to:

- Allow quantitative interpretation of LA/MS data for tank waste samples and
- Further improve the operational LA/MS capability for both data acquisition and data reduction to support routine use in the analysis of radioactive, solid sample materials.

Laboratory testing with the elementally spiked simulant materials will be continued to firmly establish the importance of sample matrix effects on the resulting LA/MS data and to evaluate the importance of a reference sample selection of LA/MS data reduction. Data analysis and comparisons will incorporate the results of the independent chemical analyses on the spiked simulant materials which were completed late in FY 1996. Analysis of the LA/MS data will include an evaluation of alternative methods identified for LA/MS data normalization (i.e., total detected ion count and particle plume mass normalization) and the development of a recommended normalization method to be used for future data reduction.

Additional LA/MS testing will be performed on Hanford tank waste samples. The effects of reference sample selection on data reduction for the actual waste samples will be evaluated using existing glass reference samples and elementally spiked simulant materials. Waste samples will be selected for these tests which have been previously characterized using independent analytical methods. Samples evaluated by multiple methods and/or laboratories will be preferred to those given single analyses.

The results of testing with both simulant and actual waste samples will be evaluated to determine reliable methods for data acquisition and data reduction.

- a) The LA/MS sample analysis experience will provide the basis for a recommended LA/MS analysis protocol which can be employed for future use with both the Hot Cell and Laboratory LA/MS instrumentation systems.
- b) The LA/MS data reduction experience will provide the basis for recommendations on a) reference sample selection to support waste sample analysis (i.e., must the reference sample be matched to the sample under test?; if yes, how good a match is required?); b) a method for LA/MS data normalization to compensate for sample and system variations; and c) reliable methods for LA/MS data reduction to meet laboratory analysis needs.

In addition, the results of LA/MS tests conducted under this task will provide clear indications on the performance capabilities of the LA/MS analytical method for the elemental and isotopic analysis of tank waste samples.

9.0 References

Anand, NK, AR McFarland, FS Wong, and CJ Kocmoud. 1993. *Optimization of Aerosol Penetration Through Transport Lines* by Aerosol Technology Laboratory, Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843, Report No. 6441/01/31/93, March 1993.

Anderson, MS and S Braymen. 1994. *Final Report - Ames Mobile Laboratory Project: The Development and Operation of Instrumentation in a Mobile Laboratory for In Situ Real-time Screening and Characterization of Soils Using the Laser Ablation Sampling Technique*, Report No. IS-5115, Ames Laboratory (DOE), Environmental Technology Development Program, Iowa State University, Ames, IA 50011, February 16, 1994.

Anderson, MS, S Braymen, R McIntosh, J Prail, MA Anderson, J Gray, D Baldwin, D Zamzow, AP D'Silva, and RD Ediger. 1994. *Laser Ablation ICP-Mass Spectrometry Determination of Th²³⁰ in Soils at the Gunnison, Colorado UMTRA Site*, Report No. IS-5106, Ames Laboratory (DOE), Environmental Technology Development Program, Iowa State University, Ames, IA 50011, February 16, 1994.

Fritts, LL. 1996. *Final Results for Tank 241-U-105, Push Mode Cores 131, 133, and 136, Rev. 1*, WHC-SD-WM-DP-182, Rev. 1, July 26, 1996.

Garcia Alonso, JI, D Thoby-Schultzendorff, L Koch. 1993. "ICP-MS for fissile material analysis in highly radioactive samples," *ESARDA 15th Annual Symposium on Safeguards and Nuclear*, p.485-9, Conference Date: 11-13 May 1993, Conference Location: Rome, Italy, Publication Date: 1993.

Hanford Analytical Services Quality Assurance Plan, DOE/RL-94-55, (Rev. 2), April 01, 1996.

McCain DJ and B Simpson. 1996. *Historical Model Evaluation Data Requirements (Rev. 1)*, WHC-SD-WM-DQO-018, June 20, 1996.

Pacific Northwest Laboratory. *Fabrication and Characterization of MCC Approved Testing Material ATM-WV/205 Glass*, PNL-5577-WV/205, UC-70, 1988.

Rapko, BM, GJ Lumetta and MJ Wagner. 1995. *Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1995 Studies*, PNL-10712, August 1995.

Smith, MR 1992. *Preliminary Evaluation of ICP/MS Analytical Methods for HWVP Sample Characterization*, PHTD-92-04.11/K905 (Rev. 0), January 27, 1992.

Wyse, EJ and MR Smith. 1993. *Summary of Round Robin Results for Interlaboratory Noble Metals Analysis of HWVP Glasses*, PHTD-C93-05.08D (Rev. 0), March 1993.

Distribution

No. of Copies		No. of Copies	
	OFFSITE		
3	U.S. Department of Energy Cloverleaf Building 19901 Germantown Rd. Germantown, MD 20874	1	Confederated Tribes of the Umatilla Indian Reservation P.O. Box 638 Pendleton, OR 97801 <i>S. Harris</i>
	<i>C.O. Bauer</i> Room 157 <i>D.W. Geiser</i> Room 183 <i>C.B. Purdy</i> Room 1172	1	Lockheed Idaho Technologies Co. MS 3423 P.O. Box 1625 Idaho Falls, ID 83415 <i>T.R. Thomas</i>
1	U.S. Department of Energy G-109/GTN 19901 Germantown Rd. Germantown, MD 20874 <i>F.J. Wobber</i>	1	Los Alamos National Laboratory PO Box 1663 Los Alamos, NM 87545 <i>P.G. Eller</i>
1	Ames Laboratory Technology Integration Program Office Iowa State University 125 South 3rd Street Ames, IA 50010-6739 <i>M.S. Anderson</i>	2	Nez Perce Tribe ERWM P.O. Box 365 Lapwai, ID 83540-0365 <i>D.L. Powaukee, Manager</i> <i>P. Danielson</i>
1	Argonne National Laboratory - West PO Box 2528 Idaho Falls, ID 83403 <i>S.G. Johnson</i>	1	Science Applications International Corp. 555 Quince Orchard Road Suite 500 Gaithersburg, MD 20878 <i>S. Wyrick</i>

No. of Copies		No. of Copies	
1	Surface Dynamics Laboratory Department of Physics Washington State University Pullman, WA 99164-2814 <i>J.T. Dickinson</i>	7	Lockheed Martin Hanford Company <i>J.N. Appel</i> G3-21 <i>H. Babad</i> S7-14 <i>K.E. Bell</i> R2-12 <i>K.A. Gasper</i> G3-21 <i>K.M. Hall</i> R2-12 <i>J.W. Hunt</i> R2-12 <i>B.C. Simpson</i> R2-12
1	Yakima Indian Nation P.O. Box 151 Toppenish, WA 98984 <i>B. Cook, Research</i>	10	Numatec Hanford Company <i>J.W. Ball (4)</i> T6-30 <i>J. Bourges</i> T6-09 <i>H.D. Chauve</i> H5-25 <i>D.A. Dodd</i> T6-50 <i>C. Dormant</i> T6-07 <i>G.L. Troyer</i> T6-50 <i>W.I. Winters</i> T6-50
ONSITE			
11	DOE Richland Operations Office <i>C.A. Babel</i> S7-54 <i>J.A. Frey</i> K8-50 <i>M.J. Glasper</i> K8-50 <i>J.P. Hanson</i> K8-50 <i>P.R. Hernandez</i> S7-54 <i>R.M. Rosselli</i> K8-50 <i>K.M. Thompson</i> H0-12 <i>A.C. Tortosa</i> H0-12 <i>M.C. Vargas</i> K8-50 <i>D.M. Wanek</i> H0-12 <i>V. Fitzpatrick, MACTEC</i> K8-50	4	Rust Federal Services Hanford Company <i>A.G. King</i> T6-03 <i>C.T. Narquis (2)</i> T6-16 <i>D.M. Thornton</i> T6-20
1	Bechtel Hanford <i>S.C. Tindall</i> H0-02	2	U.S. Environmental Protection Agency <i>D.A. Faulk</i> B5-01 <i>D.R. Sherwood</i> B5-01

**No. of
Copies**

**No. of
Copies**

5 **Washington State Department of
Ecology**
Hanford Project Office

S.L. Dahl B5-18
D.N. Goswami B5-18
W.W. Soper B5-18
G.T. Tebb B5-18
N.H. Uziemblo B5-18

W.P. Hess K2-14
E.H. Hirt K5-10
W.J. Martin K9-14
A. Mendoza K5-25
A.F. Noonan K9-91
W.R. Park K5-17
T.J. Peters K5-25
B.M. Rapko P7-25
S.C. Slate K9-14
M.R. Smith (5) P8-08
T.L. Stewart (6) K9-91
Information Release (7)
K1-06

45 **Pacific Northwest National
Laboratory**

M.L. Alexander K3-58
D.L. Blanchard P7-25
W.F. Bonner K9-14
B.J. Burghard K5-25
S. D. Colson H8-03
M.A. Hansen K5-22
J.S. Hartman (12) K5-25