

X-RAY FLUORESCENCE (XRF) ANALYSIS OF HANFORD LOW ACTIVITY WASTE SIMULANTS

ANALYTICAL DEVELOPMENT

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ADC &
Reviewing
Official: [Signature]
(Name and Title)

Date: 5/11/06

ADDITIONAL APPROVAL IF APPLICABLE:

Official: [Signature]
Date: 6/9/06

May 2006

Washington Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500



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Printed in the United States of America

**Prepared For
U.S. Department of Energy**

Key Words:

Hanford, River Protection Project
XRF, Low Activity Waste

Retention:

Permanent

Key WTP C&T References:

Statement of Work – CCN091863
Test Plan - WSRC-TR-2004-00563

X-RAY FLUORESCENCE (XRF) ANALYSIS OF HANFORD LOW ACTIVITY WASTE SIMULANTS

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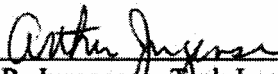
May 8, 2006


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Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-96SR18500





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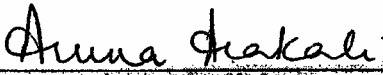

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LIST OF ACRONYMS

AD	Analytical Development
CRV	Concentrate Receipt Vessel
CVAA	Cold Vapor Atomic Absorption
ED-XRF	Energy Dispersive X-ray Fluorescence
FWHM	Full Width Half Measure
GFC	Glass Former Chemicals
HGAA	Hydride Generation Atomic Absorption
HLW	High Level Waste
ICDD	International Center for Diffraction Data
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IR	Infrared

IUPAC	International Union for Pure and Applied Chemistry
LAW	Low Activity Waste
LDR	Land Disposal Restriction
LOD	Limit of Detection
LOQ	Limit of Quantification
MDL	Method Detection Limit
MFPV	Melter Feed Preparation Vessel
NCAW	Neutralized Current Acid Waste
PDF	Powder Diffraction File
R&D	Research and Development
RPP	River Protection Project
%RSD	Percent Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TGA	Thermogravimetric Analysis
TRU	Transuranics
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WD-XRF	Wavelength Dispersive X-ray Fluorescence
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

1. Executive Summary

Savannah River National Laboratory (SRNL) was requested to develop an x-ray fluorescence (XRF) spectrometry method for elemental characterization of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) pretreated low activity waste (LAW) stream to the LAW Vitrification Plant. The WTP is evaluating the potential for using XRF as a rapid turnaround technique to support LAW product compliance and glass former batching. The overall objective of this task was to develop XRF analytical methods that provide the rapid turnaround time (<8 hours) requested by the WTP, while providing sufficient accuracy and precision to determine waste composition variations.

For Phase 1a, SRNL (1) evaluated, selected, and procured an XRF instrument for WTP installation, (2) investigated three XRF sample methods for preparing the LAW sub-sample for XRF analysis, and (3) initiated scoping studies on AN-105 (Envelope A) simulant to determine the instrument's capability, limitations, and optimum operating parameters. After preliminary method development on simulants and the completion of Phase 1a activities, SRNL received approval from WTP to begin Phase 1b activities with the objective of optimizing the XRF methodology.

Three XRF sample methods used for preparing the LAW sub-sample for XRF analysis were studied: direct liquid analysis, dried spot, and fused glass. The direct liquid method was selected because its major advantage is that the LAW can be analyzed directly without any sample alteration that could bias the method accuracy. It also is the fastest preparation technique – a typical XRF measurement could be completed in < 1hr after sample delivery. Except for sodium, the method detection limits (MDLs) for the most important analytes in solution, the hold point elements, were achieved by this method. The XRF detection limits are generally adequate for glass former batching and product composition reporting, but may be inadequate for some species (Hg, Cd, and Ba) important to land disposal restrictions. The long term precision (24-hr) also was good with percent relative standard deviations (%RSDs) < 10 % for most elements in filtered solution. There were some issues with a few elements precipitating out of solution over time affecting the long term precision of the method. Additional research will need to be performed to resolve this sample stability problem. Activities related to methodology optimization in the Phase 1b portion of the study were eliminated as a result of WTP request to discontinue remaining activities due to funding reduction.

These preliminary studies demonstrate that developing an XRF method to support the LAW vitrification plant is feasible. When funding is restored for the WTP, it is recommended that optimization of this technology should be pursued.

2. Introduction and Background

This document addresses the Savannah River National Laboratory (SRNL) Phase 1a and 1b activities detailed in task plan WSRC-TR-2004-00563, Rev1¹ in support of using x-ray fluorescence (XRF) spectrometry for elemental characterization of the Hanford Waste Treatment and Immobilization Plant (WTP) pretreated low activity waste (LAW) stream to the LAW Vitrification Plant. The WTP is evaluating the potential for using XRF as a rapid turnaround technique to support LAW product compliance and glass former batching. The overall objective of this task was to develop XRF analytical methods that provide the rapid turnaround time (<8 hours) requested by the WTP, while providing sufficient accuracy and precision to determine waste composition variations.

The LAW stream is primarily a liquid supernatant comprised of sodium hydroxide and sodium nitrate. It also contains trace metals, sulfate, aluminum, and potassium and up to 3.8-wt% entrained solids. The waste will be transferred to the Pretreatment Facility in batches up to 5,700,000-L. If required, the LAW stream will be concentrated up to a 5-molar (M) sodium concentration and filtered to remove any entrained solids. As necessary, strontium and transuranics (TRU) will be removed using a permanganate precipitation process and blended with the high level waste (HLW) feed. Cesium will be separated next using an ion exchange resin for ultimate blending with the HLW feed. The low activity treated waste will then be concentrated along with any LAW vitrification recycle solutions to 5 to 8-M sodium. The target concentration of the treated LAW batch will be defined by the relative concentrations of sodium and sulfate.

The Pretreatment Facility is designed to provide sufficient pretreated LAW feed to produce 90,000-kg of LAW glass per day. For LAW vitrification, 34,000-L batches are received from the Pretreatment Facility into Concentrate Receipt Vessels (CRV). Batches of treated LAW Feed are transferred from the Pretreatment Process to the LAW- CRV and then to the Melter Feed Preparation Vessel (MFPV) where the waste is combined with glass former chemicals (GFC). The LAW Concentrate Storage Vessel in the Pretreatment Facility is not well mixed and may change composition as new waste feeds are added during processing. As such, waste and glass formers can not be moved past the LAW - MFPV until selected analytical results are available on the LAW - CRV sample. This was the basis for identifying a product qualification hold point for CRV sample results at the MFPV- see Appendix A for the list of hold and non-hold point constituents. Each CRV batch is expected to refill an MFPV four times (or twice each for the two LAW MFPVs). The required analysis turnaround time is <15-hr with preferred turnaround time of <8-hr. Based on composition and radionuclide analyses, glass formulation calculations will specify the GFC batch to be added.

This project scope focused on testing (limits of detection, precision, resolution, and linear dynamic range) with Envelopes A (AN-105), B (AZ-101) and, C (AN-107) simulants of the LAW pretreated waste concentrates (50-60 weight % total solids; dissolved + suspended) that would be present in the Concentrate Receipt Vessel. The simulants were prepared by SRNL using the

¹ A. R. Jurgensen, D. M. Missimer, and C. C. Herman, "Task Technical and Quality Assurance Plan for X-Ray Fluorescence Method Development", WSRC-TR-2004-00563, Rev. 1, Savannah River Site, Aiken SC 29808 (March 22, 2005).

baseline concentrations for these waste tank streams (Table 1)². Although not detected in these three LAW waste tanks, other RCRA and CERCLA elements important to land disposal restrictions, including As, Hg, Sb, & Tl, were spiked at 25 or 50-µg/mL into a separate set of simulants. Although present in the waste, Ba, Ag, Cd, Ni, & Se also were spiked up to a minimum of 25- mg/mL into the second set of LAW simulants to increase their relative XRF sensitivity. The hold point elements at the top of Table 1 (Al, Cl, K, Na, and S) were given primary attention because of their relative importance in glass batching and wastefrom compliance. The additional constituents, including boron and fluorine, listed at the bottom of Table 1 cannot be determined using the proposed XRF method and, although part of the simulants matrix, were ignored during this study. The scope of the activities did not include the characterization of the treated low activity waste and glass former feed nor glass product from the melter.

For Phase 1a, SRNL:

- Evaluated, selected, and procured an XRF instrument for WTP installation (A report was previously issued on this task³.);
- Investigated three XRF sample methods for preparing the LAW sub-sample for XRF analysis; and
- Initiated scoping studies on AN-105 (Envelope A) simulant to determine the instrument’s capability, limitations, and optimum operating parameters.

After preliminary method development on simulants and the completion of Phase 1a activities, SRNL received approval from WTP to begin Phase 1b activities with the objective of optimizing the XRF methodology. Due to reduction in funding, WTP issued a notice to discontinue remaining workscope⁴ after only a fraction of the Phase 1b objectives had been completed.

Table 1. Hanford Actual Waste Tank Compositions

	Envelope A	Envelope B	Envelope C
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² R. E. Eibling and C. A. Nash, “Hanford Waste Simulants Created for Research and Development on the River Protection Project-Waste Treatment Plant”, WSRC-TR-2000-00338, Rev. 0, Savannah River Site, Aiken SC 29808 (February, 2001).

³ D. M. Missimer, A. R. Jurgensen, and R. L. Rutherford, “Support for the Selection and Procurement of the Hanford WTP X-ray Fluorescence Spectrometer”, SRNL-ADS-2005-00120, Savannah River Site, Aiken SC 29808 (March 22, 2005).

⁴ CCN 139029: Notice to Proceed BCR 06-004, Re. 0 – Discontinuing Laboratory Project Scope, April 26, 2006.

Component	Tank AN-105 Concentration mg/L	Tank AZ-101 Concentration mg/L	Tank AN-107 Concentration mg/L
Hold Point Elements			
Aluminum	39700	10670	386
Chloride	9090	200	1830
Potassium	7500	4624	1810
Sodium	233000	108990	195000
Sulfate	a	17670	a
Non-Hold Point Elements			
Calcium	40	a	591
Iron	a	a	1690
Magnesium	5	a	25
Phosphate	570	1503	1110
Silicon	211	a	a
Zinc	10	a	45
Zirconium	a	3.1	70
LDR Elements			
Barium	a	a	7
Cadmium	3	a	64
Chromium	1350	730	176
Lead	53	a	388
Nickel	a	a	530
Selenium	1	a	1
Silver	a	a	14
Additional XRF Elements			
Cerium	a	a	53
Copper	a	a	30
Lanthanum	a	a	46
Manganese	a	a	563
Molybdenum	82	a	36
Neodymium	a	a	96
Additional Constituents			
Ammonium	120	313	22
Boron	51	-	35
Carbonate	12540	23076	83936
Fluoride	190	1813	133
Hydroxide	58100	9030	340
Nitrate	165000	75632	230000
Nitrite	111000	65063	61000
Acetate	2070	a	1100
Citric Acid	a	a	8495
Ethylenediaminetetraacetic acid			5620
Formate	2880	a	10400
Glycolate	1150	a	18600
n-Hydroxyethylenediaminetriacetic acid	a	a	2140
Iminodiacetic Acid	a	a	5947
Nitilotriacetic Acid	a	a	561
Oxalate	610	a	826
Sodium Gluconate	a	a	3927

a) These constituents were not reported in reference 2.

3. Experimental

3.1 Simulant Preparation

The following LAW simulants were prepared using the baseline concentrations (Table 1) for the following waste tank streams to support the WTP XRF workscope:

- AN-105 Envelope A supernate,
- AZ-101 Envelope B supernate,
- AN-107 Envelope C supernate.

Simulants were used for this research because of cost of handling and analyzing radioactive solutions and because the effect of radiation on the instrument performance can probably be ignored, since the residual activity after waste pretreatment is low. WTP has recently adopted a design basis that limits the Cs-137 to less than 0.3-Ci/m³ of glass, which is equivalent to only 0.1 to 1- μ Ci/mL in LAW supernate. The primary problem with analyzing radioactive samples by XRF is the scattered radiation, which enters the same optical path as the x-ray radiation. The small amount of scattered γ or β radiation can be almost completely removed by careful adjustment of the pulse height analyzer, because the energies of the γ and high-energy β radiations are usually an order of magnitude greater than the x-ray radiation measured. If the XRF method proved viable with simulants, then the effect of residual radioactive Cs will have to be evaluated in the future. The source of each of these simulants and the specific issues in the preparation of these simulants will be described individually.

Reagent grade chemicals were used without any additional preparation to make these simulants. In addition, a second set of simulants was spiked with up to 50 μ g/mL LDR elements using inductively coupled plasma – atomic emission spectroscopy (ICP-AES) standard solutions. There were undissolved solids in all the simulants as indicated by the presence of floating and settled crystallized salts, even after through agitation and mixing. Simulant preparation was performed at room temperature and no attempt was made to redissolve the precipitates by heating. The supernate solutions were centrifuged for 2-hr at 3000 rpm on a Fisher Scientific Marathon 21K centrifuge to remove the majority of suspended material and then filtered through a Corning 0.2- μ m cellulose nitrate filter assembly. The filtrates were stored in Teflon bottles. The cations in the filtrates were analyzed by ICP-AES, inductively coupled plasma mass spectrometry (ICP-MS) for elements with $Z > 27$, cold vapor atomic absorption spectroscopy (CVAA) for Hg, and hydride generation atomic absorption spectroscopy (HGAA) for low concentrations of Se. Many of the constituents in the solutions, e.g. organics, can't be determined by XRF and were not analyzed. The residual solids were washed several times with deionized water to remove any soluble salts, air-dried, and analyzed to identify the crystalline compounds on a PANalytical X'Pert Pro x-ray diffractometer (XRD) and for semi-quantitative action content on a Spectro X-LAB2000 x-ray fluorescence spectrometer. The XRF scans and the XRD patterns of the filtered residues from the six simulant solutions (spiked and not spiked with LDR elements) are presented in Appendix C and Appendix D, respectively.

After the simulants were prepared and analyzed, it was conjectured the reason for the poor %-recovery was incorrect stoichiometry for some of the starting compounds. The mass loss of several of these compounds was measured by thermogravimetric analysis on a Netzsch STA409C TGA instrument. Of these compounds, only the zirconium nitrate monohydrate and the aluminum hydroxide from Aldrich had an incorrect stoichiometry because of additional waters of hydrate in the structure. The Al (AZ-101 only) and Zr (AZ-101+LDR, AN-107, & AN-107+LDR) ICP-AES results were adjusted by the correction factors listed in Table 2 in the ensuing data tables.

Table 2. TGA Mass Loss on Selected Compounds

Compound	Molecular Weight	Product	Molecular Weight	% TGA Mass Loss	Correction Factor
ZrO(NO ₃) ₂ ·H ₂ O	249.249	ZrO ₂	123.223	65.59	0.696^a
Al(NO ₃) ₃ ·9H ₂ O	375.134	Al ₂ O ₃	101.961	85.99	1.03
Na ₂ SiO ₃ ·9H ₂ O	284.201	Na ₂ SiO ₃	122.063	56.89	1.00
Al(OH) ₃ (Alcoa S-11)	78.004	Al ₂ O ₃	101.961	34.83	1.00
Al(OH) ₃ (J.T. Baker)	78.004	Al ₂ O ₃	101.961	34.21	1.01
Al(OH) ₃ (Aldrich)	78.004	Al ₂ O ₃	101.961	46.3	0.822^a
Mg(NO ₃) ₂ ·6H ₂ O	256.407	MgO	40.304	84	1.018

^a ICP-AES results were adjusted by these correction factors.

3.1.1 Envelope A

Envelope A waste was generated by evaporating the low organic content, waste supernates stored in single shell tanks and the supernate produced by the Hanford B plant. Envelope A can be generally characterized as an alkaline ([OH]⁻>1 M), high sodium (>8 M) supernate. The envelope contains ¹³⁷Cs and ⁹⁹Tc at concentrations that require removal prior to LAW vitrification. The majority of the LAW supernate to be vitrified in the initial phase of the RPP-WTP will be Envelope A.

Envelope A simulant was based on the supernate from Tank AN-105, which was decanted from the solids within the waste tank. Organic speciation data was not available for the AN-105 waste. Since a very similar waste, Tank AW-101, was also sampled and analyzed during the initial privatization studies, the values for these organic compounds were taken from that waste analysis. The composition basis used for the AN-105 simulant is listed in the first column of Table 1. The computations performed to transform Table 1 data into their relevant compounds are detailed in Appendix A in WSRC-TR-2000-00338⁵. The actual recipe

⁵ R. E. Eibling and C. A. Nash, "Hanford Waste Simulants Created for Research and Development on the River Protection Project-Waste Treatment Plant", WSRC-TR-2000-00338, Rev. 0, Appendix A, Savannah River Site, Aiken SC 29808 (February, 2001).

for this simulant with a detailed list of the chemicals, including manufacturer, part number and lot numbers, and their added weights are listed in Appendix B of this document.

The XRF measurable waste components in the test batches of AN-105 and AN-105+LDR simulants are listed in Tables 3 & 4. The elements highlighted in bold blue are unreasonably lower than targeted based on the weights of the starting reagents. The semi-quantitative XRF and qualitative XRD results are presented in Tables 5 & 6. The low values can be explained and summarized as follows:

AN-105

- **Al** - excess starting reagent, $\text{Al}(\text{OH})_3$, and the precipitation of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24}\cdot 2\text{H}_2\text{O}$, and Al_2O_3
- **Ca** - precipitation of $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24}\cdot 2\text{H}_2\text{O}$, $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, and $\text{CaPO}_3(\text{OH})\cdot 2\text{H}_2\text{O}$
- **Mg** - probably by precipitation, forming compounds similar to Ca.
- **Si** - $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24}\cdot 2\text{H}_2\text{O}$

AN-105+LDR

- **Al** - precipitation of $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24}\cdot 2\text{H}_2\text{O}$
- **Ca** - precipitation of $\text{CaC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ($K_{\text{sp}} = 2.3 \times 10^{-9}$), CaCO_3 ($K_{\text{sp}} = 3.4 \times 10^{-9}$), and $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24}\cdot 2\text{H}_2\text{O}$
- **Mg** - probably by precipitation, forming compounds similar to Ca.
- **Si** - $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24}\cdot 2\text{H}_2\text{O}$
- **Ag** - precipitation of Ag_3Hg_2 and $\text{Ag}_{1.04}\text{Cd}_{0.96}$. Even if these alloys didn't form, Ag could be lost by photoreduction to Ag or precipitation as AgOH ($K_{\text{sp}} = 2.6 \times 10^{-8}$), AgCl ($K_{\text{sp}} = 1.2 \times 10^{-10}$), Ag_2CO_3 ($K_{\text{sp}} = 8.5 \times 10^{-12}$), Ag_2CrO_4 ($K_{\text{sp}} = 1.1 \times 10^{-12}$), or $\text{Ag}_2\text{C}_2\text{O}_4$ ($K_{\text{sp}} = 5.4 \times 10^{-12}$).
- **Ba** - precipitation of BaCrO_4 ($K_{\text{sp}} = 1.2 \times 10^{-10}$).
- **Cd** - precipitation of $\text{Ag}_{1.04}\text{Cd}_{0.96}$
- **Hg** - precipitation of Ag_3Hg_2 . Even if this alloy didn't form, $\text{Hg}(\text{OH})_2$ ($K_{\text{sp}} = 3 \times 10^{-26}$), $\text{Hg}_2\text{C}_2\text{O}_4$ ($K_{\text{sp}} = 1.8 \times 10^{-13}$), or Hg_2CO_3 ($K_{\text{sp}} = 3.6 \times 10^{-17}$), could precipitate in this high OH solution.
- **Ni** - precipitation of $\text{Na}_2\text{NiAlF}_7$

Table 3. Analytical Results for AN-105 Simulant

Component	Units	Target	Measured ICP-MS	Measured ICP-AES	% of Target
Al	mg/L	39700	a	34200	87
B	mg/L	51	a	50	98
Ca	mg/L	40	a	<0.64	<2
Cd	mg/L	3	2.8	3	93, 100
Cr	mg/L	1350	a	1260	93
K	mg/L	7500	a	7860	105
Mg	mg/L	5	a	<0.1	<2
Mo	mg/L	82	82	b	100
Na	mg/L	233000	a	217000	93
P	mg/L	185	a	193	104
Pb	mg/L	53	52	b	98
Se	mg/L	1	1.3 ¹		130
Si	mg/L	211	a	168	80
Zn	mg/L	10	10	12	120
<i>Cu²</i>	<i>mg/L</i>			<i>0.2</i>	
<i>Fe²</i>	<i>mg/L</i>			<i>3.1</i>	
<i>Ni²</i>	<i>mg/L</i>			<i>5.3</i>	
<i>Sr²</i>	<i>mg/L</i>			<i>2.9</i>	
<i>Ti²</i>	<i>mg/L</i>			<i>0.6</i>	
<i>V²</i>	<i>mg/L</i>			<i>9.6</i>	
<i>Zr²</i>	<i>mg/L</i>			<i>0.5</i>	

Note: the elements in blue had unreasonably low % target values.

¹ Se concentration determined by Hydride Generation Atomic Absorption Spectrometry.

² The elements in red italic are contaminants from the reagent grade compounds.

a) These elements were not measured by ICP-MS.

b) These elements were not measured by ICP-AES.

Table 4. Analytical Results for AN-105 Simulant Spiked with LDR Elements

Component	Units	Target	Measured ICP-MS	Measured ICP-AES	% of Target
Ag	mg/L	25	0.007	<1.0	0.03
Al	mg/L	39700	a	34700	87
As	mg/L	50	53	b	106
B	mg/L	51	a	53	104
Ba	mg/L	25	1.4	1.6	5.6, 6.4
Ca	mg/L	40	a	<3.2	<8
Cd	mg/L	25	18	20	72, 80
Cr	mg/L	1350	a	1280	95
Hg	mg/L	25	0.19 ¹		0.8
K	mg/L	7500	a	7490	100
Mg	mg/L	5	a	<0.7	<14
Mo	mg/L	82	82	b	100
Na	mg/L	233000	a	228000	98
Ni	mg/L	25	a	<0.1	<0.4
P	mg/L	185	a	191	103
Pb	mg/L	53	50	57	94, 108
Sb	mg/L	25	24	b	96
Se	mg/L	25	27	b	108
Si	mg/L	211	a	140	66
Tl	mg/L	25	25	b	100
Zn	mg/L	10	10	12	100, 120
<i>Sr²</i>	<i>mg/L</i>		<i>a</i>	<i>1.6</i>	
<i>Zr²</i>	<i>mg/L</i>		<i>a</i>	<i>3.1</i>	

Note: the elements in blue had unreasonably low % target values.

¹ Hg was determined by Cold Vapor Atomic Absorption Spectrometry.

² The elements in red italic are contaminants from the reagent grade compounds.

a) These elements were not measured by ICP-MS.

b) These elements were not measured by ICP-AES.

Table 5. Semi-quantitative XRF Analysis of Tank AN-105 Simulant Filtered Residue

Tank AN-105		Tank AN-105 + LDR	
Element	Normalized Wt%	Element	Normalized Wt%
Calcium	50.1	Calcium	27.8
Aluminum	40.0	Aluminum	15.0
Silicon	6.4	Mercury	12.2
Iron	1.0	Silicon	11.1
Nickel	0.8	Nickel	9.4
Phosphorus	0.4	Silver	6.9
Titanium	0.3	Barium	6.4
Strontium	0.3	Chromium	5.7
Chromium	0.2	Phosphorus	1.4
Lead	0.2	Zirconium	1.0
Cadmium	0.1	Thallium	0.9
Manganese	0.06	Cadmium	0.9
Zinc	0.05	Iron	0.7
Zirconium	0.05	Lead	0.3
Gallium	0.02	Hafnium	0.2
Barium	0.01	Antimony	0.2
		Sulfur	0.1

Table 6. XRD Analysis of Envelope A Simulant Filtered Residue

Tank AN-105	
Compound	Mineral Name
Al(OH) ₃	Gibbsite
Ca ₃ Al ₂ (OH) ₁₂	Katoite
Na ₆ CaAl ₆ Si ₆ (CO ₃)O ₂₄ ·2H ₂ O	Cancrinite
Al ₂ O ₃	Corundum
CaPO ₃ (OH)·2H ₂ O (?)	Brushite

Tank AN-105 + LDR	
Compound	Mineral Name
CaC ₂ O ₄ ·2H ₂ O	Whewellite
BaCrO ₄	
CaCO ₃	Calcite
Na ₆ CaAl ₆ Si ₆ (CO ₃)O ₂₄ ·2H ₂ O	Cancrinite
Ag ₃ Hg ₂	Paraschachnerite
Ag _{1.04} Cd _{0.96} (?)	
Na ₂ NiAlF ₇ (?)	
CaPO ₃ (OH)·2H ₂ O (?)	Brushite

The presence of compounds in this table labeled with a “?” is questionable.

3.1.2 Envelope B

Envelope B is sometimes referred to as the supernate phase from Neutralized Current Acid Waste (NCAW). The LAW glass specifications will require ¹³⁷Cs and ⁹⁹Tc removal. Envelope B is expected to be high in glass limiting constituents such as sulfate, phosphate, and halides. Only a small part of the LAW waste to be vitrified in the initial phase is Envelope B.

Tank AZ-101 was a NCAW receiver and the supernate in the tank has been well-characterized by Battelle and Hanford 222S. The spreadsheets used to calculate the envelope B simulant composition and recipe are shown in Appendix B of WSRC-TR-2000-00338⁶. The inventory contains only a few of the major waste compounds, no organic compounds, and no trace species. The middle column of Table 1 specifies the analytical information the simple simulant is based upon. The actual recipe for this simulant with a detailed list of the chemicals, including manufacturer, part number and lot numbers, and their added weights are listed in Appendix B of this document.

⁶ R. E. Eibling and C. A. Nash, “Hanford Waste Simulants Created for Research and Development on the River Protection Project-Waste Treatment Plant”, WSRC-TR-2000-00338, Rev. 0, Appendix B, Savannah River Site, Aiken SC 29808 (February, 2001).

The XRF measurable waste elements in the AZ-101 and AZ-101+LDR simulants are presented in Tables 7 & 8. Again, the elements highlighted in bold blue are lower than targeted based on the weights of the starting reagents. The semi-quantitative XRF and qualitative XRD results are listed in Tables 9 & 10. The low values can be explained and summarized as follows:

AZ-101

- **Al** – conversion of excess amorphous starting reagent, Al(OH)₃, to two crystalline polymorphs, gibbsite and bayerite, and the precipitation of AlPO₄·xH₂O
- **Zr** - precipitation of Zr(HPO₄)₂

AZ-101+LDR

- **Al** - conversion of excess amorphous starting reagent, Al(OH)₃ to crystalline gibbsite
- **Zr** - precipitation of Zr(HPO₄)₂

Because of the voluminous Al(OH)₃ precipitate, it was difficult to identify the end products of the LDR precipitation by XRD. The XRF data confirms that these elements are present in the filtered residue. It can be speculated that the compounds are the same as in the AN-105+LDR residue.

Table 7. Analytical Results for AZ-101 Simulant

Component	Units	Target	Measured ICP-MS	Measured ICP-AES	% of Target
Al	mg/L	10668	a	7190	68
<i>Al</i>	<i>mg/L</i>	<i>8769¹</i>	<i>a</i>	<i>7190</i>	<i>83</i>
Cr	mg/L	730	a	668	92
K	mg/L	4624	a	4530	98
Na	mg/L	108989	a	96800	89
P	mg/L	490	a	478	98
S	mg/L	5898	-	6490	110
Zr	mg/L	3.1	1.2	1.4	39, 45
<i>Zr</i>	<i>mg/L</i>	<i>2.2²</i>	<i>1.2</i>	<i>1.4</i>	<i>55, 64</i>
<i>Ba³</i>	<i>mg/L</i>		<i>a</i>	<i>0.5</i>	
<i>Ca³</i>	<i>mg/L</i>		<i>a</i>	<i>1.8</i>	
<i>Ni³</i>	<i>mg/L</i>		<i>a</i>	<i>1.3</i>	
<i>Sr³</i>	<i>mg/L</i>		<i>a</i>	<i>1.5</i>	
<i>V³</i>	<i>mg/L</i>		<i>a</i>	<i>2.0</i>	
<i>Zn³</i>	<i>mg/L</i>		<i>a</i>	<i>1.0</i>	

Note: the elements in blue had unreasonably low % target values.

¹ Al concentration corrected for TGA mass loss.

² Zr concentration corrected for TGA mass loss.

³ The elements in red italic are contaminants from the reagent grade compounds.

a) These elements were not measured by ICP-MS.

Table 8. Analytical Results for AZ-101 Simulant Spiked with LDR Elements

Component	Units	Target	Measured ICP-MS	Measured ICP-AES	% of Target
Ag	mg/L	25	0.029	<0.2	1.2
Al	mg/L	10668	a	1200	11
As	mg/L	50	54	b	108
Ba	mg/L	25	0.41	0.49	1.6, 1.7
Cd	mg/L	25	5.1	5.2	20, 21
Cr	mg/L	730	a	698	96
Hg	mg/L	25	0.70 ¹		2.8
K	mg/L	4624	a	4410	95
Na	mg/L	108989	a	98600	90
Ni	mg/L	25	a	<0.07	<0.3
P	mg/L	490	a	502	102
Pb	mg/L	25	25	28	100, 112
S	mg/L	5898	a	5900	100
Sb	mg/L	25	24	b	96
Se	mg/L	25	26	b	104
Tl	mg/L	25	24	b	96
Zr	mg/L	3.1	0.93	0.89	30, 29
Zr	mg/L	2.2 ²	0.93	0.89	42, 40
Ca³	mg/L		a	41.6	

Note: the elements in blue had unreasonably low % target values.

¹ Hg was determined by Cold Vapor Atomic Absorption Spectrometry.

² Zr concentration corrected for TGA mass loss.

³ The elements in red italic are contaminants from the reagent grade compounds.

a) These elements were not measured by ICP-MS.

b) These elements were not measured by ICP-AES.

Table 9. Semi-quantitative XRF Analysis of Tank AZ-101 Simulant Filtered Residue

Tank AZ-101		Tank AZ-101+ LDR	
Element	Wt%	Element	Wt%
Aluminum	85.3	Aluminum	98.3
Calcium	11.3	Nickel	0.4
Phosphorus	2.2	Barium	0.3
Iron	0.4	Silver	0.2
Zirconium	0.2	Mercury	0.2
Zinc	0.2	Cadmium	0.2
Strontium	0.1	Calcium	0.1
Nickel	0.1	Chromium	0.1
Titanium	0.06	Iron	0.1
Chromium	0.05	Lead	0.02
Manganese	0.05	Gallium	0.02
Sulfur	0.03	Antimony	0.02
Barium	0.03	Zirconium	0.01
Gallium	0.02		
Cadmium	0.01		
Yttrium	0.01		
Thorium	0.005		
Bromine	0.0004		

Table 10. XRD Analysis of Envelope B Simulant Filtered Residue

Tank AZ-101	
Compound	Mineral Name
Al(OH) ₃	Bayerite
Al(OH) ₃	Gibbsite
Ca ₅ (PO ₄) ₃ F ₁	Fluorapatite
AlPO ₄ ·xH ₂ O (?)	
Zr(HPO ₄) ₂ (?)	

Tank AZ-101 + LDR	
Compound	Mineral Name
Al(OH) ₃	Gibbsite

The presence of compounds in this table labeled with a “?” is questionable.

3.1.3 Envelope C

Envelope C waste was produced from evaporation of wastes derived from high organic content single-shell tank waste and waste generated during the Cs/Sr separation and encapsulation process conducted at the Hanford B plant. The waste is characterized by the high organic carbon content because of the presence of organic complexing agents and their decomposition products. Due to the complexing agents, the concentration of ^{90}Sr and TRU will require removal using the Sr/TRU precipitation and filtration process. Removal of ^{137}Cs by ion exchange will also be required.

The analytical basis for the AN-107 simulant is listed in the last column of Table 1. The real waste has an extensive list of organic compounds, which can act as complexing agents, of which only the major ones are included in this formulation. The spreadsheets used to calculate the envelope C simulant composition and recipe can be found in Appendix C of WSRC-TR-2000-00338⁷. The actual recipe for this stimulant with a detailed list of the chemicals, including manufacturer, part number and lot numbers, and their added weights are listed in Appendix B of this document.

The XRF measurable waste elements in the AN-107 and AN-107+LDR simulants are presented in Tables 11 & 12. Again, the elements highlighted in bold blue are lower than targeted based on the weights of the starting reagents. The semi-quantitative XRF and qualitative XRD results are listed in Tables 13 & 14. The low values can be explained and summarized as follows:

AN-107

- **Al** - precipitation of $\text{NaAl}(\text{OH})_2(\text{CO}_3)$
- **Ca** - precipitation of CaCO_3 ($K_{\text{sp}} = 3.4 \times 10^{-9}$)
- **Mg** - probably by precipitation, forming compounds similar to Ca.
- **Ag** - photoreduction to Ag

AN-107+LDR

- **Al** - precipitation of $\text{NaAl}(\text{OH})_2(\text{CO}_3)$ and $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24} \cdot 2\text{H}_2\text{O}$
- **Ca** - precipitation of CaCO_3 ($K_{\text{sp}} = 3.4 \times 10^{-9}$) and $\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24} \cdot 2\text{H}_2\text{O}$
- **Mg** - probably by precipitation, forming compounds similar to Ca
- **Ag** - precipitation of $\text{Ag}_{13}\text{Hg}_7$ and AgCd . Ag could be lost by photoreduction to Ag or precipitation as AgOH ($K_{\text{sp}} = 2.6 \times 10^{-8}$), AgCl ($K_{\text{sp}} = 1.2 \times 10^{-10}$), Ag_2CO_3 ($K_{\text{sp}} = 8.5 \times 10^{-12}$), Ag_2CrO_4 ($K_{\text{sp}} = 1.1 \times 10^{-12}$), or $\text{Ag}_2\text{C}_2\text{O}_4$ ($K_{\text{sp}} = 5.4 \times 10^{-12}$).
- **Hg** - precipitation of $\text{Ag}_{13}\text{Hg}_7$. $\text{Hg}(\text{OH})_2$ ($K_{\text{sp}} = 3 \times 10^{-26}$), $\text{Hg}_2\text{C}_2\text{O}_4$ ($K_{\text{sp}} = 1.8 \times 10^{-13}$), or Hg_2CO_3 ($K_{\text{sp}} = 3.6 \times 10^{-17}$) could precipitate in this high OH^- solution.

⁷ R. E. Eibling and C. A. Nash, "Hanford Waste Simulants Created for Research and Development on the River Protection Project-Waste Treatment Plant", WSRC-TR-2000-00338, Rev. 0, Appendix C, Savannah River Site, Aiken SC 29808 (February, 2001).

Table 11. Analytical Results for AN-107 Simulant

Component	Units	Target	Measured ICP-MS	Measured ICP-AES	% of Target
Ag	mg/L	14	0.42	1.4	3, 10
Al	mg/L	386	a	215	56
B	mg/L	35	a	33	94
Ba	mg/L	7	6.5	8.3	93, 118
Ca	mg/L	591	a	246	42
Cd	mg/L	64	63	64	98, 100
Ce	mg/L	53	46	b	87
Cu	mg/L	30	28	28	93, 93
Cr	mg/L	176	a	157	89
Fe	mg/L	1690	a	1650	98
K	mg/L	1810	a	1900	105
La	mg/L	46	44	47	96, 102
Mg	mg/L	25	a	19	55
Mn	mg/L	563	a	550	98
Mo	mg/L	36	38	b	106
Na	mg/L	195000	a	183000	94
Ni	mg/L	530	a	543	102
Nd	mg/L	96	89	b	93
P	mg/L	362	a	379	105
Pb	mg/L	388	376	400	97, 103
Se	mg/L	1	3.6 ¹		360
Zn	mg/L	45	43	48	96, 107
Zr	mg/L	70	44	47	63, 67
Zr	mg/L	48.7 ²	44	47	90, 97
Sr³	mg/L		a	56	
V³	mg/L		a	6.7	

Note: the elements in blue had unreasonably low % target values.

¹ Se concentration determined by Hydride Generation Atomic Absorption Spectrometry.

² Zr concentration corrected for TGA mass loss.

³ The elements in red italic are contaminants from the reagent grade compounds.

a) These elements were not measured by ICP-MS.

b) These elements were not measured by ICP-AES.

Table 12. Analytical Results for AN-107 Simulant Spiked with LDR Elements

Component	Units	Target	Measured ICP-MS	Measured ICP-AES	% of Target
Ag	mg/L	25	0.16	<1.0	6.4
Al	mg/L	386	a	151	39
As	mg/L	50	57.3	b	114
B	mg/L	35	a	31	89
Ba	mg/L	25	26	25	104, 100
Ca	mg/L	591	a	298	50
Cd	mg/L	64	14	13	22, 21
Ce	mg/L	53	49	b	92
Cu	mg/L	30	28	29	93, 97
Cr	mg/L	176	a	155	88
Fe	mg/L	1690	a	1630	96
Hg	mg/L	25	0.20 ¹		0.8
K	mg/L	1810	a	1810	100
La	mg/L	46	43	45	93, 98
Mg	mg/L	25	a	14	56
Mn	mg/L	563	a	546	97
Mo	mg/L	36	38	b	106
Na	mg/L	195000	a	180000	93
Ni	mg/L	530	a	527	99
Nd	mg/L	96	91	b	95
P	mg/L	362	a	374	103
Pb	mg/L	388	353	402	91, 104
Sb	mg/L	25	25	b	100
Se	mg/L	25	28	b	112
Tl	mg/L	25	26	b	104
Zn	mg/L	45	41	47	91, 104
Zr	mg/L	70	48	47	69, 67
Zr	mg/L	48.7 ²	48	47	99, 97
<i>Sr³</i>	<i>mg/L</i>		<i>a</i>	<i>68</i>	

Note: the elements in blue had unreasonably low % target values.

¹ Hg was determined by Cold Vapor Atomic Absorption Spectrometry.

² Zr concentration corrected for TGA mass loss.

³ The element in red italic is a contaminant from the reagent grade compounds.

a) These elements were not measured by ICP-MS.

b) These elements were not measured by ICP-AES.

Table 13. Semi-quantitative XRF Analysis of Envelope C Simulant Filtered Residue

Tank AN-107		Tank AN-107 + LDR	
Element	Wt%	Element	Wt%
Calcium	84.7	Calcium	70.1
Iron	4.4	Aluminum	7.0
Aluminum	3.0	Iron	5.5
Silver	2.7	Mercury	5.5
Chromium	2.7	Silver	4.4
Manganese	1.2	Chromium	3.8
Lead	0.4	Manganese	1.2
Lanthanum	0.2	Lanthanum	0.5
Cerium	0.1	Lead	0.4
Phosphorus	0.1	Cerium	0.4
Vanadium	0.1	Barium	0.3
Nickel	0.1	Cadmium	0.3
Silicon	0.1	Vanadium	0.2
Barium	0.04	Phosphorus	0.2
Strontium	0.03	Nickel	0.1
Zirconium	0.03	Antimony	0.1
Zinc	0.03	Copper	0.04
Cadmium	0.02	Zinc	0.03
		Zirconium	0.03

Table 14. XRD Analysis of Envelope C Simulant Filtered Residue

Tank AN-107	
Compound	Mineral Name
CaCO ₃	Calcite
Ag	Silver
NaAl(OH) ₂ (CO ₃)	Dawsonite

Tank AN-107 + LDR	
Compound	Mineral Name
CaCO ₃	Calcite
NaAl(OH) ₂ (CO ₃)	Dawsonite
Na ₆ CaAl ₆ Si ₆ (CO ₃)O ₂₄ ·2H ₂ O	Cancrinite
AgCd	
Ag ₁₃ Hg ₇ (?)	

The presence of compounds in this table labeled with a “?” is questionable.

There are several general observations about the simulants that can be made with regard to the solubility of the individual cations:

- 1) The target Al composition was never attained, indicating that the real waste tank supernates are supersaturated in aluminum or that additional ligands or complexing agents are present in the waste that solubilize the excess aluminum.
- 2) Ca precipitates almost completely as the carbonate, oxalate, or as an aluminosilicate (cancrinite), except in AN-107 where there are a large number of ligands (EDTA, gluconate, etc.) that complex the element. Since Mg is also an alkaline earth element, it would behave similarly.
- 3) Si was only added to the AN-105 simulant, where it partially precipitated as cancrinite ($\text{Na}_6\text{CaAl}_6\text{Si}_6(\text{CO}_3)\text{O}_{24}\cdot 2\text{H}_2\text{O}$).
- 4) Zr is only partially soluble in AZ-101 where it precipitates as a phosphate, $(\text{Zr}(\text{HPO}_4)_2)$, but is completely soluble in AN-107, where a large number of potential complexing agents are present.
- 5) Ba partially precipitates out of AN-105 and possibly AZ-101 as the chromate BaCrO_4 , but is completely soluble in AN-107. Again this could be because of the organic ligands in this simulant.
- 6) The 25 $\mu\text{g}/\text{mL}$ antimony, 50 $\mu\text{g}/\text{mL}$ arsenic, 25 $\mu\text{g}/\text{mL}$ selenium, and 25 $\mu\text{g}/\text{mL}$ thallium spikes were completely soluble in all three high pH matrices.
- 7) In contrast, silver and mercury were very insoluble in the three simulants, forming insoluble alloys, possibly hydroxides, carbonates, and oxalates or in the case of silver photoreducing to elemental metal. The method detection limits (MDLs) for Hg and Ag cannot be determined in the simulants since the XRF intensities at their solubility limit are too low to measure on the ZSX-Mini II instrument.
- 8) Cd partially precipitates out of all three spiked solutions as a binary alloy with Ag, AgCd . It was noted that if Ag is not present in AN-107, Cd remains in solution at concentrations up to at least 64 $\mu\text{g}/\text{mL}$.

3.2 Instrumentation

As part of Phase 1a activities in support of using x-ray fluorescence spectrometry (XRF) for elemental analysis, SRNL was requested to compare and evaluate the technical attributes of several x-ray fluorescence bench top systems. This instrument will ultimately be used at the Hanford Waste Treatment and Immobilization Plant for analyzing their low activity waste (LAW) compositions in the Concentrate Receipt Vessel (CRV). Energy and wavelength dispersive instruments from five manufacturers, Spectro Analytical Instruments, Thermo Electron Corporation, PANalytical, Bruker AXS, Inc., and Rigaku/MSI, Inc., were compared. On average, the Rigaku ZSX-Mini II XRF (Figure 1) outperformed all the other small instruments in this investigation⁸. Of particular importance, the process control light element (Na-Ca) background subtracted peak intensities were orders of magnitude better. The unit is also small enough to install in a radiological hood.

⁸ D. M. Missimer and A. R. Jurgensen, "Support for the Selection and Procurement of the Hanford WTP X-Ray Fluorescence Spectrometer", SRNL-ADS-2005-0120, Westinghouse Savannah River Company, March 2005.



Figure 1. Rigaku ZSX-Mini II benchtop x-ray fluorescence spectrometer.

The Rigaku-MSZ ZSX-Mini II is a WD-XRF system that has an extended element range from fluorine (F) through plutonium (Pu). In wavelength-dispersive x-ray spectrometry (WD-XRF), the individual x-rays are separated on the basis of their wavelength by diffraction from pure crystals as described by Bragg's law. Its linear dynamic range with either a gas flow proportional detector or scintillation counter is >1Mcps compared to only 30-kcps for an energy-dispersive instrument with a Si(Li) detector. The WD-XRF is also better at resolving weak peaks from strong peaks and is significantly more sensitive for light element determinations. Its primary drawbacks are that each element x-ray line is measured sequentially increasing the analysis time compared to an energy-dispersive instrument and it is mechanically a more complex instrument. The ZSX-Mini II can accommodate a wide variety of sample matrices, including solids, pressed or loose powders and liquids in air, under vacuum or under a He purge. The maximum sample size is 42-mm diameter (in sample cup) and 60-mm height with the analyzed area fixed at 20-mm diameter. The system includes the following: 50-W Pd target x-ray tube with a 75- μ m Be window, two detectors (a flow proportional counter for light elements and a scintillation counter for heavy elements), 3 analyzing crystals for wavelength (energy) separation, and a 12 position sample tray (Figure 2). To reduce the size to make it cost competitive with the ED-XRFs, Rigaku sacrificed some sensitivity. The ZSX-Mini has a polymeric film, which isolates the sample chamber from the crystal chamber during helium analysis. This film adversely absorbs some of the sodium and magnesium x-rays produced by the sample.

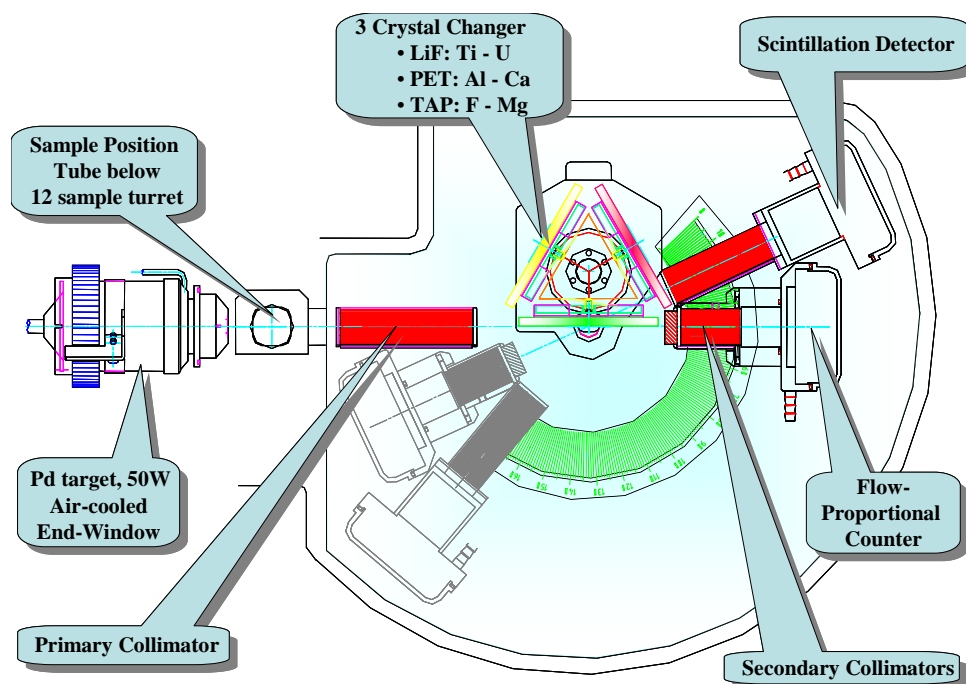


Figure 2. Rigaku ZSX-Mini II block diagram.

One important task for this program was determining the optimum instrument parameters to use for the LAW analysis. Parameters investigated included x-ray tube voltage and current settings, peak and background location selection. To reduce cost, the crystal selection and detector choice for each x-ray transition ($K\alpha$, $L\alpha$, etc.), which are selectable in larger WD-XRF systems, were fixed by the manufacturer. The hardware limitation on the goniometer range in the Rigaku ZSX-Mini II when using the preferred crystal, $LiF(200)$ ⁹, precludes its use for K and Ca analysis. Instead Ca and K are analyzed using the less sensitive PET crystal. To determine the peak and background point(s), slow scans across each analyte peak in all three matrices were run at maximum x-ray tube power, 40-kV and 1.2-mA. Element x-ray transitions (line) were selected on the basis of sensitivity and absence of overlapping spectral interferences from other elements in the matrix. The instrument conditions are listed in Table 15. Representative element scans with labeled background positions are included in Appendix E.

XRF cannot determine all waste elements required for glass former batching and product composition reporting. Notably, elements of atomic numbers lower than sodium (i.e. lower than 10) cannot be determined with the Rigaku XRF system. This excludes Li [3] and B [5], which are important to glass former addition, but should not be in the waste or are in the waste in low concentrations relative to the mass in glass formers being added; F [9] that is important to process control; and Be [3] which is important to land disposal restrictions. If needed, these species will require determination by an alternative method.

⁹ H. Bennet, XRF Analysis of Ceramics, Minerals, and Allied Materials, John Wiley and Sons, New York, 1992.

Table 15. Instrument Conditions

Element	Line	Crystal	Detector	Peak (deg)	Time (sec)	BG1 (deg)	Time (sec)	BG2 (sec)	Time (sec)
Na	K α	RX35 ¹	PC ²	25.091	200	29.000	100	a	a
Al	K α	PET ³	PC	144.610	200	140.000	100	a	a
P	K α	PET	PC	89.265	200	92.000	100	a	a
S	K α	PET	PC	75.616	200	79.000	100	a	a
Cl	K α	PET	PC	65.334	200	68.000	100	a	a
K	K α	PET	PC	50.513	200	48.500	100	a	a
Ca ⁴	K α	PET	PC	50.513	200	45.200	100	a	a
Cr	K α	LiF1 ⁵	SC ⁶	69.319	200	70.500	100	a	a
Mn	K α	LiF1	SC	62.900	200	64.500	100	a	a
Fe	K α	LiF1	SC	57.483	200	59.000	100	a	a
Ni	K α	LiF1	SC	48.607	200	50.000	100	a	a
Cu	K α	LiF1	SC	45.010	200	44.350	100	45.650	100
Zn	K α	LiF1	SC	41.780	200	41.000	100	42.500	100
Zr	K α	LiF1	SC	22.477	200	21.900	100	23.100	100
Mo	K α	LiF1	SC	20.263	200	19.700	100	20.900	100
La	L α	LiF1	SC	82.900	200	84.000	100	a	a
Ce	L α	LiF1	SC	79.000	200	80.000	100	a	a
Nd	L α	LiF1	SC	72.120	200	73.000	100	a	a
Pb	L α	LiF1	SC	33.920	200	32.950	100	34.950	100

¹W/Si multilayer diffraction crystal, 2d = 55 Å

²10% methane / 90 % argon flow proportional counter

³Pentaerythritol diffraction crystal (020), 2d = 8.808 Å

⁴Potassium spectral interference correction required at these low calcium concentrations.

⁵Lithium fluoride (200) crystal, 2d = 4.027 Å

⁶Sodium iodide scintillation detector

a) Only one background point was measured.

3.3 Sample Preparation Optimization

Three XRF sample methods used for preparing the LAW sub-sample for XRF analysis were investigated: direct liquid analysis, dried spot, and fused glass. The intent of the studies was to develop a simple XRF sample preparation scheme, which will meet the required LAW product compliance and glass former batching criteria including: rapid turn around time, good sensitivity, and low analytical errors/uncertainties. An important part of the sample preparation for x-ray fluorescence analysis is removing a representative sample from the sample bottle. The data from separate HLW studies using a vial insert and a sub-sampling method from the peanut vial will provide guidance for LAW sub-sampling and are not addressed in this report.

3.3.1 Direct Liquid Analysis

In this simplest method, 5-mL of sample liquid was pipetted into a 31-cm diameter circular sample cell, which is covered on the bottom by a thin x-ray transmitting film. The choice of polymer film is important since it may degrade rapidly in contact with the high hydroxide sample solutions. The chemical durability of five common XRF sample films to the highly corrosive simulants was investigated. The polymeric films, their thickness, and manufacturer are listed in Table 16. As shown in Table 17 only Ultralene™ (polyethylene) and polypropylene survived a 24-hr exposure to each of the three high pH LAW simulants. Ultralene™ was selected for LAW analysis, since it is thinner and has lower light element absorption (See Section 4.1.3). An alternative source of polyethylene is Prolene™ from Chemplex Industries.

Table 16. Film Description

Film	Polymer	Thickness	Manufacturer Part No.
Ultralene™	Polyethylene	4-μm	Spex #3526
Polypropylene	Polypropylene	5-μm	Spex #3521
Polycarbonate	Polycarbonate	5-μm	Spex #3522
Kapton™	Polyimide	7.5-μm	Chemplex #447
Mylar™	Polyester (Polyethylene Terephthalate)	4-μm	Somar #3615-33

The upper cup surface was covered with a microporous Teflon™ film that allows for pressure equalization during the analysis. This prevents the sample surface film from distending outwards as the sample is heated, changing the sample to source and detector distances. The sample cells were placed in stainless steel holders in the 12-position sample wheel and were analyzed under a He atmosphere to minimize light element x-ray absorption by the chamber atmosphere.

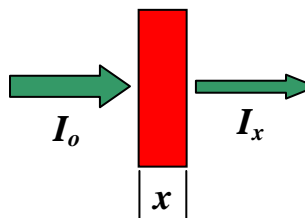
Table 17. Film Chemical Resistance – 24-hr Exposure

Film	Tank AN105 Simulant	Tank AZ101 Simulant	Tank AN107 Simulant
Ultralene™	OK	OK	OK
Polypropylene	OK	OK	OK
Polycarbonate	Ate thru film	Ate thru film	Leaked
Kapton™	Film was frosted, very soft, and pliable	Film was very soft and pliable	OK
Mylar™	Ate thru film	Ate thru film	Ate thru film

Ideally for quantitative XRF analysis, the sample should be infinitely thick. In an infinitely thick sample, the secondary or fluorescing x-rays are produced from a given element by the primary or incident x-ray beam (Pd x-ray tube) at a depth from which they can't emerge. An increase in sample thickness doesn't result in an increase in x-ray intensity.

The required sample thickness as a function of analyte wavelength for the Rigaku Mini-ZSX II can be determined as follows. X-ray intensity (or any electromagnetic radiation) decreases exponentially as it passes through and is absorbed by matter. The Beer-Lambert Law can be used to calculate the magnitude of this attenuation as a function of distance.

$$I_x = I_o \exp(-\mu_l x)$$



where

I_x is the transmitted intensity

I_o is the incident intensity

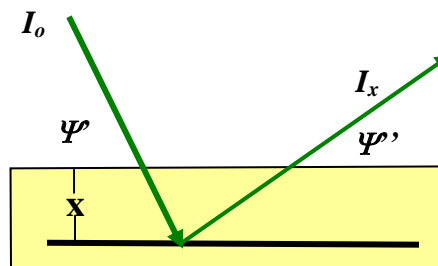
μ_l is the linear absorption coefficient in cm^{-1} , which represents the fraction of the intensity absorbed per cm of material transversed. The linear absorption coefficient is the product of the material density (ρ) and the mass absorption coefficient (μ), which is a measure of loss of intensity from photoelectric absorption and Rayleigh and Compton scatter.

The mass absorption coefficient is energy and material dependent and decreases with increasing energy of the penetrating X-rays and decreasing atomic number of the absorbing material. The mass absorption coefficient of a material is calculated as the weighted average of the mass absorption coefficients of the constituent elements.

x is the distance transversed in cm.

Rearranging the above relationship with $I_x/I_o = 0.001$ or at 99.9 % absorption with the spectrometer angles of incidence and secondary fluorescence, the analysis or penetration depth can be calculated from:

$$x_{99.9} = \frac{6.91}{(\mu_{\lambda_{pri}} \rho / \sin \Psi' + (\mu_{\lambda_{sec}} \rho / \sin \Psi''))}$$



where

- x is the maximum analysis depth (analyte wavelength dependent) in cm
- $\mu_{\lambda_{pri}}$ is the mass absorption coefficient of the material at the Pd-K α (primary x-ray beam) wavelength in $\text{cm}^2 \text{g}^{-1}$
- $\mu_{\lambda_{sec}}$ is the mass absorption coefficient of the material at the analyte wavelength in $\text{cm}^2 \text{g}^{-1}$
- ρ is the density of the material in g cm^{-3}
- Ψ' is the angle made by the primary Pd incident beam and the sample plane (72° for the Rigaku ZSX-Mini II).
- Ψ'' is the angle made by the secondary analyte fluorescence and the sample plane (30° for the Rigaku ZSX-Mini-II).

The mass absorption coefficients for nine elements in the three simulants were calculated using the software program XrfTable for Windows, Version 1.5c. The program accuracy was checked by manually calculating two mass absorption coefficients. The mass absorption coefficients were input into the above relationship to calculate the penetration depths (Table 18).

Table 18. Calculated LAW Penetration Depths at 99.9% Absorption

Element	Line	Penetration Depth (mm)		
		AN-105	AZ-101	AN-107
Na	K α	0.010	0.009	0.009
Al	K α	0.016	0.018	0.016
Si	K α	0.022	0.027	0.024
P	K α	0.033	0.040	0.036
S	K α	0.048	0.059	0.053
Cl	K α	0.069	0.078	0.077
Cr	K α	0.50	0.62	0.61
Mo	K α	11.2	13.6	11.5
Pb	L α	3.3	4.1	3.5

Since LAW is primarily water, which has a small mass absorption coefficient, it is difficult to obtain an infinitely thick sample at all the analyte wavelengths, particularly for heavy elements in this small sample cup (max height ~2-cm). The LAW simulants would be infinitely thick for all elements up to but not including Mo, in 5-mL of solution which is ~ 11-mm high in the 31-mm diameter sample cup. Even if you fill the cup to the brim with sample, Sn-K α and higher energy x-rays would penetrate completely through the liquid. It should be emphasized that the depths in Table 18 are for **99.9%** absorption. If we consider **99%** absorption to be

sufficient, these depths are reduced by $\ln 0.001/\ln 0.01$ or 1.5. An alternative strategy to infinitely thick samples is to use fixed volumes of matrix matched standards and samples in which the relative transmittance of any analyte x-ray would be constant.

This procedure has two major disadvantages, absorption of low energy x-rays by the support film and large background caused by scattered radiation from water (low Z). Both of these can lead to poor light element signal to background ratios. In addition, suspended solids, although small, may fall out of solution onto the film and bias the results if the analysis time is too long. Its major advantage is that the LAW can be analyzed directly without any sample alteration that could bias the method accuracy. It is also the fastest preparation technique – a typical XRF measurement could be completed in < 1hr after sample delivery. The liquid limit of detection and precision results for all three LAW envelopes can be found in Sections 4.1.4 and 4.1.5.

3.3.2 Dried Film

In this approach a small sample volume of solution was pipetted onto the bottom side of a thin film, which is stretched across a plastic XRF cell, and air-dried or dried under a heat lamp leaving a small solid deposit for XRF analysis. Since the deposit is adhered to the film, it can be inverted and measured directly. Although not employed in this study, sometimes a wax ring is pressed onto the film to contain the sample and define the analysis area. The x-ray scattering and hence the background is reduced significantly and the analyte elements are concentrated as the water is removed via evaporation. The dry sample can now be analyzed under vacuum to further minimize light element x-ray absorption by the chamber atmosphere. All of these factors can lower the trace element detection limits compared to direct liquid analysis.

Samples of 100-, 200-, and 300- μL of LAW simulants were deposited on Ultralene™ film and air dried in a hood with 100-lfm air flow. Even for the small 100- μL sample, the alkaline simulant did not completely dry until the hydroxide absorbed CO_2 from air and converted to the carbonate (Table 19). This required ~10-days, a time period too long to support the LAW vitrification process (See Figures 60-62 in Appendix F for pictures). It was conjectured that acidified simulants would dry more quickly than the original basic solutions. Several experiments were performed mixing simulant with water and nitric acid to determine the minimum combination to produce a clear acidified solution (Table 20). A 1:1:1 ratio of simulant to water to nitric acid (3x simulate dilution factor) produced a solution free of suspended solids.

Table 19. Drying Time for 100- μl of LAW Simulant on Ultralene™ Film in Hood with 100-lfm Air Flow

Time (hr)	Tank AN105 Simulant	Tank AZ101 Simulant	Tank AN107 Simulant
8	Liquid	Liquid	Liquid
24	Solid with liquid core	Solid with liquid core	Solid with liquid core
240*	Completely dry	Completely dry	Completely dry

* NaOH absorbed CO_2 and converted to the carbonate.

Table 20. LAW Simulant Diluted with Concentrated HNO₃

Dilution Sample/Acid/Water	Tank AN105 Simulant	Tank AZ101 Simulant	Tank AN107 Simulant
5-mL/5-mL/0	Solids	Minimal Solids	Solids
5-mL/5-mL/5-mL	Clear solution	Clear solution	Clear solution
5-mL/5-mL/10-mL	Clear solution	Clear solution	Clear solution
5-mL/-2.5mL/2.5-mL	Solids	Clear solution	Clear solution

In addition, the drying process was accelerated by using a 240-W infrared (IR) drying lamp. The lamp was positioned 10-in from the film surface; any closer and the film would deform. After only 1.5-hr, 100- μ l of acidic simulant dried completely on the film (Table 21). In contrast, the pure basic simulant was not dry after 6-hr (See Figures 63-66 in Appendix F for pictures).

Table 21. Drying Time for 100- μ l of LAW simulant on Ultralene™ film under 240-W IR Lamp at a Distance of 10-in.

Time (hr)	Tank AN105 Simulant	Tank AZ101 Simulant	Tank AN107 Simulant
<u>Basic</u>			
1.5	Solid with liquid core	Solid with liquid core*	Solid with liquid core
6	Solid with liquid core	Solid with liquid core*	Solid with liquid core
<u>Acidic</u>			
1.5	Solid	Solid	Solid

*Envelope B dried more completely than the other two.

Unfortunately, taking the sample to dryness on film does cause experimental problems which can be seen in the photographs in Appendix F:

- fractional crystallization (mineralogical and particle size effects)
- splashing of sample as it reaches dryness (very common with high salt solutions)
- spalling of the sample cake from the film surface, since it was not bound strongly to the film
- non-uniform deposition of the sample on the hydrophilic film (sample tends to dry in a toriodal shape).

Using a hydrophilic filter paper as the sample support can avert some of these problems. The paper absorbs the sample solution in a more uniform manner and is less likely to flake off. The downside is the higher scattering power of this substrate (~10 x that of thin polymeric films), which results in higher background and poorer limits of detection. Basic and acidic AN-107 simulant aliquots (100- μ L, 200- μ L, 500- μ L, 1000- μ L, and 2000- μ L) were deposited on a Bruker # 7KP19018BH-Z 50-mm cellulose filter paper with a 25-mm ink retaining ring and dried under the

IR lamp. As shown in Figure 67, the acidic solution completely dried in 1.5-hr and was contained within the ink ring. However, because of the high salt contents, too much crystalline material (several mm thick for the 2000- μL aliquot) was concentrated in this ring for all but the 100- μL sample. The basic solution took too long (~ 8-hr) and dried non-uniformly in concentric circles for this application (Figure 68).

The dried sample on filter paper limits of detection and precision results for AN-107 simulant on filter paper can be found in Sections 4.1.4 and 4.1.5 of this document. A stop order was issued by WTP before the remaining simulants could be prepared or analyzed.

3.3.3 Fused Glass

The third sample preparation technique listed in the Task Plan is glass bead fusion method. This is the most effective way of preparing a homogeneous sample devoid of particle size and mineralogy effects. It involves the fusion of the dried sample at ~1000 °C with lithium metaborate, lithium tetraborate, or a combination of the two. The fused disk is homogeneous, durable, and easy to handle, analyze, and store. These characteristics make it an ideal medium for XRF analysis of complex matrices, e.g., rocks, cements, and slags. For LAW analysis, the fused disk would have to be polished to a 1- μm finish to flatten the disk (tends to be convex) and eliminate surface roughness effects, both of which can be detrimental for light element analysis. Because of the sample drying, fusion, and polishing steps, this procedure would be the most time consuming, complex, and labor intensive of the three possible sample preparation techniques. Also, volatile land disposal elements, e.g. Hg, As, Se, etc., will be lost during the high temperature fusion process. The final disadvantage is that the sample is diluted 5 –10x by the addition of the fusion flux. Because of these disadvantages and after consultation with WTP, this approach was not pursued.

4. Results and Discussion

4.1 Rigaku ZSX-Mini II Instrument Performance

4.1.1 Detector Linear Dynamic Range

The primary, non-matrix related, reason for non-linear calibration curves at high count rates in x-ray analysis is detector dead time. Dead time refers to the time interval during which a detector gives no response to an arriving x-ray photon because it has arrived too soon after the previous photon has generated an electronic pulse. The Rigaku ZSX-Mini II x-ray spectrometer, like most commercial wavelength dispersive instruments, has automatic dead time correction that extends the linear range to at least 10^6 counts per second. Two calibration curves were generated to verify the linearity of both the scintillation and flow proportional detectors in this instrument. Two pure element disks (Mo for the scintillation detector and Al for the gas flow proportional counter) were analyzed under vacuum at 40-kV and several x-ray tube currents. Normally more data points are acquired at higher count rates, but the Rigaku ZSX-Mini II x-ray tube current is adjustable only in 0.15, 0.3, 0.6, and 1.2-mA increments.

As expected, Figure 3 clearly illustrates that both detectors are linear up to the maximum count rates (~200-kcps) achievable on pure element samples at maximum tube power. Since this x-ray instrument is only a small benchtop system, the Pd x-ray tube was designed to operate at only 40-kV and 1.2-mA or 48-W maximum input power, well below the 4000-W commonly attainable on larger units using the same detectors. The analysis of undiluted Hanford low activity waste solutions will not be detector dead time limited using the Rigaku ZSX-Mini II x-ray fluorescence spectrometer even when operated at full power.

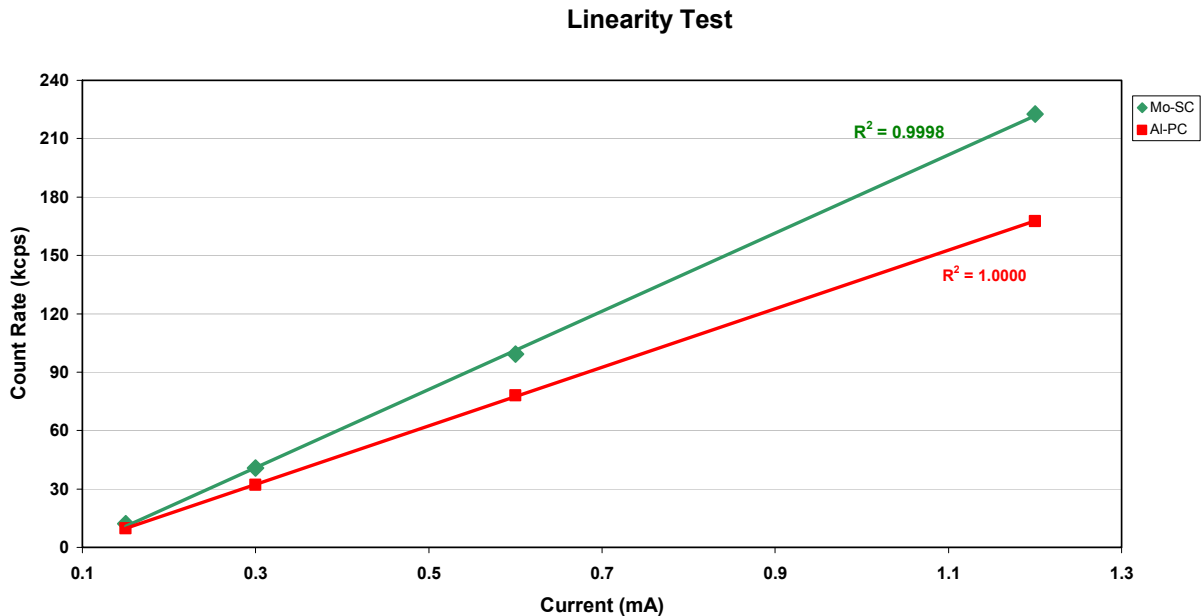


Figure 3. Detector Linearity

4.1.2 Spectrometer Resolution

The spectral resolution of a x-ray spectrometer is a measure of its power to resolve features and is usually defined as the full width half maximum (FWHM) of a completely resolved spectral line. For an energy dispersive spectrometer, the resolution is primarily dependent on the detector amplifier and the type and size of solid state detector, ~ 155 eV for a lithium drifted silicon (Si(Li)) detector, and only changes slightly with the energy of the analyte radiation. In contrast, the wavelength dispersive spectrometer resolution can vary significantly with fluorescent radiation energy and is only marginally affected by the poor inherent detector resolution, 3638 eV for the scintillation detector and 1086 eV for the gas flow proportional counter¹⁰. The analyzing crystal interplanar spacing, goniometer radius, collimator spacing, and the wavelength of the analyte radiation have a much more significant impact on this parameter, particular at low energies where resolutions of < 10 eV are achievable.

To determine the instrument resolution, slow sequential scans with a 0.01 degree step size were performed over the Na (NIST SRM 1412 glass), Al (Rigaku Al disk), Mn (NIST SRM 1263 steel), and Mo (Alfa Aesar Mo disk) peaks. These elements cover the two detectors and three diffracting crystals found in this system.

By using the **Bragg** equation:

$$n\lambda = 2d \sin \Theta$$

where

n is the order of the transition - normally first order

λ is the x-ray wavelength in Å

d is the interplanar or d spacing of the diffracting crystal in Å

Θ is the goniometer angle in radians

the x-ray fluorescence wavelengths can be calculated from the goniometer angles Full Width Half Maxima (FWHM). The x-ray wavelength then can be converted to energy by the well-known relationship:

$$E = \frac{hc}{\lambda}$$

where

h is Planck's constant, 4.133×10^{-15} eV s⁻¹

c is light speed, 3.0×10^{18} Å s⁻¹

λ is wavelength in Å

E is energy in eV

$$E_{(eV)} = \frac{12398}{\lambda}$$

¹⁰ R. Jenkins, *X-ray Fluorescence Spectrometry*, John Wiley and Sons, New York, 1988.

The results are summarized in Table 22. The instrument resolution is sufficient to separate the light element K shell x-ray fluorescence peaks from potential spectral interferences, particularly from heavy element L and M x-ray fluorescence transitions. This is a major advantage for using a WD-XRF for Hanford LAW analysis, since the hold point analytes as listed in the memo in Appendix A are low atomic number (light) elements. The impact of analyte energy on resolution can be seen when comparing the Mo (315-eV) and Mn (34-eV) resolution, even though the same diffraction crystal (LiF(200)) and scintillation detector were utilized.

Table 22. Rigaku ZSX-Mini II Measured Resolution

	Na	Al	Mn	Mo
	Gas Flow Proportional Counter		Scintillation Detector	
Crystal	RX35 ¹	PET ²	LiF (200) ³	
2 Θ ₁	24.38	143.95	62.74	20.11
2 Θ ₂	25.92	145.4	63.15	20.48
2d (Å)	55	8.808	4.0273	4.0273
λ ₁ (Å)	11.6135	8.3757	2.0965	0.7031
λ ₂ (Å)	12.3349	8.4095	2.1088	0.7159
E ₁	1067.55	1480.23	5913.77	17632.33
E ₂	1005.12	1474.28	5879.31	17317.09
ΔE	62	6	34	315

¹ W/Si multilayer diffraction crystal, 2d = 55 Å

² Pentaerythritol diffraction crystal (020), 2d = 8.808 Å

³ Lithium fluoride (200) crystal, 2d = 4.027 Å

As shown in Figures 4 & 5, scans across the major Al and Si peaks in NIST SRM 1411 glass and in Figures 6 & 7, across Mn and Cr in NIST SRM 1263 steel, dramatically illustrate the difference in resolution between energy dispersive and wavelength dispersive x-ray instrumentation.

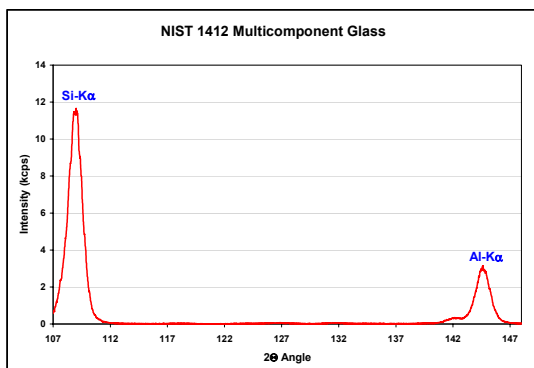


Figure 4. Rigaku ZSX-Mini II WD-XRF NIST SRM 1412 glass spectrum.

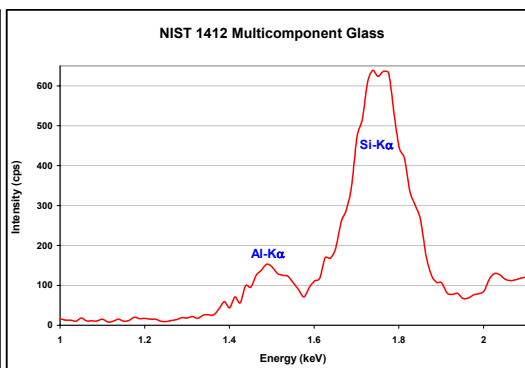
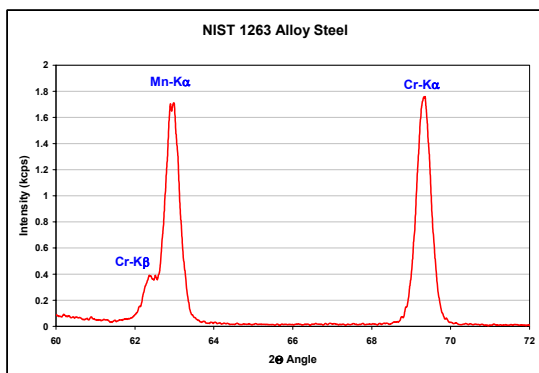
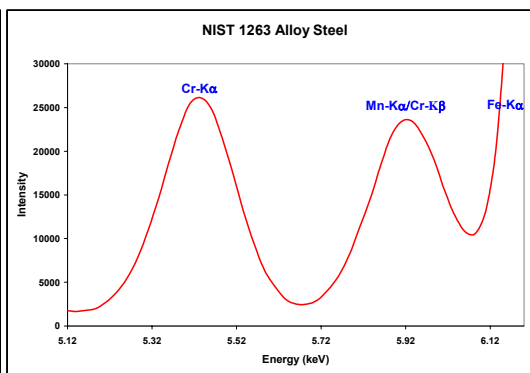


Figure 5. Spectro X-LAB2000 ED-XRF NIST SRM 1412 glass spectrum.



**Figure 6. Rigaku ZSX-Mini II WD-XRF
 NIST SRM 1236 steel spectrum**



**Figure 7. Spectro X-LAB2000 ED-XRF
 NIST SRM 1263 steel spectrum**

The Rigaku ZSX-Mini II resolution can be improved by using higher dispersion crystals, e.g., thallium hydrogen phthalate (TAP) for sodium analysis and LiF(220) or even better LiF(420) for elements heavier than scandium. As always, there is a concurrent loss in intensity with these higher resolution crystals. Since intensity, especially for Na, is important in LAW analysis and there don't appear to be any undesirable spectral interferences using the original analyzing crystals, there is no reason for replacing them.

4.1.3 Atmosphere

In order to obtain good light element sensitivity, it is essential that any absorbing atmospheric gases (oxygen, nitrogen, and argon) be removed or replaced in the analysis path length of the instrument. The easiest and most common effective method for solid monoliths and loose powders is by evacuation down to ~1-mbar pressure. For liquids, the normal technique is to purge the optics with helium, a light weakly absorbing gas. In large XRF systems, the sample is moved from the autosampler to a small secondary analysis chamber, which can be readily evacuated or purged. To reduce the size and cost of the ZSX-Mini II, the sample is not moved to a smaller chamber: it is analyzed directly in the autosampler in the large sample chamber. Because of this, Rigaku uses a polymeric film, which isolates the large sample chamber from the analysis portion of the instrument during helium analysis. This polymeric film must have high low-energy x-ray transmission (light elements) and be reasonably durable in an intense x-ray beam. Five common XRF films were investigated for this application including: Ultralene™ (polyethylene), polypropylene, Kapton™ (polyimide), polycarbonate, and Mylar™ (polyethylene terephthalate). The NIST SRM 620 soda-lime-silicate glass sodium XRF intensity was measured through these films. Kapton™ is pre-installed by Rigaku because of its excellent resistance to x-rays. However, as shown in Figure 8, its sodium transmittance is 35 times poorer than for Ultralene™, the film with the lowest absorption. The trade-off is that Ultralene™'s durability in an x-ray beam is much poorer than Kapton. Since sodium sensitivity is important, Ultralene™ was selected as the instrument film. Ultralene™ will have to be replaced daily, which will add ~1-hr to the analysis time to properly purge the instrument with He before sample measurements.

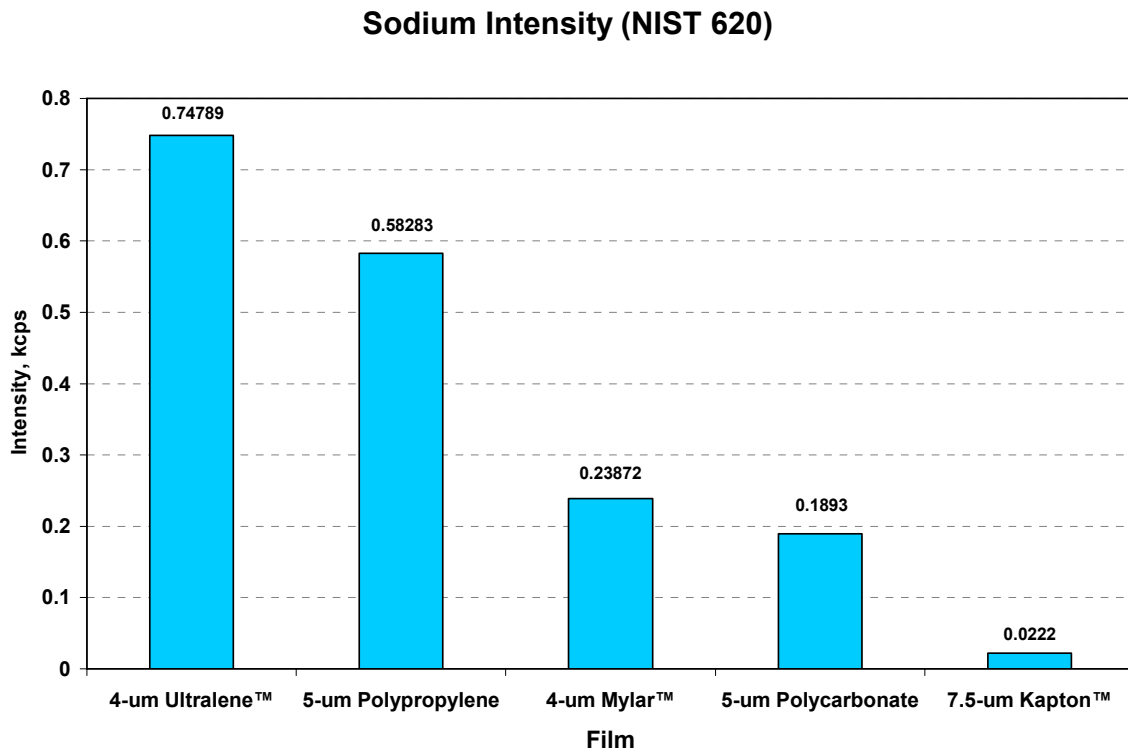


Figure 8. Relative sodium intensity for different x-ray films

The sodium intensity from the NIST 620 glass was also measured under different atmospheric conditions (Figure 9):

- under vacuum without a sample cup or instrument film (film between the analysis chamber and sample chamber); used for solid monoliths
- under vacuum with a sample cup film; used for loose powders
- under helium purge with an instrument film
- under helium purge with both sample cup and instrument films; this combination is required for light element determinations in liquid specimens.

Sodium Intensity (NIST 620)

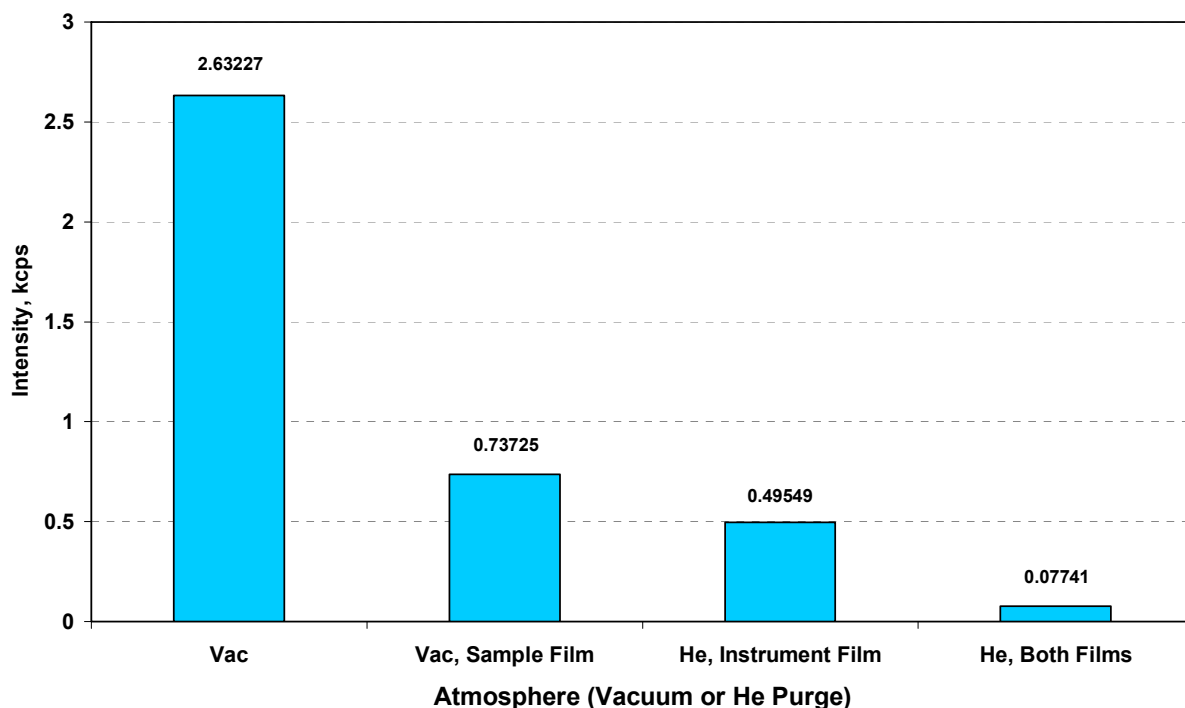


Figure 9. Relative sodium intensity under different atmospheres

The results indicate that there is a 35-fold reduction in sodium intensity when using both films in a helium atmosphere. Several attempts were made to measure the liquid sample in a sample cup with sample film without the instrument film or under vacuum. None were successful. Under vacuum, the liquid sample continuously outgassed water (concentrated) until it froze into a non-uniform pellet after ~1-hr. Without the instrument film separating the sample chamber from the analysis chamber, the helium purge gas could not effectively remove residual air from the analysis path even after several hours of gas flow. For LAW measurements, both films with a He purge will have to be used.

4.1.4 Limit of Detection

A plethora of mathematical expressions and widely ranging terminology exists for calculating the limit of detection (LOD). Only three of these will be discussed in this document: 1) International Union of Pure and Applied Chemistry LOD, 2) XRF LOD based on counting statistics, and 3) the Environmental Protection Agency's method detection limit (MDL).

4.1.4.1 IUPAC

As defined by the International Union for Pure and Applied Chemistry (IUPAC), the limit of detection (LOD) of an instrument technique is a number expressed in units of concentration (or amount) of an analyte that describes the lowest concentration (or amount) that an analyst can determine to be statistically different from an analytical blank¹¹. A common misconception is that the LOD is the smallest concentration that can be measured not simply detected. The concentration limit of detection can be calculated with the following equation:

$$C_L = \frac{kS_{Blk}}{S}$$

where:

C_L = limit of detection, $\mu\text{g/mL}$

k = constant for normally distributed data (Table 23). The IUPAC recommendation is $k = 3$, although $k = 2$ is commonly used by instrument manufacturers to obtain a lower LOD.

Table 23. Probability Constant, k , for Normally Distributed Data¹²

k	Gaussian Probability (%)
1.00	68.27
1.64	90.00
1.96	95.00
2.00	95.45
2.58	99.00
2.81	99.50
3.00	99.73
3.29	99.90
4.00	99.99

¹¹ J. Inczedy, T. Lengyel, and A. Lire, "Compendium of Analytical Nomenclature, International Union of Pure and Applied Chemistry", 3rd Edition, 1997

¹² Eric W. Weisstein, "Confidence Interval", From *MathWorld*--A Wolfram Web Resource.
<http://mathworld.wolfram.com/ConfidenceInterval.html>

s_{Blk} = standard deviation of a finite number of blanks in cts/s. The blank is defined as the signal resulting from a matrix-matched sample minus the analyte of interest.

S = standard sensitivity or background subtracted standard count rate in cts/sec divided by the standard concentration, in $\mu\text{g/mL}$.

In XRF analysis, s_{Blk} , standard deviation of the blank, is routinely replaced with s_{Bkg} , the standard deviation of the background count rate, because of the difficulty in making matrix matched blanks. Water cannot be used as a substitute for the matrix blank since water's mass absorption coefficient is lower than for the matrix (See Figure 40). The background count rate can be based on one (horizontal background) or two (sloping background) measurements.

$$C_L = \frac{k s_{Bkg}}{S}$$

In this expression, an assumption is made that the background variance is equal to the variance of a matrix-matched blank. This is probably not true, especially if multiple background points are measured, so the LODs would be slightly higher.

This method of treating the blank signal considers only one type of error. If you take into account the two types of errors, that is an element is not detected even though it is present (Type 1 or α) and an element is detected even though it is absent (Type 2 or β) the 3 sigma confidence interval reduces from 99.7 to 93%¹³. Currie¹⁴ recommends the use of a more conservative $k=3.29$, where the confidence interval is 95% if the type 1 and 2 errors are equal ($\alpha = \beta = 0.05$). IUPAC further suggests that, because the values for the blank and standard deviation are estimates based on limited measurements and the distributions are almost never Gaussian, the 3 sigma value actually corresponds to a confidence level of about 90%¹⁵. Since IUPAC recommends $k=3$, this value was used for all LOD calculations in this report.

4.1.4.2 Environmental Protection Agency (EPA)

The method detection limit (MDL) is a statistical detection limit, defined as the minimum analyte concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero¹⁶. The MDL is determined from analyte analysis in a given matrix type and is calculated by multiplying the appropriate one-sided 99% t-statistic (Table 24) by the standard deviation from a minimum of three analyses of a matrix spike containing the analyte at a concentration three to five times the estimated MDL.

¹³ J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, John Wiley and Sons, New York, 1988.

¹⁴ L .A. Currie, "Limits for Qualitative Detection and Quantitative Determination", *Anal. Chem.* **40**, 586-593 (1968).

¹⁵ V. Thomsen, D. Schatzlein, and D. Mercurio, "Limits of Detection in Spectroscopy", *Spectroscopy*, **18(12)**, 112-114 (2003).

¹⁶ U. S. Environmental Protection Agency, "Test Methods for Analyzing Hazardous Waste", SW-846, 2006

Table 24. t-Statistic

No. of samples	t-Statistic
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

$$MDL = k\sigma_{std}$$

where:

MDL = method limit of detection, $\mu\text{g/mL}$

k = 2.82 for ten samples

σ = standard deviation of analyte concentration in $\mu\text{g/mL}$ at three to five times the estimated MDL

The EPA's MDL method was designed for determining low hazardous element concentrations, not major matrix element values. The LOD measurements for matrix elements were not made because of the degree of difficulty in making matrix matched standards without a major analyte and the time needed to pursue this method, and most importantly without altering the mass absorption coefficient of the sample. The program was canceled before minor Land Disposal Restriction (LDR) elements MDLs in spiked simulants could be made.

4.1.4.3 X-ray Fluorescence (XRF) Counting Statistics

The standard deviation for counting photons emitted at completely random time interval (Poisson distribution) can be approximated as the square root of the number of counts:

$$s_N = \sqrt{N}$$

where

s_N is the standard deviation of the individual measurement

N is the number of counts

The standard deviation expected in a calculated average is:

$$s_{Bkg} = \sqrt{\bar{N}} = \sqrt{n_{Bkg} t_{Bkg}}$$

where

s_{Bkg} = standard deviation of the individual measurement

\bar{N}_{Bkg} = average number of background counts
 n_{Bkg} = background count rate in cts/s
 t_{Bkg} = time spent counting the background in seconds

To convert counts to count rate:

$$s_{Bkg} = \frac{\sqrt{n_{Bkg} t_{Bkg}}}{t_{Bkg}} = \sqrt{\frac{n_{Bkg}}{t_{Bkg}}}$$

Since two count rate measurements (peak and background) are normally made in XRF analysis, the total variance is equal to the sum of the variances of the two statistically independent distributions¹⁷:

$$s_{Total}^2 = s_{Peak}^2 + s_{Bkg}^2$$

where

s_{Total}^2 = total variance
 s_{Peak}^2 = peak variance
 s_{Bkg}^2 = background variance

At the LOD, $s_{Peak}^2 = s_{Bkg}^2$

$$s_{Total}^2 = 2s_{Bkg}^2$$

$$s_{Total} = \sqrt{2}s_{Bkg}$$

Combining these relationships and changing to concentration units:

$$C_L = k \frac{\sqrt{2}}{S} \sqrt{\frac{n_{Bkg}}{t_{Bkg}}}$$

where:

C_L = limit of detection, $\mu\text{g/mL}$
 $k = 3$
 n_{Bkg} = background count rate in cts/s
 t_{Bkg} = time spent counting the background in seconds
 S = standard sensitivity or background subtracted standard count rate in cts/sec divided by the standard concentration, in $\mu\text{g/mL}$

¹⁷ E. P. Bertin, *Principles and Practice of X-Ray Spectrometric Analysis*, Plenum Press, New York, (1970).

As this equation indicates, one way of decreasing the LOD if the system is detector shot noise (random fluctuations) limited is by increasing count time. Normally this is not the case; instrument instability errors usually dominate.

4.1.4.4 Experimental and Data

A discernible amount of solids, particularly in Envelope B, was observed in the simulants after storage for several months, even though the simulants had been filtered immediately after preparation. Consequently, before the LOD measurements were performed, the simulants were filtered through a 0.45 μm syringe filter. Five 5-mL aliquots of each of the filtered solutions were pipetted into the sample cups, placed in five random autosampler positions, and analyzed in triplicate under a helium atmosphere. A NIST SRM 1411 glass standard was also analyzed for comparison. Since the Rigaku WD-XRF system is a sequential instrument, ~ 20 min were required for each sample analysis. More details on the instrument setup can be found in Section 3.2. The background and background subtracted peak intensities are tabulated in Appendix G.

Table 25. Summary of LAW Simulant and NIST 1411 Glass Detection Limits

	AN-105 Simulant		AZ-101 Simulant		AN-107 Simulant		NIST 1411 Glass	
	IUPAC (3 σ) ($\mu\text{g/mL}$)	XRF (3 σ) ($\mu\text{g/mL}$)	IUPAC (3 σ) ($\mu\text{g/mL}$)	XRF (3 σ) ($\mu\text{g/mL}$)	IUPAC (3 σ) ($\mu\text{g/mL}$)	XRF (3 σ) ($\mu\text{g/mL}$)	IUPAC (3 σ) ($\mu\text{g/g}$)	XRF (3 σ) ($\mu\text{g/g}$)
Na	641	578	717	477	527	584	483	116
Al	69	43	26	26	25	25	25	23
Si	21	25	a	a	a	a	101	57
P	6	9	9	7	9	8	b	b
S	a	a	5	5	a	a	b	b
Cl	13	14	7	6	8	7	b	b
K	23	19	31	13	22	13	23	25
Ca	a	a	a	a	42	29	19	17
Cr	5	4	3	3	3	3	b	b
Mn	a	a	a	a	3	3	b	b
Fe	a	a	a	a	3	3	4	4
Ni	a	a	a	a	2	2	b	b
Cu	a	a	a	a	2	2	b	b
Zn	a	a	a	a	1	2	b	b
Zr	a	a	a	a	4	2	b	b
Mo	8	3	a	a	6	3	b	b
Pb	a	a	a	a	9	7	b	b

a) These elements were not measured.

b) These elements were not listed on the NIST certificate of analysis and consequently not measured.

As shown in Table 25, the XRF detection limits increase dramatically towards longer wavelengths (lighter elements), because of lower light element fluorescence quantum efficiencies and increasing absorption of the low energy analyte fluorescence by the sample matrix. The LODs will also be lower in lighter element matrices. The degree of absorption decreases in light matrices and, therefore, the measured intensity is higher. The commonly listed instrument detection limits (IDLs) determined in pure water will always be lower than

the more accurate MDLs measured in the sample matrix. The NIST 1411 LODs are approximately the same as for the LAWs because their mass absorption coefficients were similar.

The LODs for a set of ten filter papers containing the dried residue from 100- μ L or 200- μ L of acidified AN-107 simulant solution were determined under vacuum or in a He atmosphere (Table 26). There is only a slight improvement in LODs for a majority, but not all, the elements measured under vacuum versus a helium atmosphere. The almost negligible improvement in sodium LOD was unexpected, since it had been previously demonstrated that the sodium intensity for NIST 1411 glass in vacuum was five times higher than in a helium atmosphere (Section 4.1.3). The reason for the small change can be seen by examining the data in Tables 44 and 46. Although the average sample intensity for AN-107 increases \sim 5-fold when switching from He atmosphere to vacuum, the standard deviation of the background also increases by approximately the same factor. The net result is no change in the MDLs. There is also no significant decrease in LODs by increasing the sample size from 100- to 200- μ L. There is no justification for using the dried filter paper method for LAW analysis. The LODs for dried filter paper samples are only marginally better than for liquids; the sample preparation time is much longer and, as will be shown in the next section, the precision is substantially poorer.

Table 26. Summary of Dried Spot LAW Simulant Detection Limits

	100 μ L Aliquot (Helium Purge)		200 μ L Aliquot (Helium Purge)		100 μ L Aliquot (Vacuum)		200 μ L Aliquot (Vacuum)	
	IUPAC (3 σ) (μ g/mL)	XRF (3 σ) (μ g/mL)	IUPAC (3 σ) (μ g/mL)	XRF (3 σ) (μ g/mL)	IUPAC (3 σ) (μ g/mL)	XRF (3 σ) (μ g/mL)	IUPAC (3 σ) (μ g/mL)	XRF (3 σ) (μ g/mL)
Na	623	308	585	256	602	128	245	110
Al	11	9	7	7	5	6	5	5
P	3	4	3	2	3	3	2	2
Cl	48	36	52	43	28	29	73	38
K	40	14	36	12	15	12	21	11
Ca	13	14	39	19	17	14	43	19
Cr	3	3	4	3	3	3	2	3
Mn	5	5	4	4	4	5	5	4
Fe	6	5	5	4	5	4	4	3
Ni	9	5	5	4	6	5	4	4
Cu	6	4	4	3	5	4	4	3
Zn	10	5	7	4	6	4	5	4
Zr	37	15	26	9	23	14	26	8
Mo	24	12	24	8	16	11	24	8
Pb	50	27	38	19	41	25	39	17

Table 27 contains the list of target MDL's based on ICP-AES sensitivity from the Task Plan and the LAW solution IUPAC MDLs for those elements measured before the program was cancelled. It's not surprising that some MDLs could not be attained using the ZSX-Mini II XRF system, since ICP-AES is typically orders of magnitude more sensitive than XRF. The main advantage of XRF is that no or minimal sample preparation is required for most materials. Except for sodium, the

MDLs for the most important analytes, the hold point elements, were achieved by this method. And the sodium LODs were only 2 to 3 times higher than the desired upper threshold. Based on this data, the XRF detection limits are generally adequate for glass former batching and product composition reporting, but may be inadequate for some species (Hg, Cd, and Ba) important to land disposal restrictions.

Table 27. List of Target MDLs¹⁸

Analyte	Target MDL (mg/L)	AN-105 MDL (mg/L)	AZ-101 MDL (mg/L)	AN-107 MDL (mg/L)
<u>Hold Point Elements</u>				
Aluminum	20 - 45	69	26	25
Chlorine	100 - 500	13	7	8
Potassium	10 - 50	23	31	22
Sodium	60 - 250	641	717	527
Sulfur	150 - 500	a	5	a
<u>Non-Hold Point Elements</u>				
Calcium	10 - 50	a	a	42
Iron	2 - 20	a	a	3
Magnesium	9.5 - 30	a	a	a
Phosphorus	150 - 500	6	9	9
Silicon	50 - 100	21	a	a
Titanium	10 - 50	a	a	a
Zinc	3.5 - 5.5	a	a	1
Zirconium	2.5 - 125	a	a	4
<u>LDR Elements</u>				
Antimony	15 - 20	a	a	a
Arsenic	10 - 50	a	a	a
Barium	0.55 - 1.75	a	a	a
Cadmium	1.75 - 2.5	a	a	a
Chromium	0.75 - 8.5	5	3	3
Lead	15 - 45	a	a	9
Mercury	1 - 2	a	a	a
Nickel	6.5 - 15	a	a	2
Selenium	20 - 30	a	a	a
Silver	2 - 7.5	a	a	a
Thallium	5.5 - 15	a	a	a
<u>Additional Elements</u>				
Cerium	10 - 50	a	a	a
Copper	2 - 8.5	a	a	2
Lanthanum	10 - 50	a	a	a
Manganese	0.55 - 1.75	a	a	3
Molybdenum	3 - 15	8	a	6
Neodymium	10 - 50	a	a	a

Note: Goal is to achieve MDLs below target values. In some cases the values may be higher due to lack of sensitivity or matrix effects.
a) These elements were not measured. The elements in red had MDLs > the target values.

4.1.4.5 Limit of Quantification

The limit of quantification, LOQ, or limit of determination refers to the smallest concentration or the mass, which can be quantitatively analyzed with reasonable reliability by a given

¹⁸ D. Blumenkranz, "Quality Assurance Project for Testing Programs Generating Environmental Regulatory Data", PL-24590-QA00001, Revision 0, June 2001.

procedure. Quantification is generally agreed to begin at a concentration equal to 10 standard deviations of the blank¹⁹. Therefore, LOQ = 3.3 LOD for k =3 and 3.04 LOD for k = 3.29.

4.1.5 Precision

Precision is commonly defined as the agreement or repeatability among a group of independent experimental results and should only be impacted by random or indeterminate errors in an experimental system. The smaller the random part of the experimental errors that affect the results, the more precise the procedure. Random errors cause the individual measurements to distribute uniformly around the mean, whereas systematic errors affect the measurement accuracy by causing the results to generate a positive or negative bias from the true value²⁰. In x-ray analysis, systematic errors arise primarily from sample preparation and instrument calibration, including the conversion of intensities into concentrations and the analytical method used for the correction of matrix effects. Modern x-ray instruments are very stable so that the standard deviation due to the instrumental errors (generator, tube, crystal, detector, goniometer, specimen chamber, etc.) is negligible.

The goal in x-ray fluorescence analysis is to minimize all systematic and random errors through rigorous sample preparation and calibration protocols so that the inherent counting error, which is associated with the intrinsic random nature of the fluorescing x-ray, dominates the error function. X-ray intensity, which is measured from the number of accumulated counts of x-ray photons per unit time, is always accompanied by a small counting statistical fluctuation which conforms to the Gaussian distribution with a standard deviation equal to the square root of the total counts. The best achievable precision of an x-ray measurement can, therefore, be predicted by the measured intensity. This count rate value is related to two measurements, one for the peak count n_{pk} , and one representing the background n_{Bkg} , both observations carry a statistical uncertainty. The precision based on counting statistics can be determined from the following equation²¹:

$$\text{Precision} = 100 * \frac{\sqrt{n_{pk} / t_{pk} + n_{Bkg} / t_{Bkg}}}{n_{pk} - n_{Bkg}}$$

where:

n_{pk} = peak count rate in cts/s

t_{pk} = time spent counting the peak in sec

n_{Bkg} = background count rate in cts/s

t_{Bkg} = time spent counting the background in sec

¹⁹ L .A. Currie, "Nomenclature in Evaluation of Analytical Methods Including Detection and Quantification Capabilities", *Pure and Applied Chemistry*, **67**, 1699-1723 (1995).

²⁰ J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, John Wiley and Sons, New York, 1988.

²¹ R. E. Van Griekbe and A. A. Markowicz, *Handbook of X-ray Spectrometry*, Marcel Dekker Inc., New York, 1992.

The total precision or more accurately the relative error is commonly expressed as percent relative standard deviation (%RSD) or coefficient of variation (CV) and the percent standard error of the mean (% $s_{\bar{x}}$). The %RSD can be calculated from the following relationship:

$$\%RSD = 100 * \frac{s}{\bar{x}}$$

where

s is the standard deviation of a finite number of measurements and
 \bar{x} is the average or arithmetic mean of a finite number of measurements.

The standard deviation of the sampling distribution of the mean is smaller than the standard deviation of the population and can more accurately reflect the true measurement precision. The standard deviation of the sampling distribution of the mean is called the standard error of the mean:

$$\%s_{\bar{x}} = 100 * \frac{s}{\sqrt{n}}$$

where

$s_{\bar{x}}$ is the standard error of the mean
 s is the standard deviation of all samples
 n is the number of independent samples

To determine the ZSX-Mini II system stability, a pure aluminum block was analyzed 10 times in one autosampler position over 2-hr and in 10 different sample cups and autosampler locations over an 8-hr time period. Aluminum was selected for this test because the PET crystal, used for Al measurements, is the least stable of the three analyzing crystals and will register even the smallest temperature fluctuation in the crystal chamber. The results in Table 28 verify that the instrument is very stable and that there is only a small increase in the system's relative error from instrument instability (0.02%) and from differences in the sample cups or autosampler positions (0.01%) over the counting statistics error. The precisions for the six elements in a NIST glass standard measured over 10-hr, although not as good as for the Al block since the total number of measured counts was lower, were also excellent.

Table 28. Aluminum Disk and NIST SRM 1411 Glass Precision

Element	Pure Al ¹ – 2-Hr		Pure Al ² – 8-hr		NIST SRM 1411 Glass ³	
	Total %RSD	Counting Statistics %RSD	Total %RSD	Counting Statistics %RSD	Total %RSD	Counting Statistics %RSD
Si	a	a	a	a	0.09	0.05
Na	a	a	a	a	0.29	0.17
Al	0.03	0.01	0.04	0.01	0.14	0.14
K	a	a	a	a	0.13	0.16
Ca	a	a	a	a	0.16	0.17
Fe	a	a	a	a	0.84	0.89

¹ Al was analyzed ten times in one autosampler position over 2-hr time period.

² Al was analyzed once in ten autosampler positions over 8-hr time period.

³ Glass was analyzed twenty times in one autosampler position over 10-hr time period.

a) These elements are not present in the pure Al block.

For the LAW precision analysis three separate tests were made:

1. Triplicate analysis of ten **unfiltered** solutions in fixed autosampler positions
2. Triplicate analysis of **unfiltered** solutions, which were moved into **random** autosampler locations between each of the triplicate determinations.
3. Triplicate analysis of ten **filtered** solutions in fixed autosampler positions

Ten 5-mL aliquots of each of the filtered solutions were pipetted into the sample cups, placed in ten autosampler positions, and analyzed in triplicate under a helium atmosphere. A NIST SRM 1411 glass standard was also analyzed for comparison. Since the Rigaku WD-XRF system is a sequential instrument, ~ 20 min were required for each sample analysis. More details on the instrument setup can be found in Section 3.2. The background and background subtracted peak intensities, sub-sampling, replicate, residual, and total precisions are tabulated in Appendix H and precision as total %RSD and total % standard error of the mean are summarized in Tables 29-31. A thorough statistical analysis of this data can be found in SRNL-SCS-2006-00013²². These results indicate that there is sample degradation over the 18-hr total analysis time, particularly for Al, K, and Si. The reason for these intensity drifts is unknown. The Al block precision study proved that the XRF system is very stable and doesn't drift. The poor precision could be from sample heating by the x-ray source and distension of the sample film toward the x-ray tube as it heats or possibly degradation of the solutes and/or complexing agents by the intense x-ray beam. A simple 1:1 dilution of the sample might correct this problem. A thorough investigation to understand these interactions and improve the long-term precision needs to be initiated. Even with this systematic error, the long-term precision for almost all the elements in the three simulants is <10%.

²² T. B. Edwards, "A Statistical Evaluation of XRF Measurements of WTP LAW Simulants (U)", SRNL-SCS-2006-00013, Washington Savannah River Company, March 31, 2006.

Table 29. AN-105 Simulant Precision

	Unfiltered - 3 Sets of 10		Unfiltered - 3 Sets of 10 (Randomized)		Filtered - 3 Sets of 10	
	%RSD	%Std Error of Mean	%RSD	%Std Error of Mean	%RSD	%Std Error of Mean
Na	3.4	0.8	2.7	0.7	6.6	3.7
Al	2.8	1.5	14.5	7.8	3.1	1.8
P	4.0	1.2	8.3	4.2	3.3	0.8
Cl	0.6	0.2	5.4	2.9	0.4	0.2
K	10.5	5.7	2.8	1.5	4.5	2.4
Cr	2.0	1.0	1.3	0.6	0.8	0.3

Table 30. AZ-101 Simulant Precision

	Unfiltered - 3 Sets of 10		Unfiltered - 3 Sets of 10 (Randomized)		Filtered - 3 Sets of 10	
	%RSD	%Std Error of Mean	%RSD	%Std Error of Mean	%RSD	%Std Error of Mean
Na	11.6	6.4	4.8	1.8	15.1	8.0
Al	4.8	2.6	9.6	4.7	5.3	2.3
P	4.0	2.1	4.3	2.4	2.1	6.7
S	a	a	a	a	4.1	1.7
Cl	4.5	2.5	3.5	1.9	6.9	3.7
K	6.8	3.7	2.6	1.2	2.1	1.2
Cr	2.9	1.6	2.7	1.3	2.4	1.2

a) Sulfur was not measured in the first two data sets.

Table 31. AN-107 Simulant Solution Precision

	Unfiltered - 3 Sets of 10		Unfiltered - 3 Sets of 10 (Randomized)		Filtered - 3 Sets of 10	
	%RSD	%Std Error of Mean	%RSD	%Std Error of Mean	%RSD	%Std Error of Mean
Na	11.4	6.1	5.3	2.2	2.1	0.7
Al	7.5	2.1	22.7	12.5	8.0	2.7
P	3.4	a	8.5	4.8	2.4	0.8
Cl	2.5	1.3	2.3	1.1	0.9	0.3
K	9.4	5.3	1.2	0.3	0.7	0.2
Cr	2.1	0.7	3.9	2.0	1.8	0.6

a) Phosphorous % standard error of mean was not reported for this data set in reference 22.

The precision for a set of ten filter papers containing the dried residue from 100- μ L of acidified AN-107 simulant solution was determined in a He atmosphere (Table 32). The relative errors are higher than for the direct measurement of the solution. And since the LODs for dried filter paper samples are only marginally better than for liquids and the sample preparation time is much longer, there is no reason for using the dried filter paper method for LAW analysis.

Table 32. AN-107 Simulant Dried Spot (100- μ L) Precision

Unfiltered - 3 Sets of 10 (Randomized)		
	%RSD	%Std Error of Mean
Na	12.2	3.9
Al	11.4	3.6
P	20.7	6.6
Cl	12.7	5.1
K	3.5	1.1
Cr	5.4	1.8

To determine if there is any difference in precision between the unfiltered, unfiltered randomized, and filtered samples, a one-sided F-Test was performed. The F-test is a significance test that compares the variances (squares of the standard deviations), i.e. the precision of two sets of data and can be calculated as follows:

$$F = s_1^2 / s_2^2$$

where

s_1^2 and s_2^2 are the two sample set variances

The one-tailed version only tests in one direction that is the standard deviation from the first population is either greater than or less than (but not both) the second population standard.

The two tests were at the 95% confidence interval (p=0.05):

1. Does filtering the samples improve precision?
2. Do the random samples (different sample cups and autosampler positions) have poorer precision?

The results (SRNL-SCS-2006-00013) show that filtering the sample improves the precision for several analytes in some of the simulants, but not for all the simulants. The other conclusion from the F-Test results is that there are no statistical differences in the precision data using different samples cups and the autosampler for LAW analysis. The relative error from sampling and sample degradation with time dominate the precision error.

4.1.6 Calibration

X-ray spectrometry is essentially a comparative technique. It is absolutely vital that both calibration reference materials and samples to be analyzed are prepared in an identical and reproducible manner and presented and analyzed by the spectrometer under the same experimental conditions. Since no standards exist for LAW supernates, appropriate synthetic standards will have to be produced. These standards will be used to calibrate the instrument and to ensure that the necessary quality controls are met. It is envisioned that the standards used by the RPP-WTP analytical laboratory will have validated compositions, which may not be NIST traceable and will encompass the projected LAW composition range. After

consultation with WTP, it was decided to have an offsite vendor prepare and certify a set of standards that covered the anticipated CRV major element concentrations from the first five processed LAW tanks: AY-102, AP-101, AZ-101, AZ-102, and AP-103. The proposed standards are listed in Table 33 and are based on the waste tank data summarized in Appendix I. The concentrations of the AP-101 and AP-103 standards (using the most current Best Basis Inventory) may have to be revised since these are holding tanks whose compositions can vary from year to year. The program was cancelled before the standards were prepared.

Table 33. Proposed Hanford LAW XRF Calibration Standards.

Element	AY-102 µg/mL	AP-101 µg/mL	AZ-101 µg/mL	AZ-102 µg/mL	AP-103 µg/mL
Aluminum	6747	6314	5280	798	18316
Calcium	a	a	a	67	76
Chromium	128	130	570	1018	588
Molybdenum	77	a	85	a	60
Nickel	a	a	a	6	78
Potassium	633	25755	3800	4555	6470
Silicon	96	a	52	56	106
Sodium	115028	111500	99000	95039	178139
Chloride	216	1364	a	200	4284
Phosphate	6824	883	1600	704	2381
Sulfate	3212	2975	16500	26300	4756

a) These elements were not reported for these waste tanks.

The XRF instrument will be calibrated using the fundamental parameters algorithm supplied by Rigaku/MSC. The fundamental parameters approach is the derivation of mathematical expressions quantifying fluorescence emissions in terms of fundamental physical parameter and instrumental parameters. Although this method can be standardless, more accurate determinations can be made by analyzing known matrix-matched standards to adjust the primary and secondary absorption and fluorescence factors, jump ratios, and other coefficients in the fundamental parameter algorithm. Relative intensities are calculated from theoretical principles using the fundamental parameter algorithm based on the Sherman equation. These theoretical intensities are compared with the measured intensities, the projected sample composition is adjusted to match these theoretical intensities, and the process is repeated until convergence. As an example of the technique, the three LAW simulants were analyzed as calibration standards for sodium using the Rigaku fundamental parameters software program. As shown in Figure 10, the correlation coefficient for the calibration curve is very good even without matrix correction, considering that the sodium values are not certified and came from a single ICP-AES analysis of these solutions. After matrix correction with the fundamental parameters algorithm, there is noticeable improvement in the linearity of the calibration curve (Figure 11). Better correlation coefficients covering a larger dynamic range will be obtained from the proposed set of five standards.

Sodium Calibration Curve

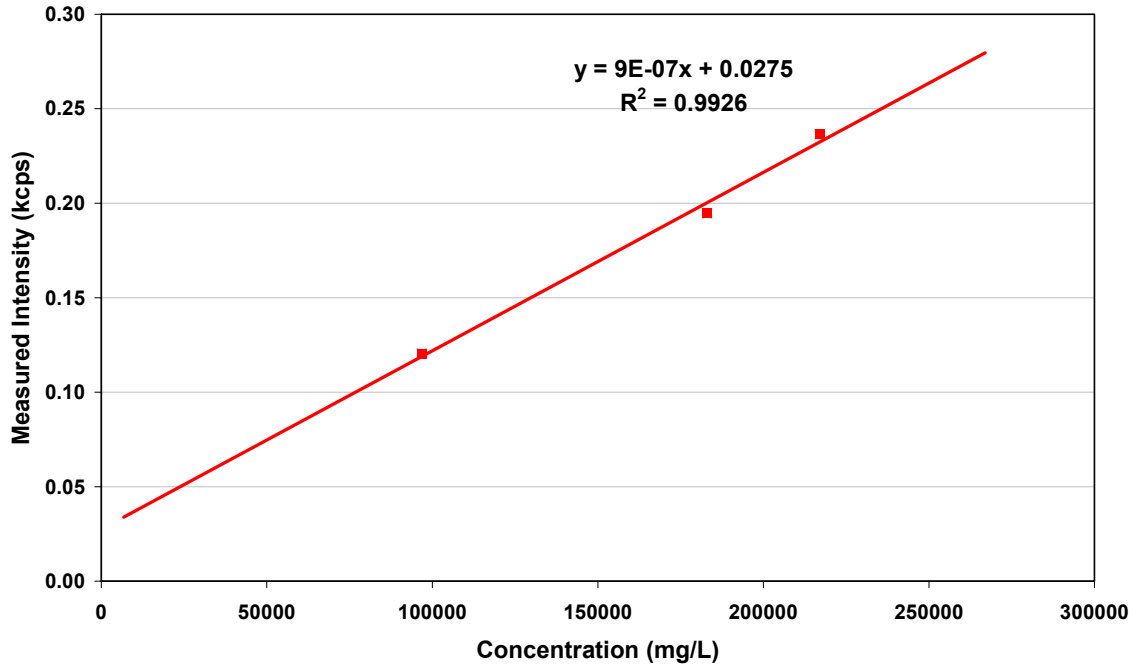


Figure 10. Sodium calibration curve using LAW simulants

Sodium Calibration Curve

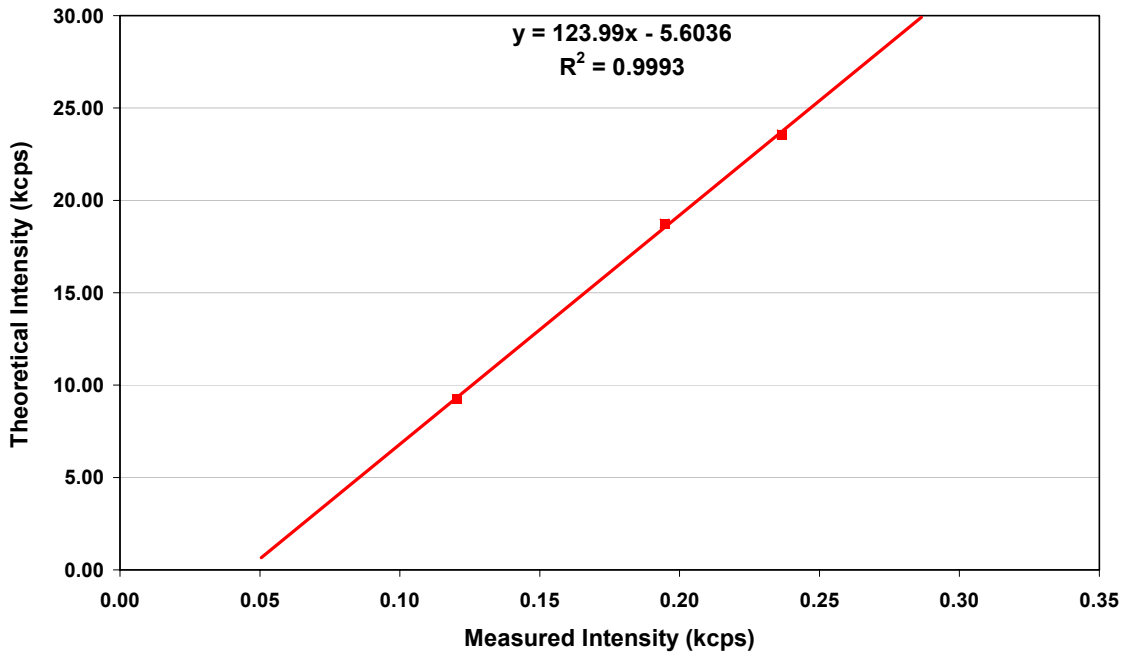


Figure 11. Sodium calibration curve using LAW simulants after matrix correction

5. Quality Assurance

The Quality Assurance measures identified in the Task Technical and Quality Assurance Plan¹ were followed in the performance of these activities. The WSRC program applied the appropriate quality assurance requirements from 10 CFR 830 Subpart A, NQA-1-1989 (Part I, Basic and Supplementary Requirements), and NQA-2a-1990, Part 2.7, as indicated by the QA Plan Checklist in Section VIII of the Task Technical and Quality Assurance Plan. A surveillance of the activities was performed by SRNL QA to verify conformance to the QA Plan Checklist. All items that were checked “Yes” in this list were followed with the exception of procedures related to stop work, non-conformance, and the corrective action system. These were not necessary since no issues were identified. SRNL was also requested to perform work in accordance with the requirements established in the Quality Assurance Project Plan for Testing Programs Generating Environmental Regulatory Data (PL-24590-QA00001)¹⁸ since the activity supports regulatory and environmental testing for the RPP-WTP.

5.1 Significant Figures

The number of significant figures used in this document was based on the following criteria:

- Data obtained from other sources, including waste tank compositions, calculated variances, and standard error of means, were entered as tabulated in the original report.
- XRF raw data in kcps was input as listed in the instrument printout.
- The number of significant figures for the data set averages, MDLs, %RSDs, etc. was based on an estimate of what was appropriate for that particular method at that concentration level.

6. Conclusions/ Recommendations

The evaluation, selection, and procurement of XRF instrument for WTP installation as part of Phase 1a activities per the approved task plan was completed and a report was issued on this task²³. The results from the investigation of three XRF sample methods for preparing the LAW sub-sample for XRF analysis, and initial scoping studies on AN-107 (Envelope C) simulant for determining the capabilities, limitations, and parameters of XRF instrument are discussed.

SRNL recommends optimizing the XRF methodology for WTP LAW vitrification process support after developing valid calibration and verification standards using the proposed set of representative LAW compositional ranges.

²³ D. M. Missimer, A. R. Jurgensen, and R. L. Rutherford, “Support for the Selection and Procurement of the Hanford WTP X-ray Fluorescence Spectrometer”, SRNL-ADS-2005-00120, Savannah River Site, Aiken SC 29808 (March 22, 2005).

7. Appendices

7.1 Appendix A: LAW Analyte List



Memorandum

To: Bruce Kaiser
From: Jim L. Nelson
Ext: 371-3203
Fax: 371-3004

Date: June 28, 2004
CCN: 093539

Subject: ILAW Analyte List for Product Compliance

Reference: CCN 087928; Meeting Minutes “LAW Compliance Needs and XRF Trend Input” June 2, 2004

The following listing of ILAW analytes has been prepared in response to Action Item 1 of the reference meeting minutes.

Hold Point

Non-Radioactive Components

Existing in SAP: TOC, Na, S, K, Cl, NO₂, NO₃, wt% solids, pH, density
ADD to next list: Al

Radioactive Components

Existing in SAP: Sr-90, Cs-137, Tc-99

Non-Hold Point Reporting Requirements

Non-Radioactive Components

Components expected to be > 0.5wt% of waste form: Al, B, Ca, Cl, F, Fe, K, Li, Mg, Na, P, Si, S, Ti, Zn, Zr

Radioactive Components

Reportable Quantities of Hazardous Materials from 49CFR172.101: See Reduced List worksheet

Components at >1% in the final waste form from Full 172.101 worksheet
(See E&NS for requirements basis and detection limits)

RCRA Components

Reportable quantities of Hazardous Components

TC: Ag, As, Ba, Cd, Cr, Hg, Pb, Se

UHC: Be, Ni, Sb, Tl

Jim L. Nelson
R&T Product Qualification

Distribution

PDC	MS11-B
Rueff, S.	MS7-ANW
Dodd, D.	MS7-ANW
Vienna, J	MS5-L
Westsik, J	MS5-L
Musick, A	MS5-L

7.2 Appendix B: Simulant Recipes

Table 34. Envelope A Recipe: Tank AN-105 Simulant

Volume of Feed: 1000 mL

Balance Manufacturer	Model #	M&TE #	Calibration Date	Calibration Mass (g)	Actual Mass (g)	M&TE #
OHAUS	E04130	AD-1001	4/7/2004	10	9.998	DW-493

Add 200 mL of deionized water to the volumetric flask.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Boric Acid	H ₃ BO ₃	0.292	0.292	Reagents Inc.	1-10430	11191N
Cadmium Nitrate	Cd(NO ₃) ₂ ·4H ₂ O	0.008	0.007	Fisher Scientific	C13-100	005642
Calcium Nitrate	Ca(NO ₃) ₂ ·4H ₂ O	0.236	0.238	J. T. Baker	1395-01	K12332
Lead Nitrate	Pb(NO ₃) ₂	0.085	0.084	Fisher Scientific	L61-3	033934
Magnesium Nitrate	Mg(NO ₃) ₂ ·6H ₂ O	0.053	0.054	Fisher Scientific	M46-500	033942
Potassium Nitrate	KNO ₃	19.221	19.222	Fisher Scientific	P263-500	926781
Zinc Nitrate	Zn(NO ₃) ₂ ·6H ₂ O	0.045	0.046	Fisher Scientific	Z45-500	005554
Glycolic Acid	HOCH ₂ COOH, 70 wt%	1.665	1.672	Aldrich	42060-3	08229CG
Sodium Chloride	NaCl	14.984	14.982	Fisher Scientific	S271-500	035509
Sodium Fluoride	NaF	0.420	0.420	Fisher Scientific	S299-500	991559
Sodium Chromate	Na ₂ CrO ₄	4.205	4.206	Fisher Scientific	S272-500	006038
Potassium Molybdate	K ₂ MoO ₄	0.204	0.203	NOAH Technologies	90143	13938/1.1
Ammonium Acetate	CH ₃ COONH ₄	0.513	0.516	Fisher Scientific	A637-500	926443B

In a separate Teflon container mix the following:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Aluminum Trihydroxide	Al(OH) ₃	114.77	114.767	J.T. Baker	0518-05	N27599
Sodium Hydroxide	NaOH	196.68	196.640	Fisher Scientific	S318-3	035670
Selenium Dioxide	SeO ₂	0.001	0.001	Aldrich	32547-3	91922EW
Sodium Meta-silicate	Na ₂ SiO ₃ ·9H ₂ O	2.135	2.135	Sigma	S4392-250g	102K0535
Sodium Acetate	CH ₃ COONa·3H ₂ O	3.865	3.867	Fisher Scientific	S209-500	985293
Sodium Formate	HCOONa	4.351	4.350	Fisher Scientific	S648-500	025952
Sodium Oxalate	Na ₂ C ₂ O ₄	0.929	0.928	Fisher Scientific	S487-500	026000
Sodium Phosphate	Na ₃ PO ₄ ·12H ₂ O	2.281	2.280	Fisher Scientific	S377-500	030202
Water	H ₂ O	300	300			

Mix thoroughly. Then add this solution to the volumetric flask.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Carbonate	Na ₂ CO ₃	22.149	22.148	Fisher Scientific	S263-500	037406

Mix thoroughly.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Nitrate	NaNO ₃	209.73	209.733	Fisher Scientific	S343-500	037721
Sodium Nitrite	NaNO ₂	166.48	166.479	Fisher Scientific	S347-500	035602

Mix thoroughly and dilute to the mark.

Table 35. Envelope A Recipe: Tank AN-105 Simulant Spiked with LDR Elements

Volume of Feed: 1000 mL

Balance Manufacturer	Model #	M&TE #	Calibration Date	Calibration Mass (g)	Actual Mass (g)	M&TE #
OHAUS	E04130	AD-1001	4/7/2004	10	10.000	DW-493

Add 200 mL of deionized water to the volumetric flask.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Barium Nitrate	Ba(NO ₃) ₂	0.048	0.045	Fisher Scientific	B-53	721327
Boric Acid	H ₃ BO ₃	0.292	0.291	Reagents Inc.	1-10430	11191N
Cadmium Nitrate	Cd(NO ₃) ₂ ·4H ₂ O	0.069	0.066	Fisher Scientific	C13-100	005642
Calcium Nitrate	Ca(NO ₃) ₂ ·4H ₂ O	0.236	0.237	J. T. Baker	1395-01	K12332
Lead Nitrate	Pb(NO ₃) ₂	0.085	0.084	Fisher Scientific	L61-3	033934
Magnesium Nitrate	Mg(NO ₃) ₂ ·6H ₂ O	0.053	0.054	Fisher Scientific	M46-500	033942
Mercuric Nitrate Monohydrate	Hg(NO ₃) ₂ ·H ₂ O	0.043	0.043	Fisher Scientific	M168-100	935946
Nickel Nitrate	Ni(NO ₃) ₂ ·6H ₂ O	0.124	0.125	Mallinckrodt	6384-04	NA
Potassium Nitrate	KNO ₃	19.221	19.222	Fisher Scientific	P263-500	926781
Silver Nitrate	AgNO ₃	0.039	0.040	Colonial Metals	9007	907-922206
Thallium Chloride	TlCl	0.029	0.031	Acros	318480100	A011131401
Zinc Nitrate	Zn(NO ₃) ₂ ·6H ₂ O	0.045	0.046	Fisher Scientific	Z45-500	005554
Glycolic Acid	HOCH ₂ COOH, 70 wt%	1.665	1.664	Aldrich	42060-3	08229CG
Sodium Chloride	NaCl	14.984	14.984	Fisher Scientific	S271-500	035509
Sodium Fluoride	NaF	0.420	0.420	Fisher Scientific	S299-500	991559
Sodium Chromate	Na ₂ CrO ₄	4.205	4.206	Fisher Scientific	S272-500	006038
Potassium Molybdate	K ₂ MoO ₄	0.204	0.203	NOAH Technologies	90143	13938/1.1
Ammonium Acetate	CH ₃ COONH ₄	0.513	0.511	Fisher Scientific	A637-500	926443B

In a separate Teflon container mix the following:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Aluminum Trihydroxide	Al(OH) ₃	114.77	114.771	ALCOA	S-11	NA
Arsenic III Oxide	As ₂ O ₃	0.066	0.065	Johnson Matthey	14667	H18C07
Sodium Hydroxide	NaOH	196.68	196.636	Fisher Scientific	S318-3	035670
Selenium Dioxide	SeO ₂	0.035	0.033	Aldrich	32547-3	91922EW
Sodium Meta-silicate	Na ₂ SiO ₃ ·9H ₂ O	2.135	2.134	Sigma	S4392-250g	102K0535
Sodium Acetate	CH ₃ COONa·3H ₂ O	3.865	3.865	Fisher Scientific	S209-500	985293
Sodium Formate	HCOONa	4.351	4.353	Fisher Scientific	S648-500	025952
Sodium Oxalate	Na ₂ C ₂ O ₄	0.929	0.930	Fisher Scientific	S487-500	026000
Sodium Phosphate	Na ₃ PO ₄ ·12H ₂ O	2.281	2.279	Fisher Scientific	S377-500	030202
Water	H ₂ O	300	300			

Mix thoroughly. Then add this solution to the volumetric flask.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Carbonate	Na ₂ CO ₃	22.149	22.146	Fisher Scientific	S263-500	037406

Mix thoroughly.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Nitrate	NaNO ₃	209.55	209.548	Fisher Scientific	S343-500	037721
Sodium Nitrite	NaNO ₂	166.48	166.482	Fisher Scientific	S347-500	035602

Add 25 mL of 1000 ppm Sb ICP-ES standard

Pipet		ICP-ES Standard		
M&TE #	Cal. Date	Manufacturer	Part #	Lot #
GT1-ML85 Eppendorf	11/14/2003	High Purity	10002-3	224815

Mix thoroughly and dilute to the mark.

Table 36. Envelope B Recipe: Tank AZ-101 Simulant

Volume of Feed: 1000 mL

Balance Manufacturer	Model #	M&TE #	Calibration Date	Calibration Mass (g)	Actual Mass (g)	M&TE #
OHAUS	E04130	AD-1001	4/7/2004	10	9.998	DW-493

Add 200 mL of deionized water to the volumetric flask.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Ammonium Nitrate	NH ₄ NO ₃	1.470	1.472	Fisher Scientific	A-676	865813
Potassium Nitrate	KNO ₃	11.956	11.958	Fisher Scientific	P263-500	926781
Zirconyl Nitrate	ZrO(NO ₃) ₂ .xH ₂ O	0.008	0.008	Acros	222635000	A017866301
Sodium Chloride	NaCl	0.329	0.331	Fisher Scientific	S271-500	035509
Sodium Fluoride	NaF	4.008	4.009	Fisher Scientific	S299-500	991559
Sodium Chromate	Na ₂ CrO ₄	2.274	2.274	Fisher Scientific	S272-500	006038

In a separate container mix the following

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Aluminum Trihydroxide	Al(OH) ₃	30.839	30.839	Sigma Aldrich	239186-500G	11515KA
Sodium Hydroxide	NaOH	37.194	37.330	Fisher Scientific	S318-3	040412
Sodium Phosphate	Na ₃ PO ₄ .12H ₂ O	6.015	6.016	Fisher Scientific	S377-500	030202
Water	H ₂ O	300	300			

Mix thoroughly. Then add this solution to the volumetric flask.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Carbonate	Na ₂ CO ₃	40.757	40.755	Fisher Scientific	S263-500	037406
Sodium Sulfate	Na ₂ SO ₄	26.128	26.126	Fisher Scientific	S421-500	007048

Mix thoroughly.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Nitrate	NaNO ₃	92.051	92.049	Fisher Scientific	S343-500	037721
Sodium Nitrite	NaNO ₂	97.583	97.585	Fisher Scientific	S347-500	035602

Mix thoroughly and dilute to the mark.

Table 37. Envelope B Recipe: Tank AZ-101 Simulant Spiked with LDR Elements

Volume of Feed: 1000 mL

Balance Manufacturer	Model #	M&TE #	Calibration Date	Calibration Mass (g)	Actual Mass (g)	M&TE #
OHAUS	E04130	AD-1001	4/7/2004	10	9.998	DW-493

Add 200 mL of deionized water to the volumetric flask.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed		Actual Mass		
		(g)	(g)	Manufacturer	Part #	Lot #
Ammonium Nitrate	NH ₄ NO ₃	1.470	1.472	Fisher Scientific	A-676	865813
Barium Nitrate	Ba(NO ₃) ₂	0.048	0.048	Fisher Scientific	B-53	721327
Cadmium Nitrate	Cd(NO ₃) ₂ ·4H ₂ O	0.069	0.070	Fisher Scientific	C13-100	5642
Lead nitrate	Pb(NO ₃) ₂	0.040	0.043	Fisher Scientific	L61-3	033934
Mercuric Nitrate Monhydrate	Hg(NO ₃) ₂ ·H ₂ O	0.043	0.043	Fisher Scientific	M168-100	935946
Nickel Nitrate	Ni(NO ₃) ₂ ·6H ₂ O	0.124	0.127	Mallinckrodt	6384-04	NA
Potassium Nitrate	KNO ₃	11.956	11.954	Fisher Scientific	P263-500	926781
Silver Nitrate	AgNO ₃	0.039	0.038	Colonial Metal Inc	9007	907-922206
Thallium Chloride	TlCl	0.029	0.029	Acros	318480100	A011131401
Zirconyl Nitrate	ZrO(NO ₃) ₂ ·xH ₂ O	0.008	0.007	Acros	222635000	A017866301
Sodium Chloride	NaCl	0.329	0.330	Fisher Scientific	S271-500	035509
Sodium Fluoride	NaF	4.008	4.008	Fisher Scientific	S299-500	991559
Sodium Chromate	Na ₂ CrO ₄	2.274	2.276	Fisher Scientific	S272-500	006038

In a separate container mix the following

Compound	Formula	Mass Needed		Actual Mass		
		(g)	(g)	Manufacturer	Part #	Lot #
Aluminum trihydroxide	Al(OH) ₃	30.839	30.839	J. T. Baker	0518-05	N27599
Arsenic III Oxide	As ₂ O ₃	0.066	0.066	Johnson Matthey	14667	H18C07
Selenium Dioxide	SeO ₂	0.035	0.034	Aldrich	32547-3	91922EW
Sodium Hydroxide	NaOH	37.290	37.298	Fisher Scientific	S318-3	035670
Sodium Phosphate	Na ₃ PO ₄ ·12H ₂ O	6.015	6.016	Fisher Scientific	S377-500	030202
Water	H ₂ O	300	300			

Mix thoroughly. Then add this solution to the volumetric flask.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed		Actual Mass		
		(g)	(g)	Manufacturer	Part #	Lot #
Sodium Carbonate	Na ₂ CO ₃	40.757	40.758	Fisher Scientific	S263-500	015085
Sodium Sulfate	Na ₂ SO ₄	26.128	26.130	Fisher Scientific	S421-500	007048

Mix thoroughly.

Add the following compounds to the volumetric flask:

Compound	Formula	Mass Needed		Actual Mass		
		(g)	(g)	Manufacturer	Part #	Lot #
Sodium Nitrate	NaNO ₃	91.845	91.846	Fisher Scientific	S343-500	037721
Sodium Nitrite	NaNO ₂	97.583	97.582	Fisher Scientific	S347-500	035602

Add 25 mL of 1000 ppm Sb ICP-ES standard

M&TE #	Pipet Cal. Date	ICP-ES Standard		
		Manufacturer	Part #	Lot #
GT1-ML85 Eppendorf	11/14/2003	High Purity	10002-3	412525

Mix thoroughly and dilute to the mark.

Table 38. Envelope C Recipe: Tank AN-107 Simulant

Balance Manufacturer	Model #	M&TE #	Calibration Date	Calibration Mass (g)	Actual Mass (g)	M&TE #
OHAUS	E04130	AD-1001	4/7/2004	10	9.999	DW-493

Add 200 mL of deionized water to the volumetric flask.

Add the following compounds to the volumetric flask:

Compounds	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Barium Nitrate	Ba(NO ₃) ₂	0.013	0.012	Fisher Scientific	B-53	721327
Cadmium Nitrate	Cd(NO ₃) ₂ ·4H ₂ O	0.176	0.177	Fisher Scientific	C13-100	005642
Calcium Nitrate	Ca(NO ₃) ₂ ·4H ₂ O	3.48	3.482	J.T Baker	1395-1	K12332
Cerium Nitrate	Ce(NO ₃) ₃ ·6H ₂ O	0.16	0.158	Aldrich	23853-8	108PY
Copper Nitrate	Cu(NO ₃) ₂ ·2.5H ₂ O	0.11	0.110	Fisher Scientific	C467-500	884348
Ferric Nitrate	Fe(NO ₃) ₃ ·9H ₂ O	12.23	12.230	Spectrum	F1030	LW0212
Lanthanum Nitrate	La(NO ₃) ₃ ·6H ₂ O	0.14	0.138	Barker Industries	NA	NA
Lead Nitrate	Pb(NO ₃) ₂	0.62	0.620	Fisher Scientific	L61-3	033934
Magnesium Nitrate	Mg(NO ₃) ₂ ·6H ₂ O	0.26	0.259	Fisher Scientific	M46-500	033942
Manganous Chloride	MnCl ₂ ·4H ₂ O	2.03	2.032	J. T. Baker	2540-01	T20150
Neodymium Nitrate	Nd(NO ₃) ₃ ·6H ₂ O	0.29	0.287	Barker Industries	NA	NA
Nickel Nitrate	Ni(NO ₃) ₂ ·6H ₂ O	2.63	2.631	Mallinckrodt	6384-04	NA
Potassium Nitrate	KNO ₃	4.60	4.602	Fisher Scientific	P263-500	926781
Silver Nitrate	AgNO ₃	0.022	0.022	Colonial Metals	9007	907-922206
Zinc Nitrate	Zn(NO ₃) ₂ ·6H ₂ O	0.206	0.206	Fisher Scientific	Z45-500	005554
Zirconyl Nitrate	ZrO(NO ₃) ₂ ·xH ₂ O	0.19	0.191	Acros	222635000	A01786301
EDTA	Na ₂ EDTA	7.26	7.259	Fisher Scientific	S311-500	995102
HEDTA	HEDTA	2.16	2.160	Aldrich	H2650-2	11515C1
Sodium Gluconate	C ₆ H ₁₁ NaO ₇	3.93	3.929	Aldrich	18633.3	99930CT
Glycolic Acid	HOCH ₂ COOH	26.93	26.930	Aldrich	42060-3	08229CG
Citric Acid	C ₆ H ₈ O ₇	9.44	9.442	Fisher Scientific	A104-500	017360
Nitrioltriactic Acid	N(CH ₂ COOH) ₃	0.57	0.569	Acros	29252-5000	68134/1
Iminodiactic Acid	CH ₂ NHCH ₂ COOH	6.04	6.039	Aldrich	22000-0	06116TU
Boric acid	H ₃ BO ₃	0.20	0.198	Reagents Inc	1-10430	11191N
Sodium Chloride	NaCl	1.82	1.819	Fisher Scientific	S271-500	035509
Sodium Fluoride	NaF	0.29	0.292	Fisher Scientific	S299-500	991559
Sodium Chromate	Na ₂ CrO ₄	0.55	0.551	Fisher Scientific	S272-500	006038
Potassium Molybdate	K ₂ MoO ₄	0.089	0.089	NAOH Technologies	90143	13938/1.1

In separate Teflon container mix the following

Compounds	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Aluminum Nitrate	Al(NO ₃) ₃ ·9H ₂ O	5.37	5.367	Fisher Scientific	A586-500	035726
Selenium Dioxide	SeO ₂	0.001	0.001	Aldrich	32547-3	91922EW
Sodium Hydroxide	NaOH	25.27	25.263	Fisher Scientific	S318-3	035670
Sodium Phosphate	Na ₃ PO ₄ ·12H ₂ O	4.44	4.440	Fisher Scientific	S317-500	030202
Sodium Formate	NaHCOO	15.71	15.711	Fisher Scientific	S648-500	025952
Sodium Acetate	NaCH ₃ COO·3H ₂ O	2.37	2.367	Fisher Scientific	S209-500	985293
Sodium Oxalate	Na ₂ C ₂ O ₄	1.26	1.260	Fisher Scientific	S487-500	026000
Water		200	200			

Mix thoroughly. Then add this solution to the volumetric flask.

Add the following compound to the volumetric flask:

Compounds	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Carbonate	Na ₂ CO ₃	148.25	148.253	Fisher Scientific	S263-500	015085

Mix thoroughly.

Add the following compounds to the volumetric flask:

Compounds	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Nitrate	NaNO ₃	297.29	297.287	Fisher Scientific	S343-500	037721
Sodium Nitrite	NaNO ₂	91.49	91.489	Fisher Scientific	S347-500	035602
Water	H ₂ O	100	100			

Mix thoroughly and dilute to the mark.

Table 39. Envelope C Recipe: Tank AN-107 Simulant Spiked with LDR Elements

Volume of Feed: 1000 mL

Balance Manufacturer	Model #	M&TE #	Calibration Date	Calibration Mass (g)	Actual Mass (g)	M&TE #
OHAUS	E04130	AD-1001	4/7/2004	10	9.999	DW-493

Add 200 mL of deionized water to the volumetric flask.

Add the following compounds to the volumetric flask:

Compounds	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Barium Nitrate	Ba(NO ₃) ₂	0.048	0.047	Fisher Scientific	B-53	721327
Cadmium Nitrate	Cd(NO ₃) ₂ ·4H ₂ O	0.18	0.182	Fisher Scientific	C13-100	5642
Calcium Nitrate	Ca(NO ₃) ₂ ·4H ₂ O	3.48	3.482	J.T Baker	1395-1	K12332
Cerium Nitrate	Ce(NO ₃) ₃ ·6H ₂ O	0.16	0.164	Aldrich	23853-8	108PY
Copper Nitrate	Cu(NO ₃) ₂ ·2.5H ₂ O	0.11	0.114	Fisher Scientific	C467-500	884348
Ferric Nitrate	Fe(NO ₃) ₃ ·9H ₂ O	12.23	12.232	Spectrum	F1030	LW0212
Lanthanum Nitrate	La(NO ₃) ₃ ·6H ₂ O	0.14	0.139	Barker Industries	NA	NA
Lead Nitrate	Pb(NO ₃) ₂	0.62	0.618	Fisher Scientific	L61-3	033934
Magnesium Nitrate	Mg(NO ₃) ₂ ·6H ₂ O	0.26	0.262	Fisher Scientific	M46-500	033942
Manganous Chloride	MnCl ₂ ·4H ₂ O	2.03	2.030	J. T. Baker	2540-01	T20150
Mercuric Nitrate Monohydrate	Hg(NO ₃) ₂ ·H ₂ O	0.043	0.043	Fisher Scientific	M168-100	935946
Neodymium Nitrate	Nd(NO ₃) ₃ ·6H ₂ O	0.29	0.294	Barker Industries	NA	NA
Nickel Nitrate	Ni(NO ₃) ₂ ·6H ₂ O	2.63	2.633	Mallinckrodt	6384-04	NA
Potassium Nitrate	KNO ₃	4.60	4.558	Fisher Scientific	P263-500	926781
Silver Nitrate	AgNO ₃	0.04	0.042	Colonial Metal Inc	9007	907-922206
Thallium Chloride	TlCl	0.029	0.029	Acros	318480100	A011131401
Zinc Nitrate	Zn(NO ₃) ₂ ·6H ₂ O	0.21	0.209	Fisher Scientific	Z45-500	005554
Zirconyl Nitrate	ZrO(NO ₃) ₂ ·xH ₂ O	0.19	0.192	Acros	222635000	A01786301
EDTA	Na ₂ EDTA	7.26	7.262	Fisher Scientific	S311-500	995102
HEDTA	HEDTA	2.16	2.162	Aldrich	H2650-2	11515C1
Sodium Gluconate	C ₈ H ₁₁ NaO ₇	3.93	3.930	Aldrich	18633.3	99930CT
Glycolic Acid	HOCH ₂ COOH	26.93	26.932	Aldrich	42060-3	08229CG
Citric Acid	C ₆ H ₈ O ₇	9.44	9.441	Fisher Scientific	A104-500	017360
Nitrioltriacetic Acid	N(CH ₂ COOH) ₃	0.57	0.569	Acros	29252-5000	68134/1
Iminodiacetic Acid	CH ₂ NHCH ₂ COOH	6.04	6.037	Aldrich	22000-0	06116TU
Boric acid	H ₃ BO ₃	0.20	0.198	Reagents Inc	1-10430	11191N
Sodium Chloride	NaCl	1.82	1.822	Fisher Scientific	S271-500	035509
Sodium Fluoride	NaF	0.29	0.291	Fisher Scientific	S299-500	991559
Sodium Chromate	Na ₂ CrO ₄	0.55	0.550	Fisher Scientific	S272-500	006038
Potassium Molybdate	K ₂ MoO ₄	0.089	0.088	NAOH Technologies	90143	13938/1.1

In separate Teflon container mix the following

Compounds	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Aluminum Nitrate	Al(NO ₃) ₃ ·9H ₂ O	5.37	5.369	Fisher Scientific	A586-500	035726
Arsenic III Oxide	As ₂ O ₃	0.066	0.066	Johnson Matthey	14667	H18C07
Selenium Dioxide	SeO ₂	0.035	0.035	Aldrich	32547-3	91922EW
Sodium Hydroxide	NaOH	25.27	25.247	Fisher Scientific	S318-3	035670
Sodium Phosphate	Na ₃ PO ₄ ·12H ₂ O	4.44	4.440	Fisher Scientific	S317-500	030202
Sodium Formate	NaHCOO	15.71	15.709	Fisher Scientific	S648-500	025952
Sodium Acetate	NaCH ₃ COO·3H ₂ O	2.37	2.369	Fisher Scientific	S209-500	985293
Sodium Oxalate	Na ₂ C ₂ O ₄	1.26	1.260	Fisher Scientific	S487-500	026000
Water		200	200			

Mix thoroughly. Then add this solution to the volumetric flask.

Add the following compound to the volumetric flask:

Compounds	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Carbonate	Na ₂ CO ₃	148.25	148.252	Fisher Scientific	S263-500	037406

Mix thoroughly.

Add the following compounds to the volumetric flask:

Compounds	Formula	Mass Needed (g)	Actual Mass (g)	Manufacturer	Part #	Lot #
Sodium Nitrate	NaNO ₃	297.16	297.260	Fisher Scientific	S343-500	037721
Sodium Nitrite	NaNO ₂	91.49	91.491	Fisher Scientific	S347-500	035602
Water	H ₂ O	100	100			

Add 25 mL of 1000 ppm Sb ICP-ES standard

Pipet		ICP-ES Standard		
M&TE #	Cal. Date	Manufacturer	Part #	Lot #
GT1-ML85 Eppendorf	11/14/2003	High Purity	10002-3	224815

Mix thoroughly and dilute to the mark.

7.3 Appendix C: X-ray Fluorescence Scans

AN105 Simulant Residue (HOPG Target)

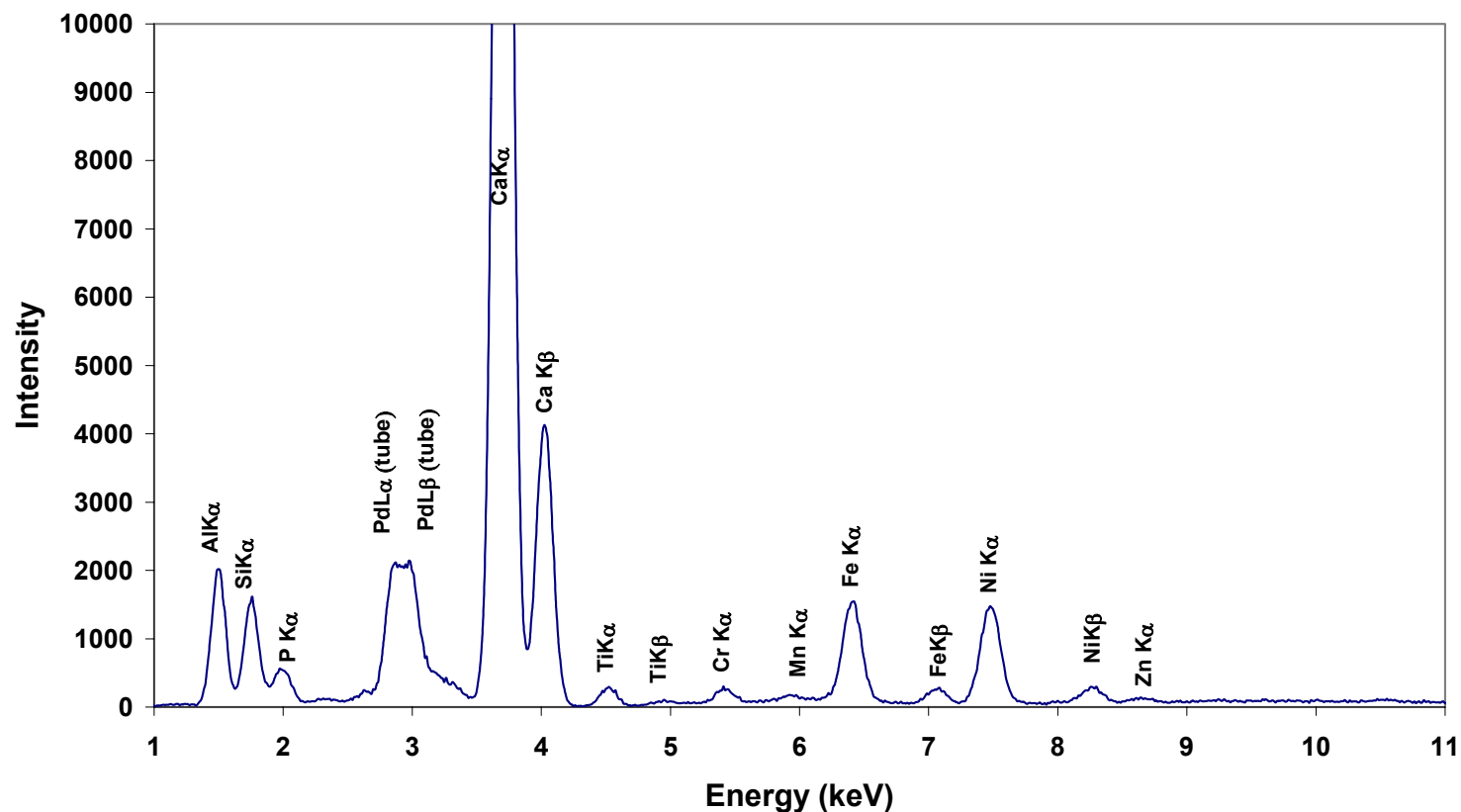


Figure 12. X-ray fluorescence pattern of AN-105 simulant filtered residue (HOPG target)

AN105 Simulant Solids (Mo Target)

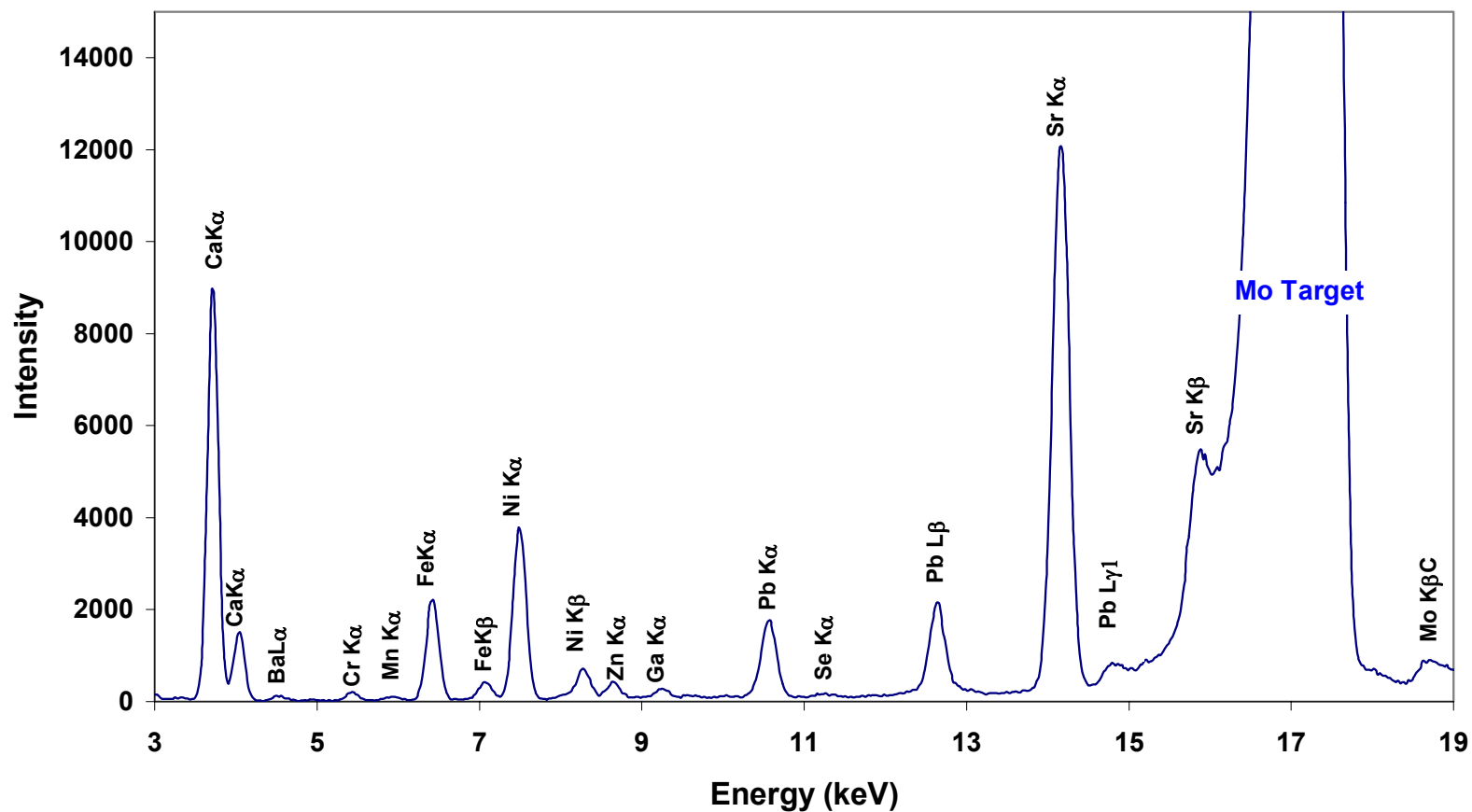


Figure 13. X-ray fluorescence pattern of AN-105 simulant filtered residue (Mo target)

AN105 Simulant Residue (Al₂O₃ Target)

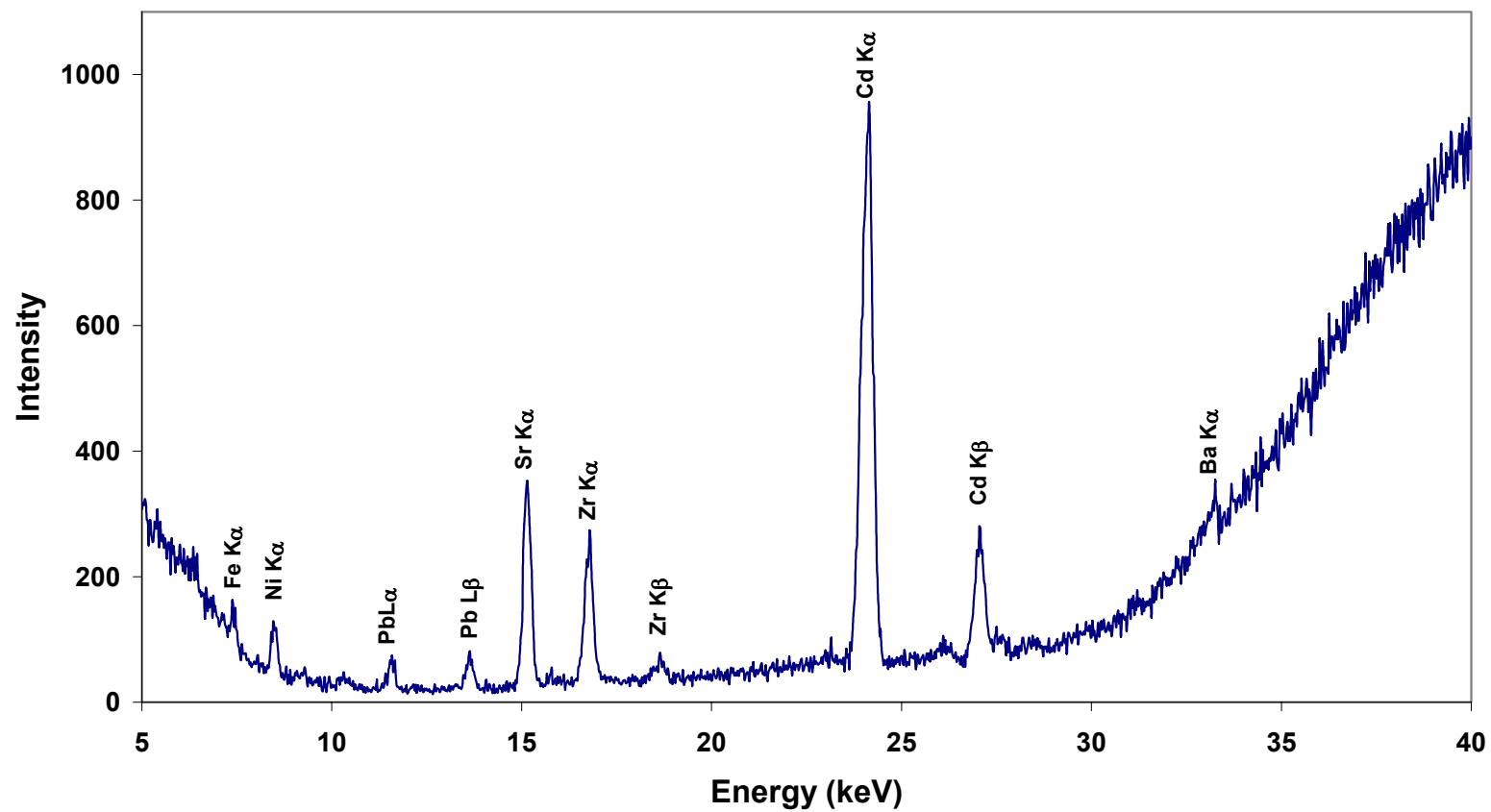


Figure 14. X-ray fluorescence pattern of AN-105 simulant filtered residue (Al₂O₃ target)

AN-105 Land Disposal Simulant Residue (HOPG Target)

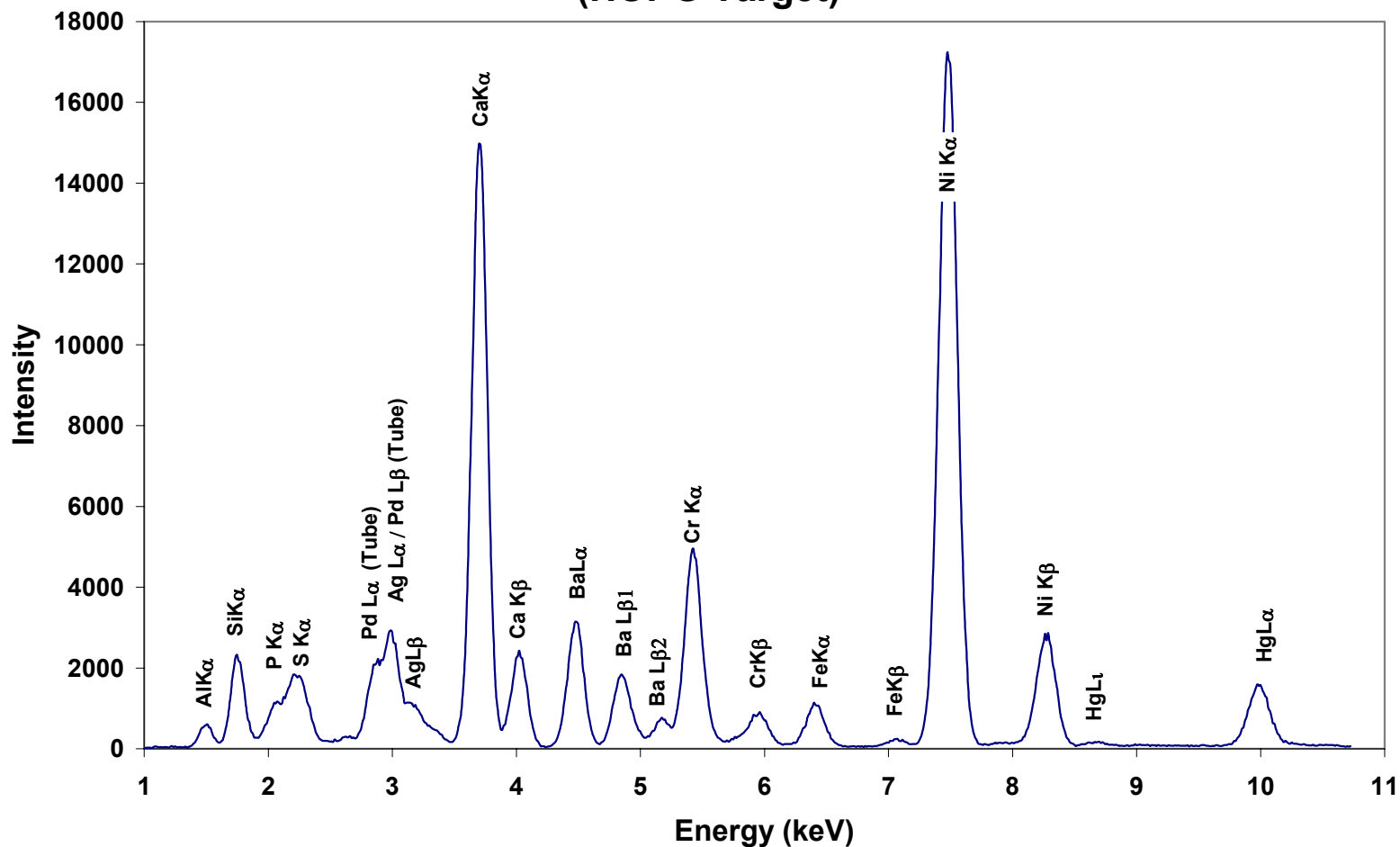


Figure 15. X-ray fluorescence pattern of AN-105 LDR simulant filtered residue (HOPG target)

AN-105 Land Disposal Simulant Residue (Mo Target)

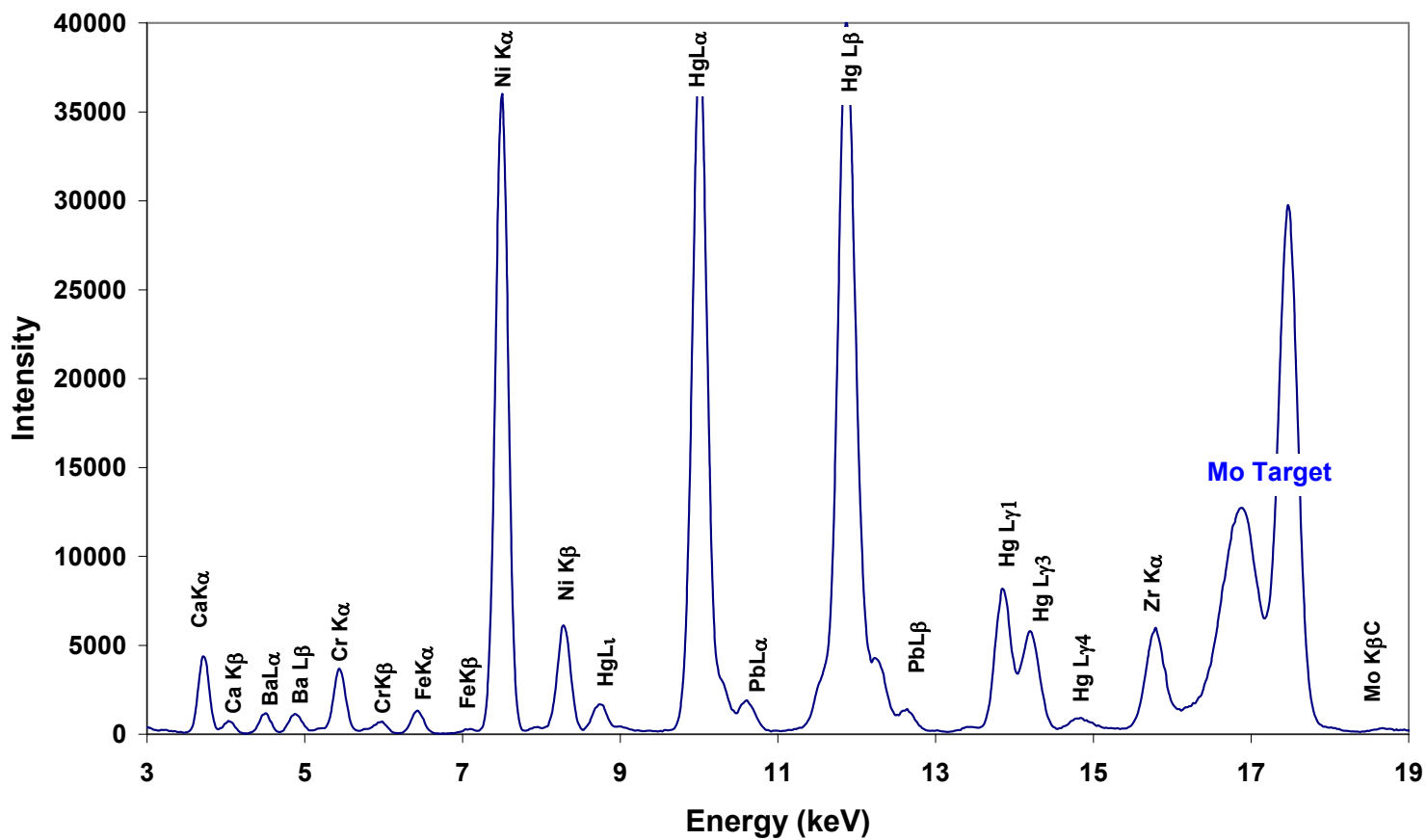


Figure 16. X-ray fluorescence pattern of AN-105 LDR simulant filtered residue (Mo target)

AN-105 Land Disposal Simulant Residue (Al₂O₃ Target)

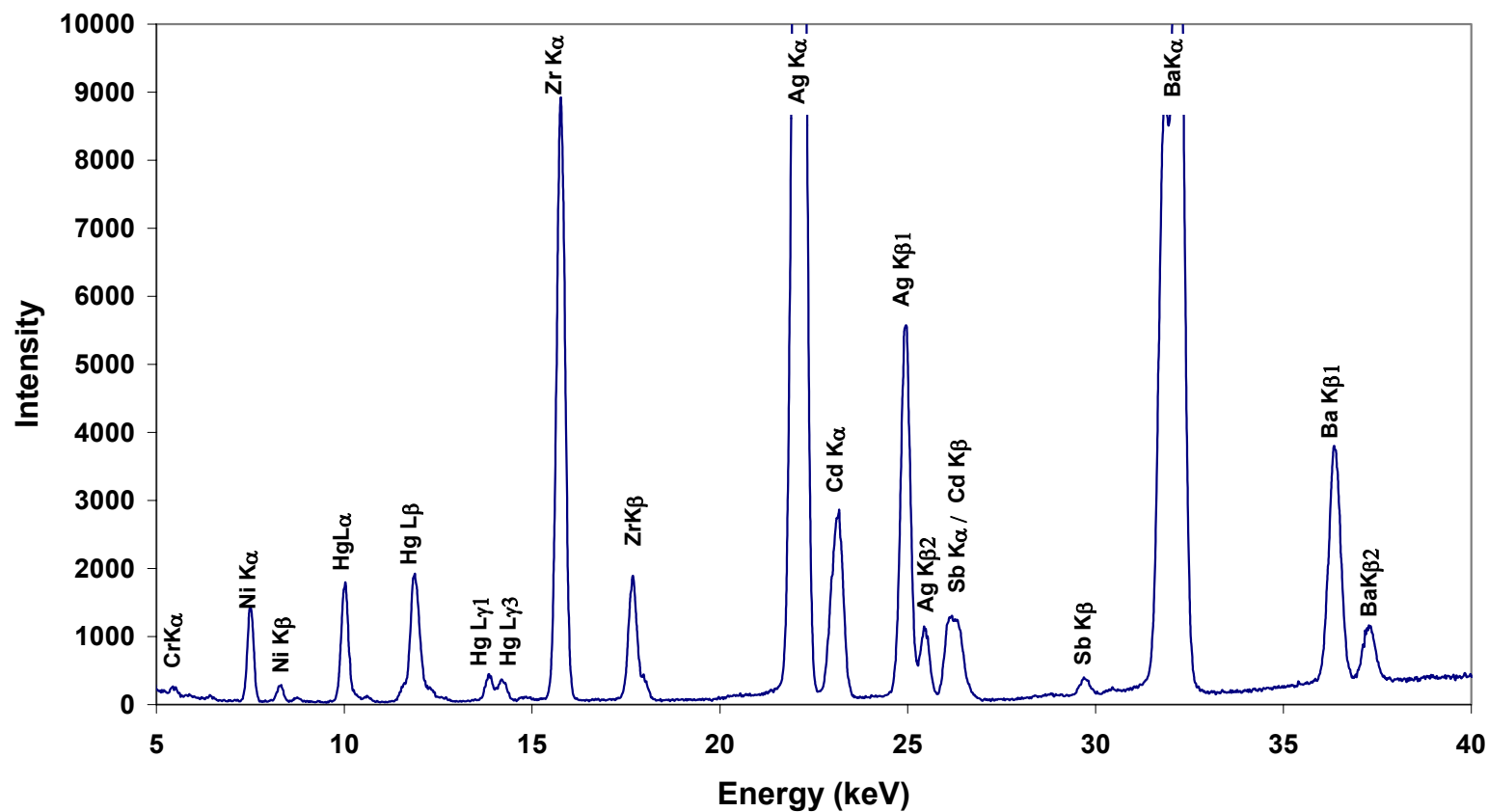


Figure 17. X-ray fluorescence pattern of AN-105 LDR simulant filtered residue (Al₂O₃ target)

AZ101 Simulant Residue (HOPG Target)

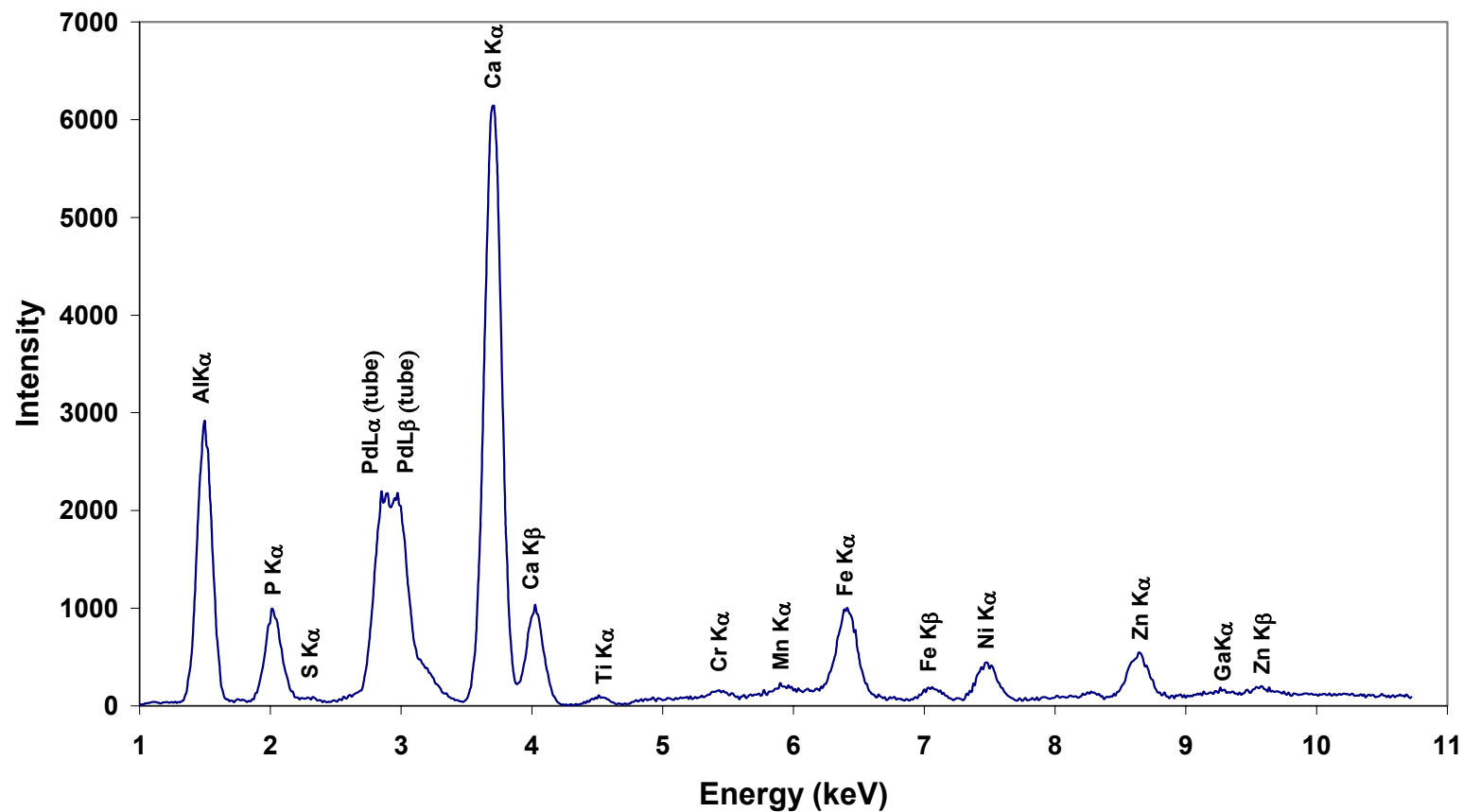


Figure 18. X-ray fluorescence pattern of AZ-101 simulant filtered residue (HOPG target)

AZ101 Simulant Residue (Mo Target)

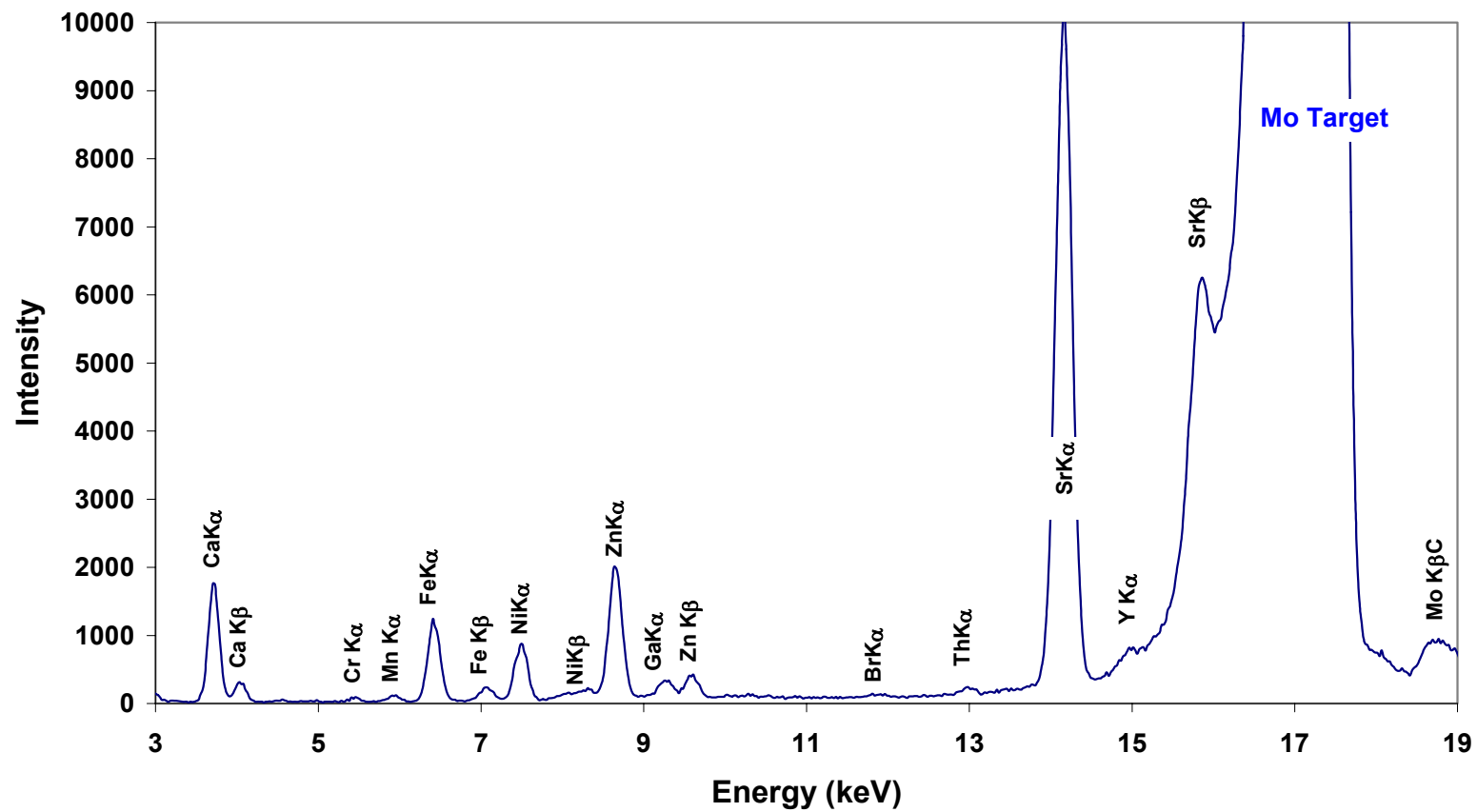


Figure 19. X-ray fluorescence pattern of AZ-101 simulant filtered residue (Mo target)

AZ101 Simulant Residue (Al₂O₃ Target)

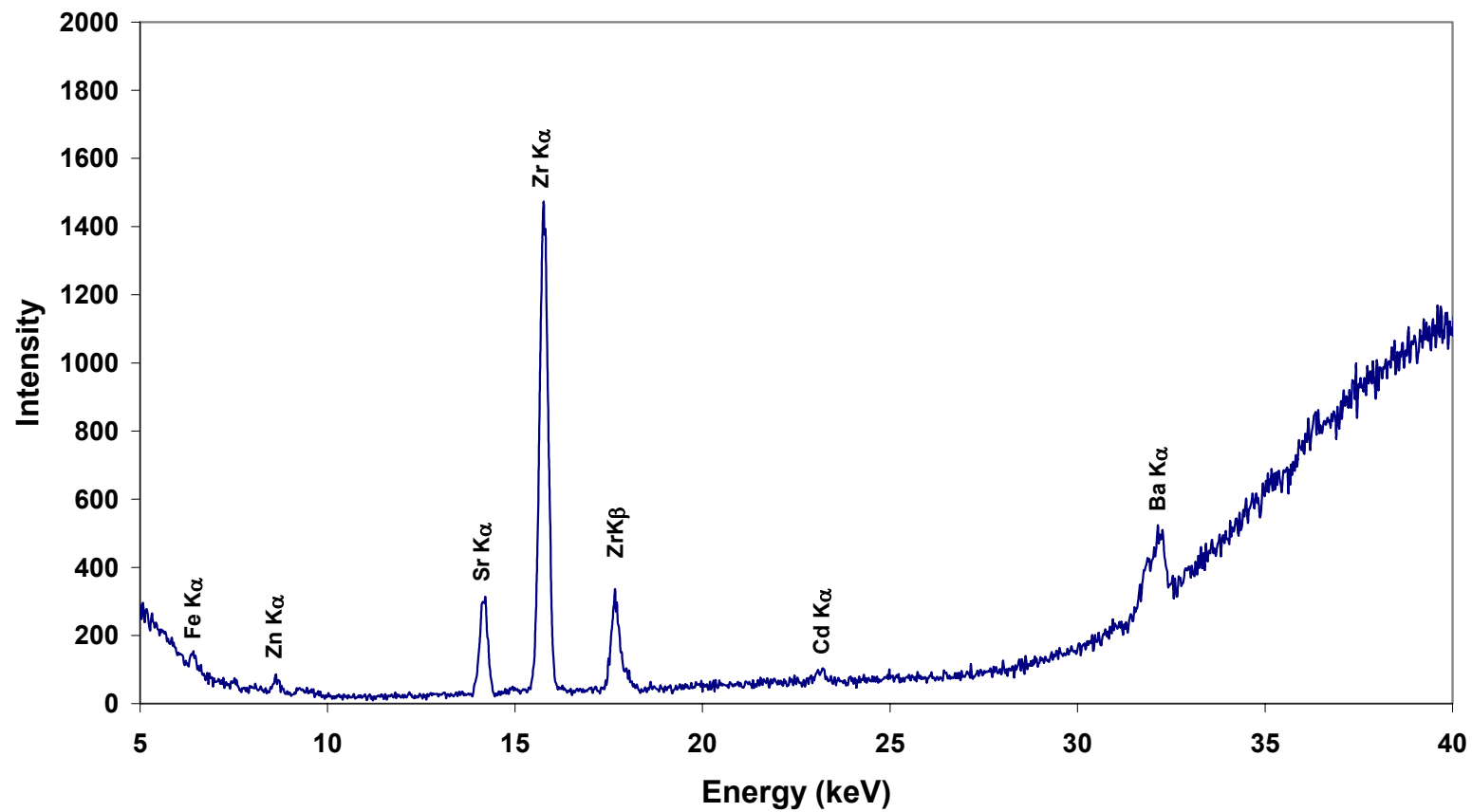


Figure 20. X-ray fluorescence pattern of AZ-101 simulant filtered residue (Al₂O₃ target)

AZ-101 Land Disposal Simulant Residue (HOPG Target)

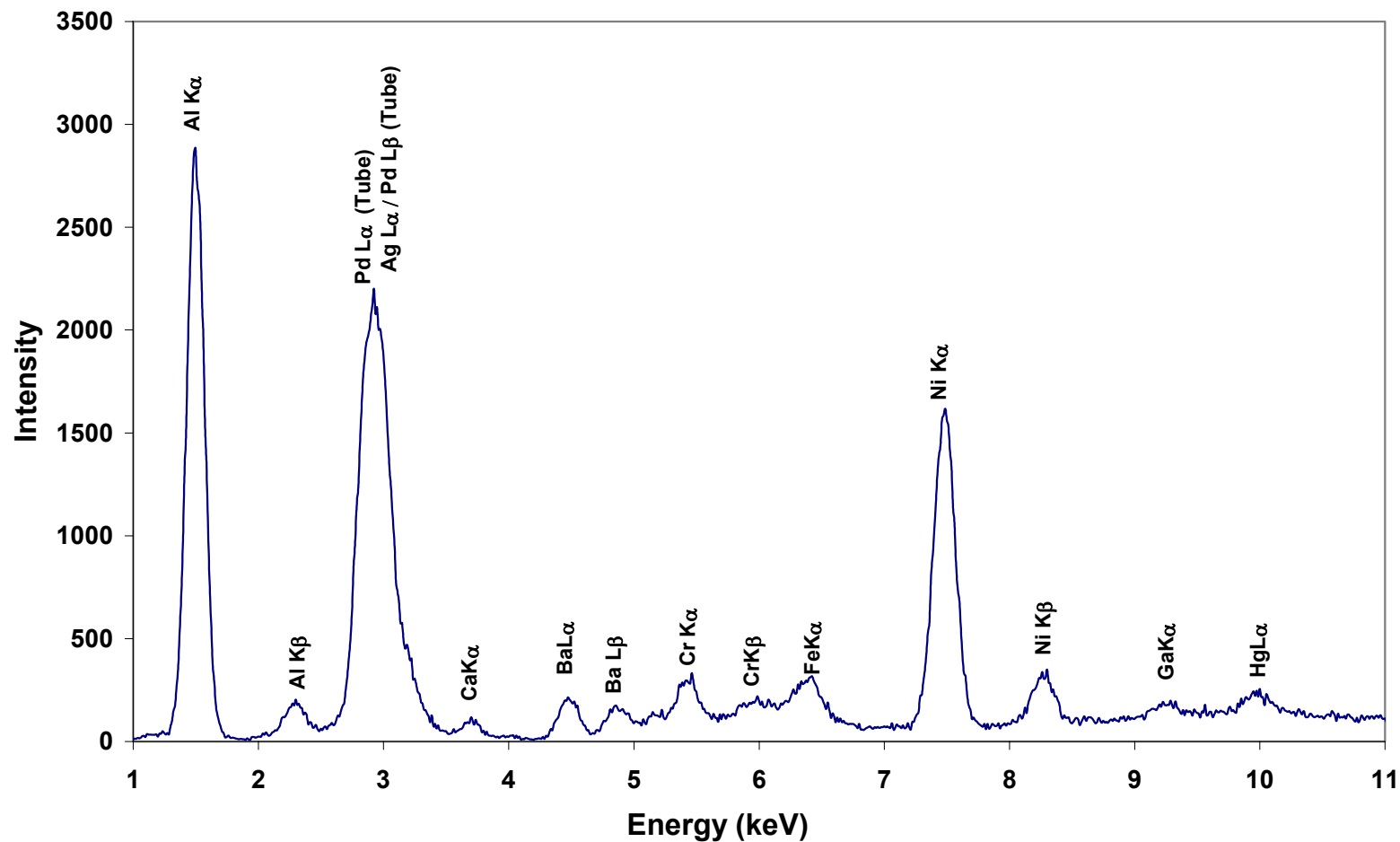


Figure 21. X-ray fluorescence pattern of AZ-101 LDR simulant filtered residue (HOPG target)

AZ-101 Land Disposal Simulant Residue (Mo Target)

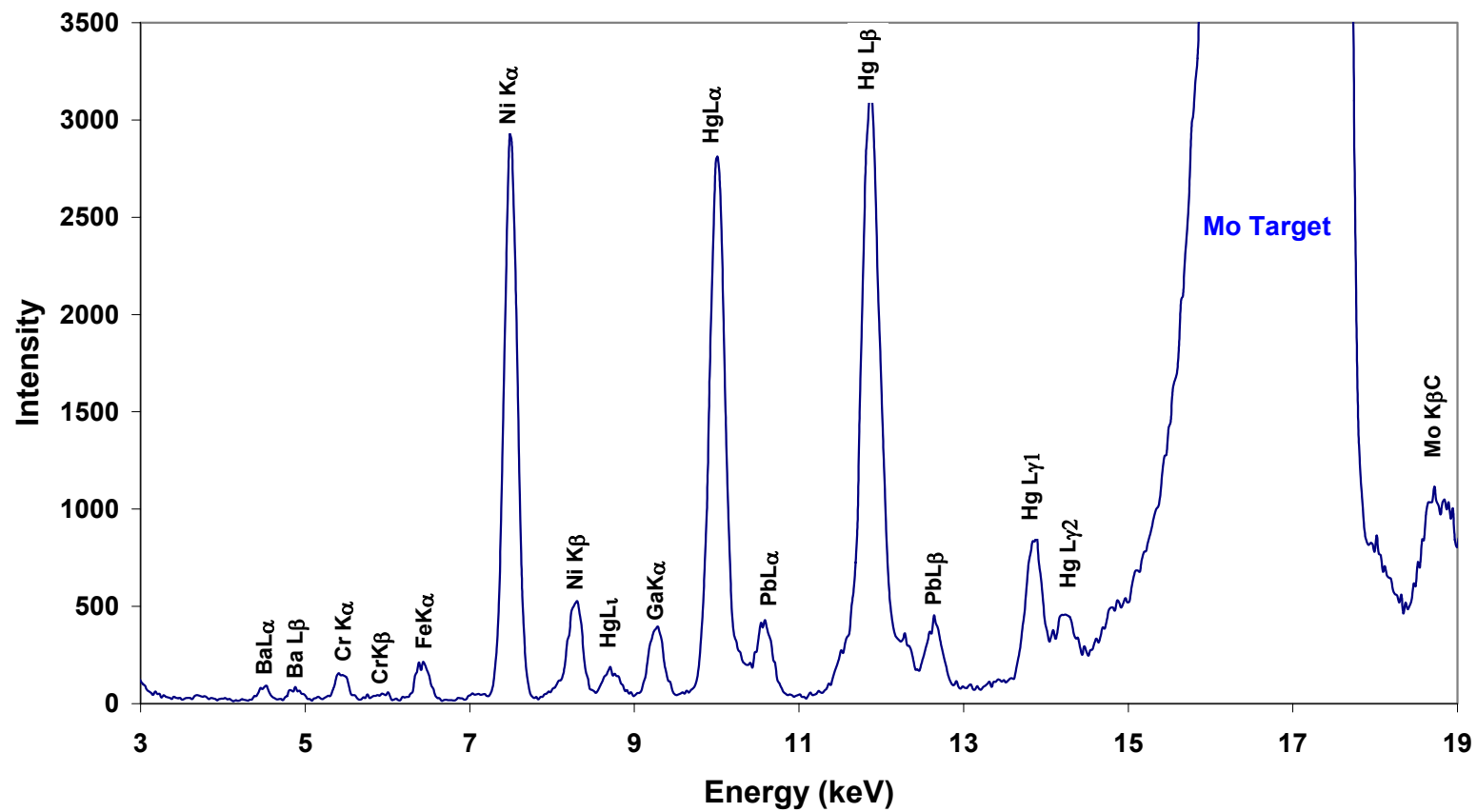


Figure 22. X-ray fluorescence pattern of AZ-101 LDR simulant filtered residue (Mo target)

AZ-101 Land Disposal Simulant Residue (Al₂O₃ Target)

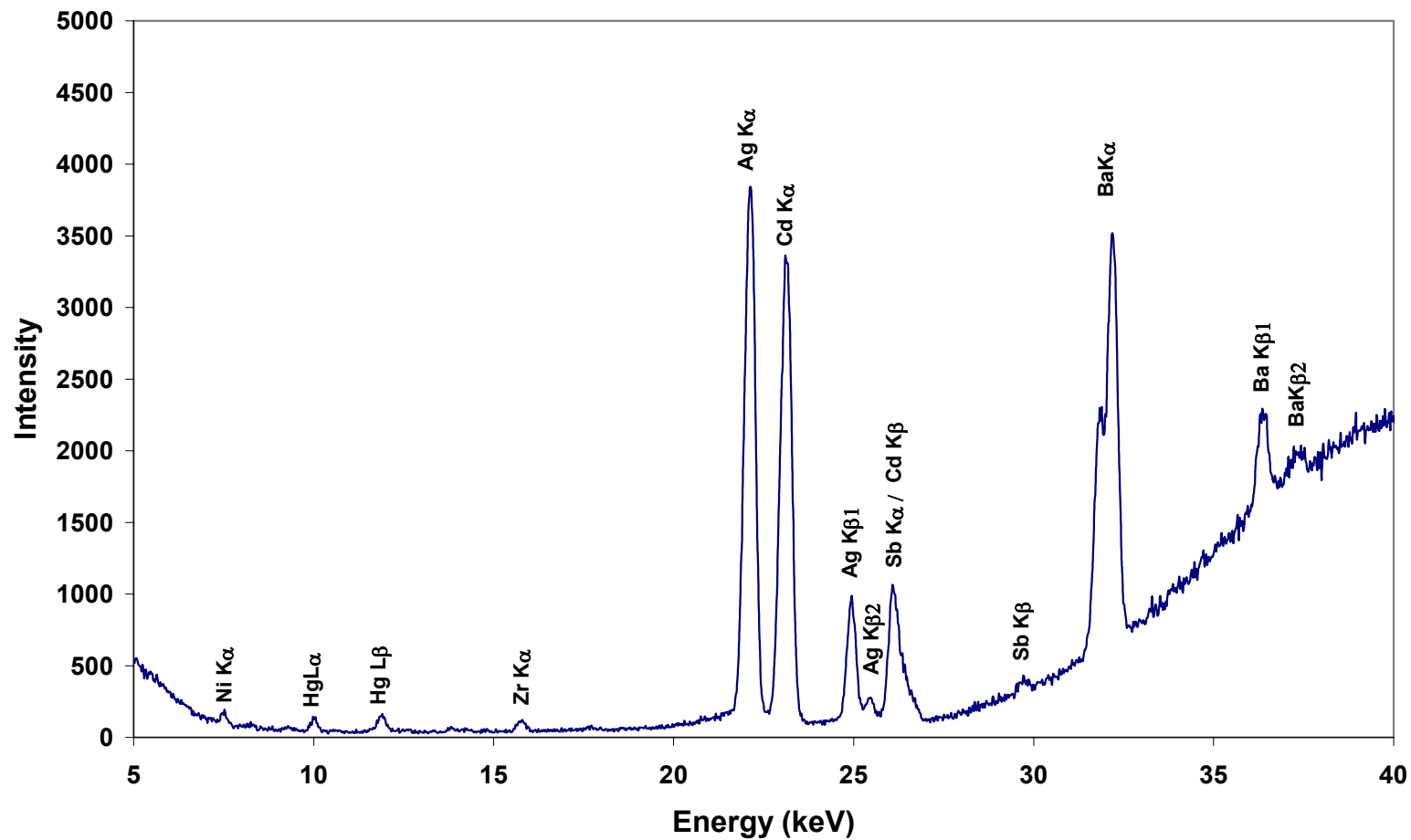


Figure 23. X-ray fluorescence pattern of AZ-101 LDR simulant filtered residue (Al₂O₃ target)

AN107 Simulant Residue (HOPG Target)

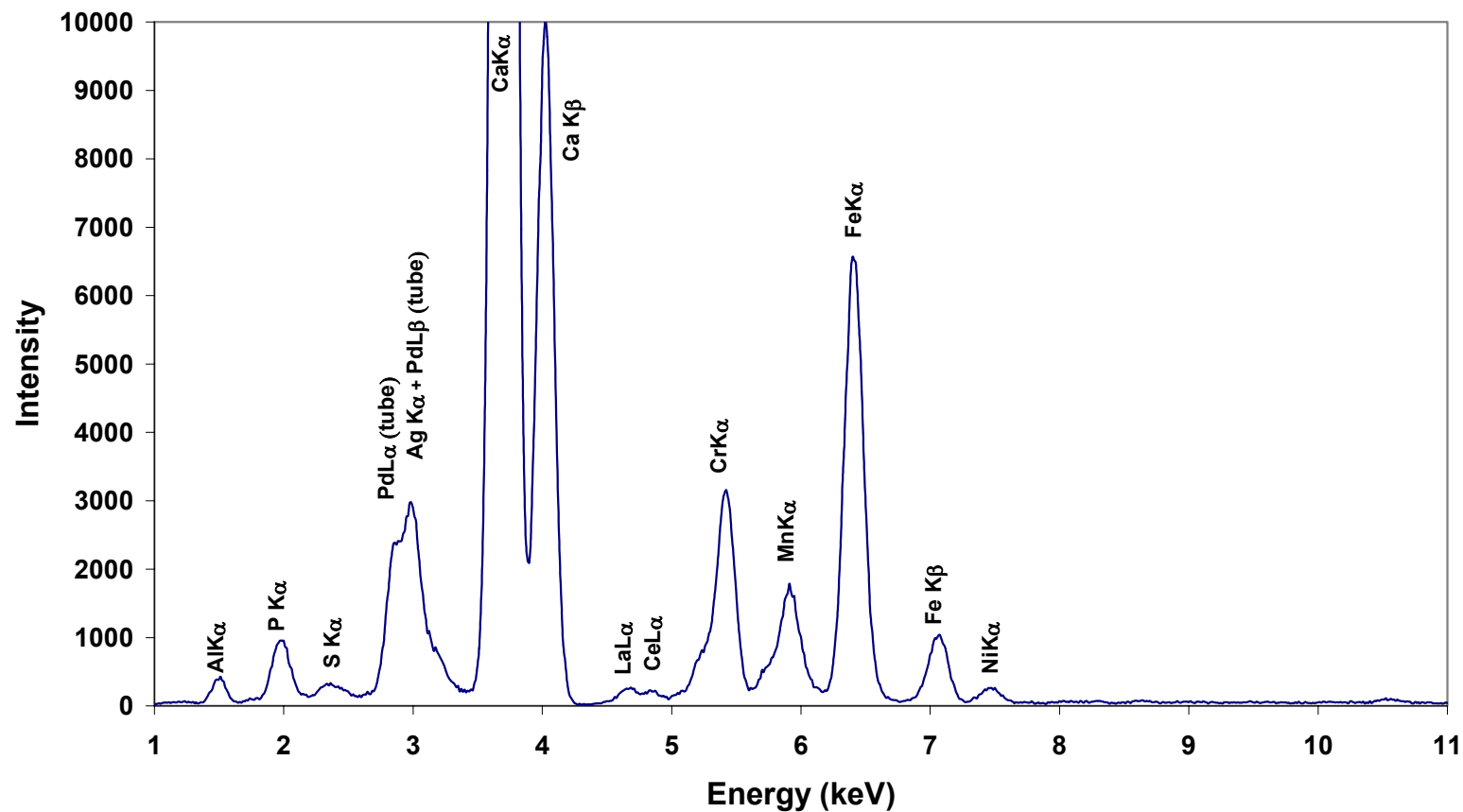


Figure 24. X-ray fluorescence pattern of AN-107 simulant filtered residue (HOPG target)

AN107 Simulant Residue (Mo Target)

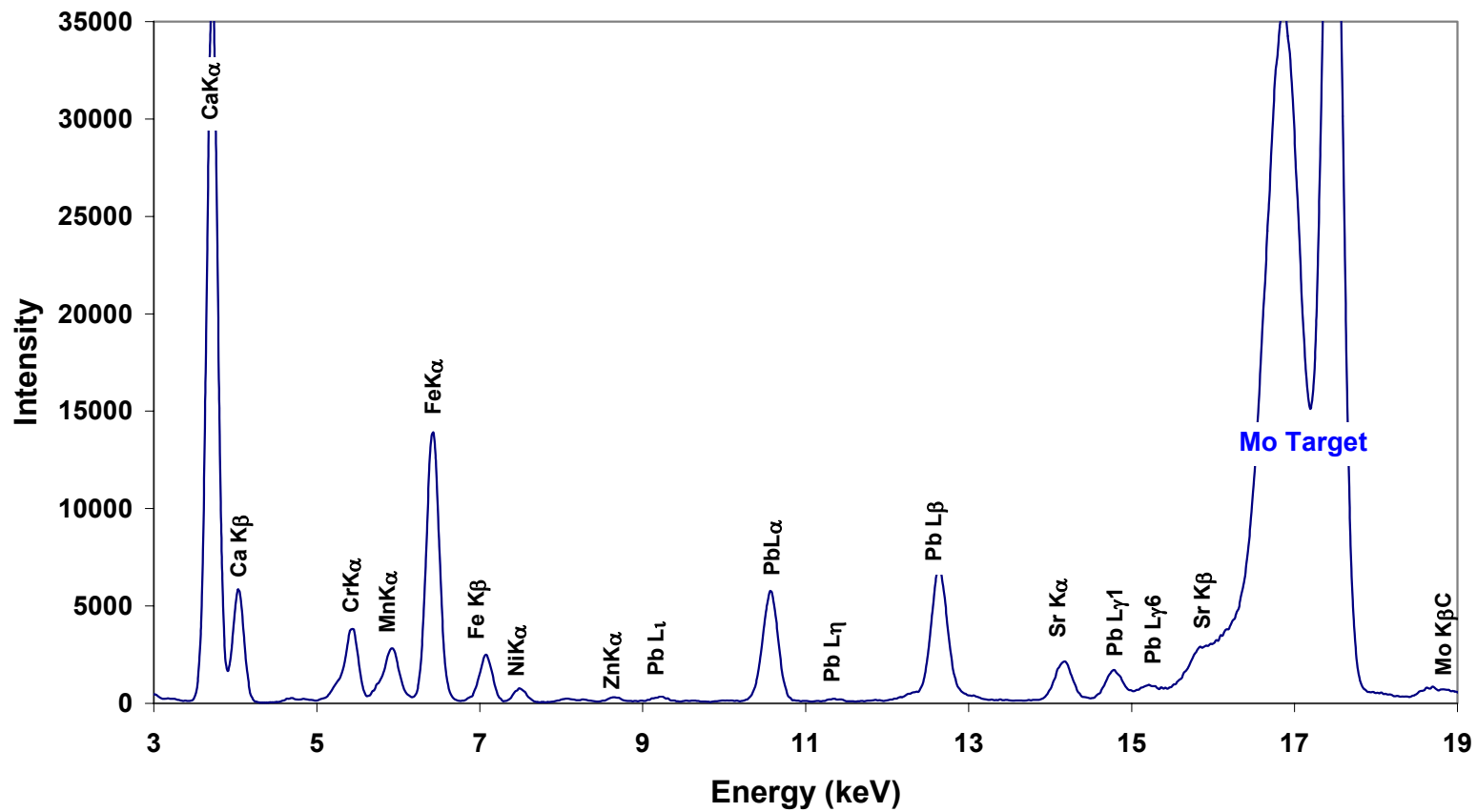


Figure 25. X-ray fluorescence pattern of AN-107 simulant filtered residue (Mo target)

AN107 Simulant Residue (Al₂O₃ Target)

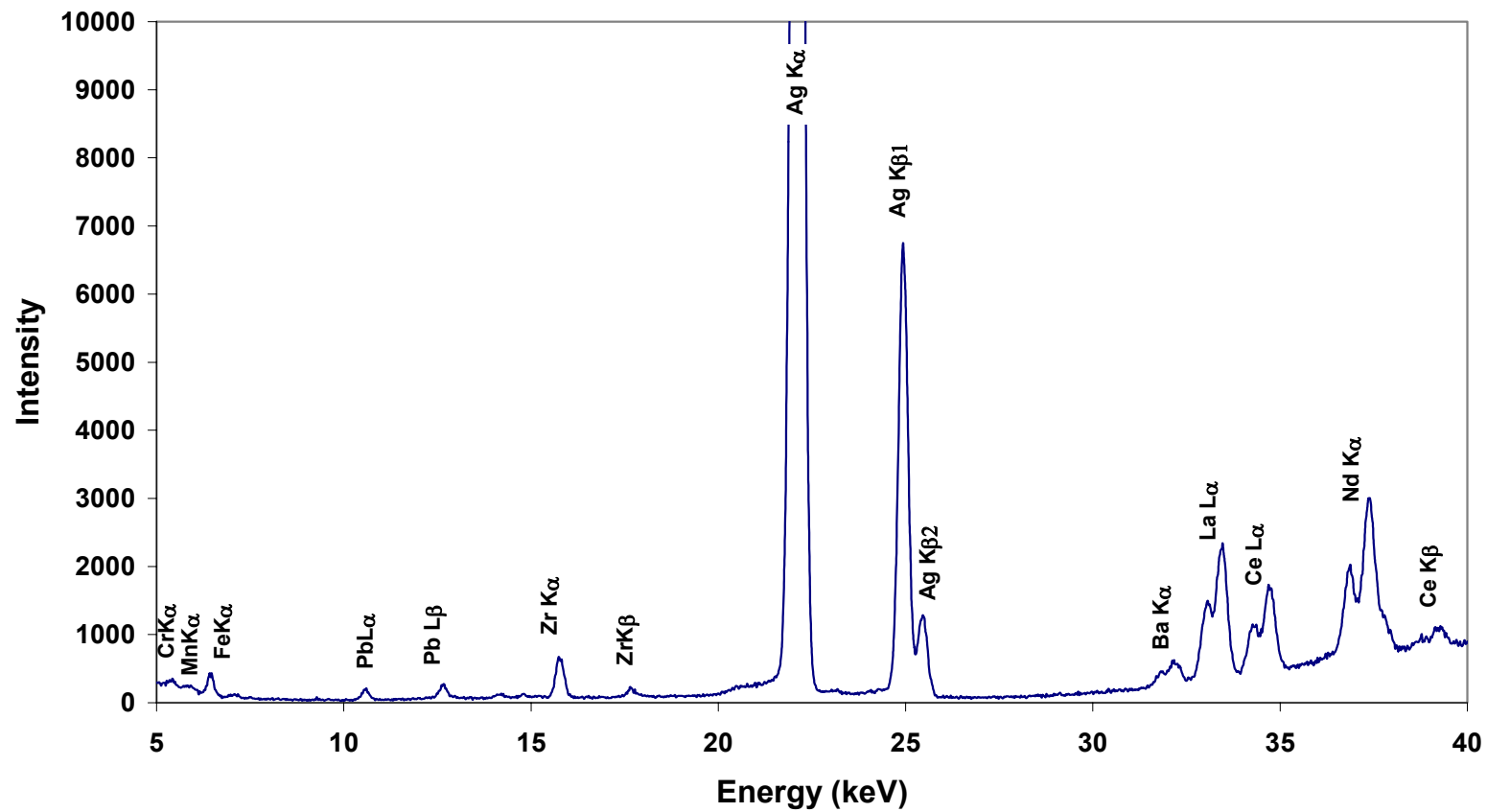


Figure 26. X-ray fluorescence pattern of AN-107 simulant filtered residue (Al₂O₃ target)

AN-107 Land Disposal Simulant Residue (HOPG Target)

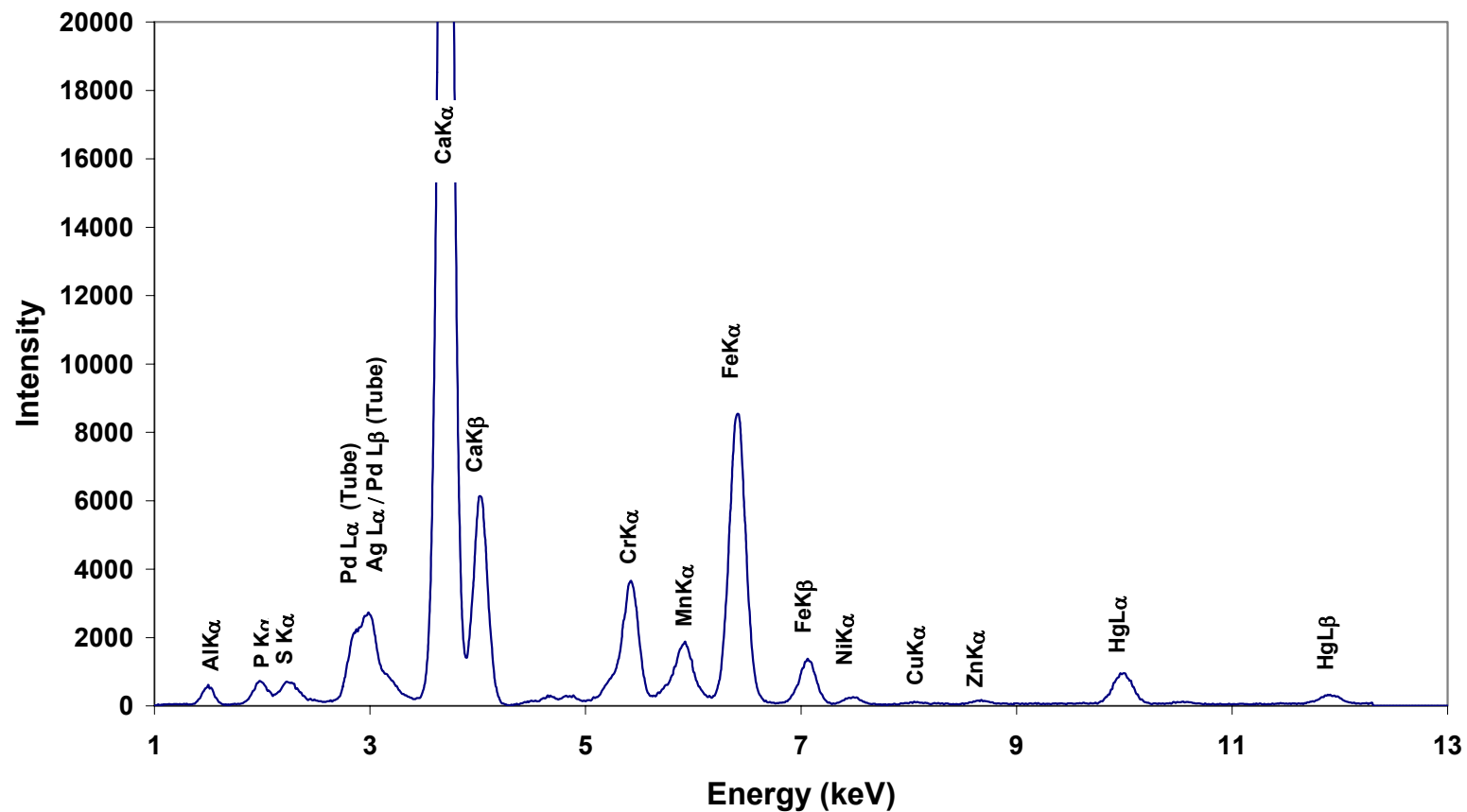


Figure 27. X-ray fluorescence pattern of AN-107 LDR simulant filtered residue (HOPG target)

AN-107 Land Disposal Simulant Residue (Mo Target)

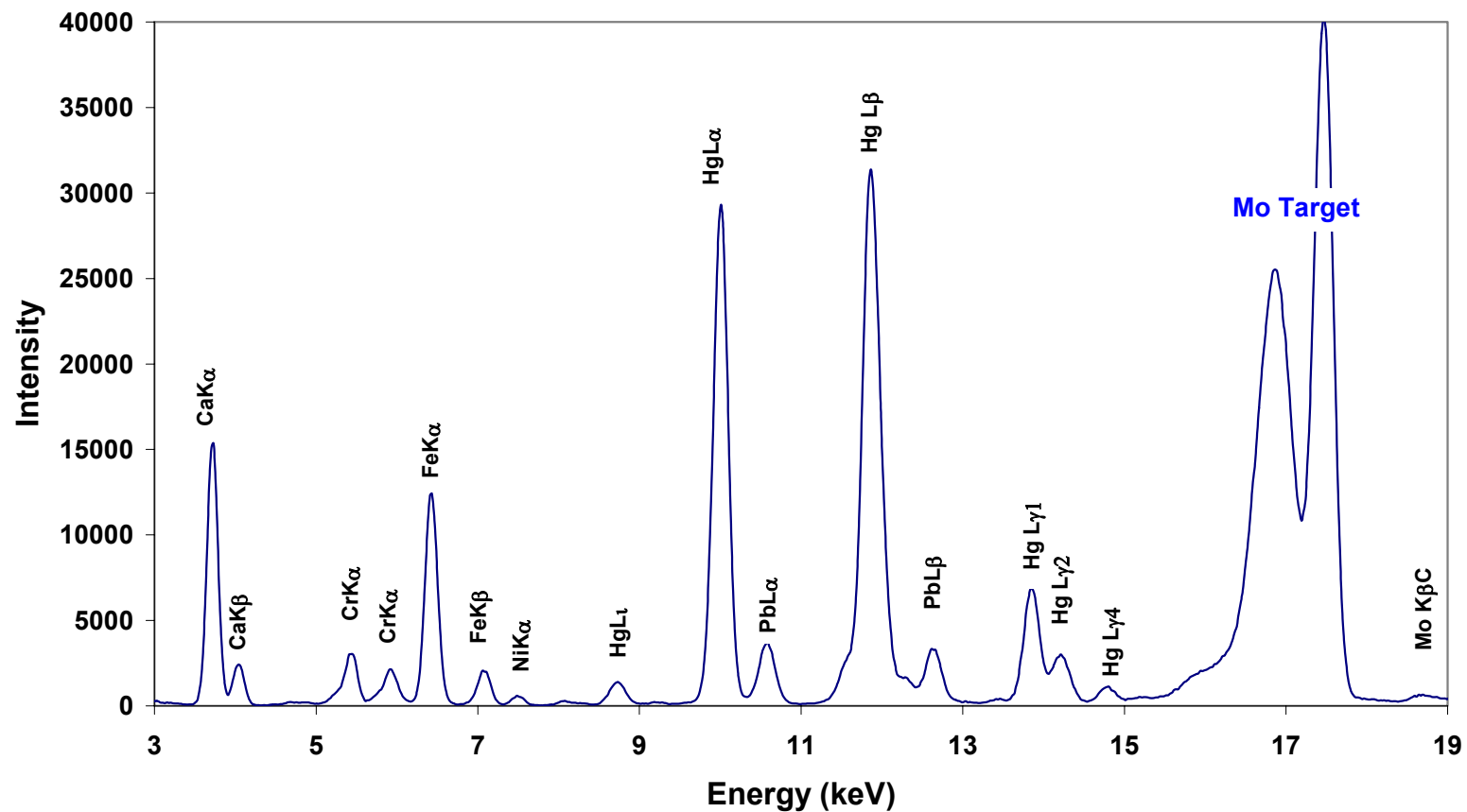


Figure 28. X-ray fluorescence pattern of AN-107 LDR simulant filtered residue (Mo target)

AN-107 Land Disposal Simulant Residue (Al₂O₃ Target)

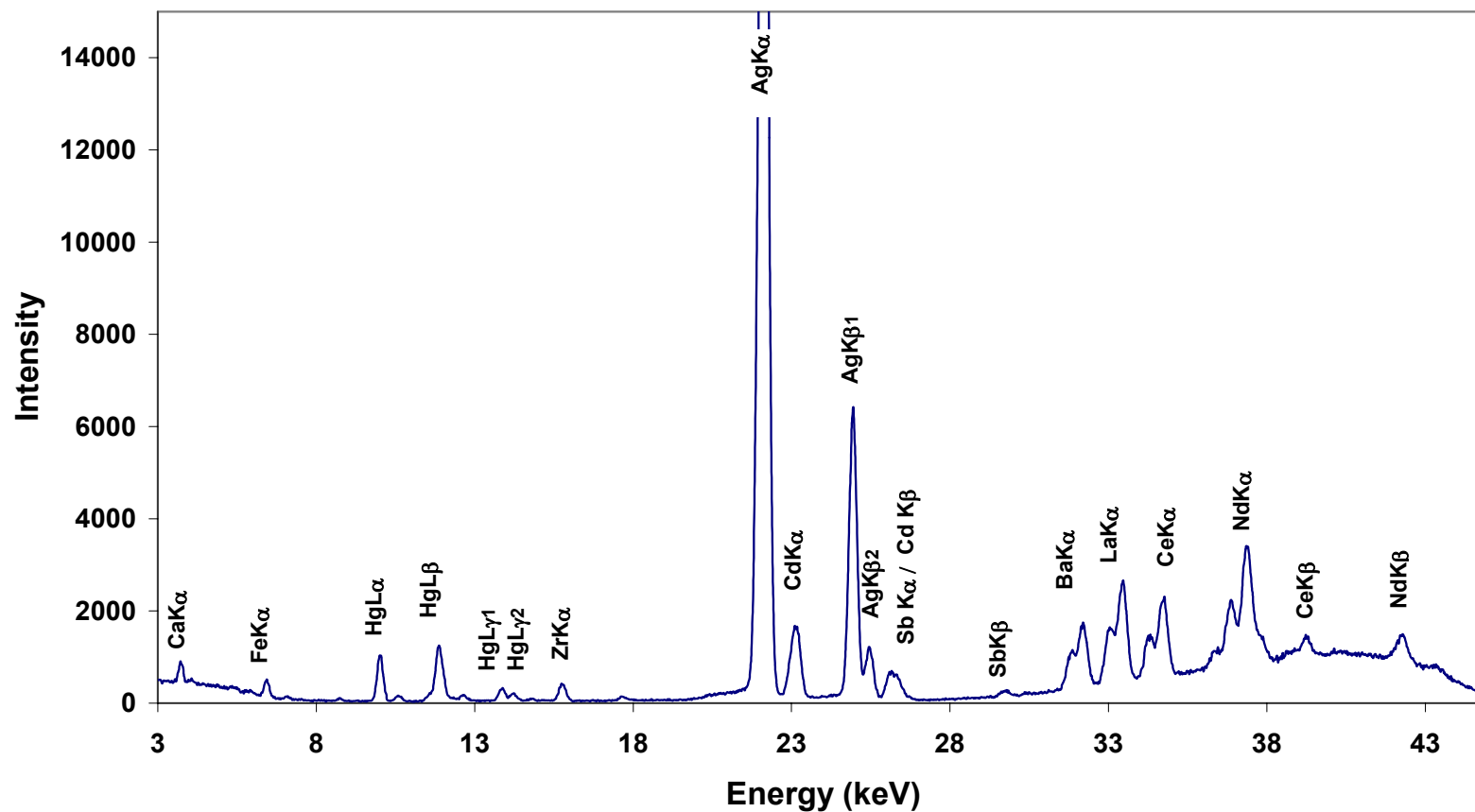


Figure 29. X-ray fluorescence pattern of AN-107 LDR simulant filtered residue (Al₂O₃ target)

7.4 Appendix D: X-ray Diffraction Scans

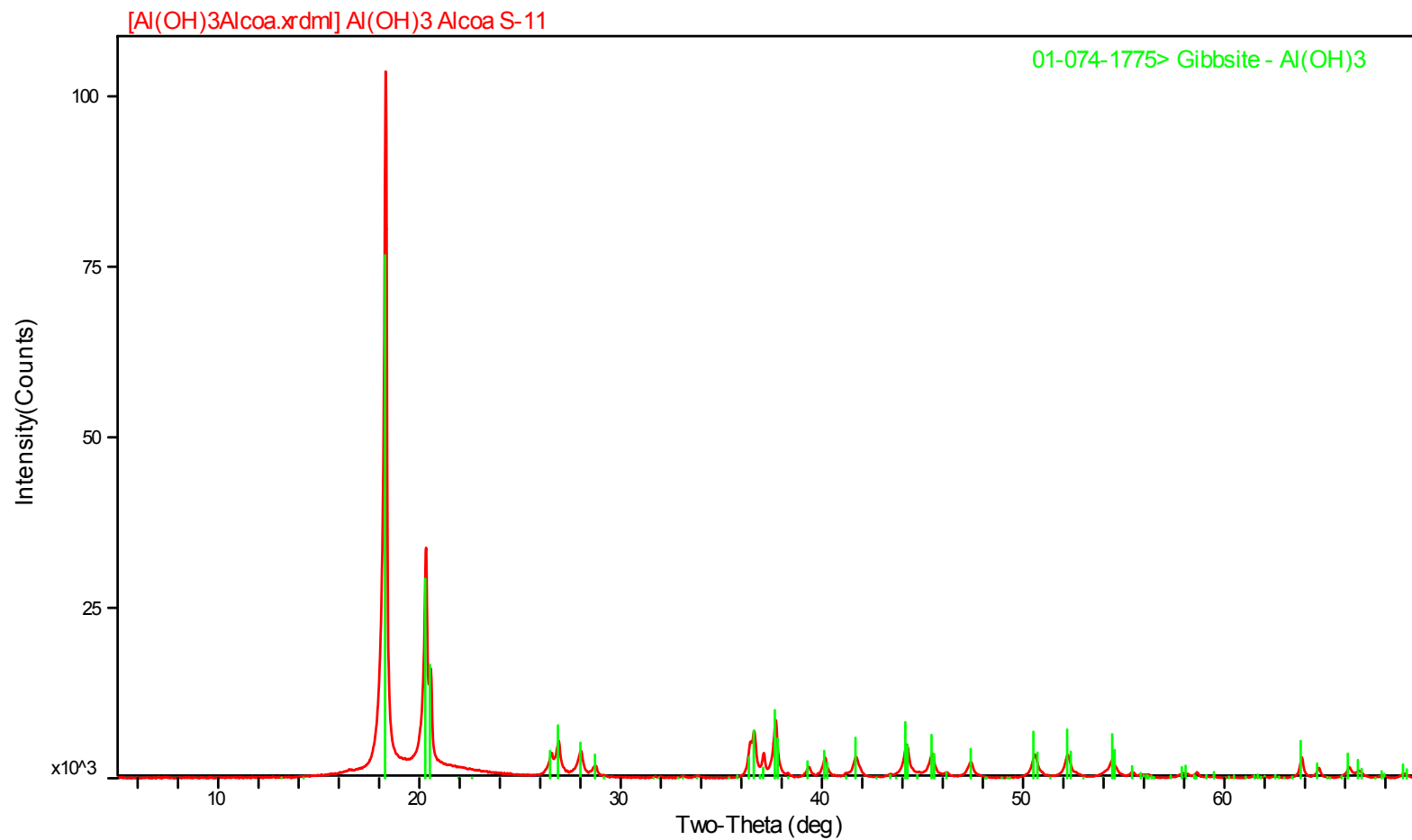


Figure 30. X-ray diffraction pattern of Al(OH)_3 from Alcoa

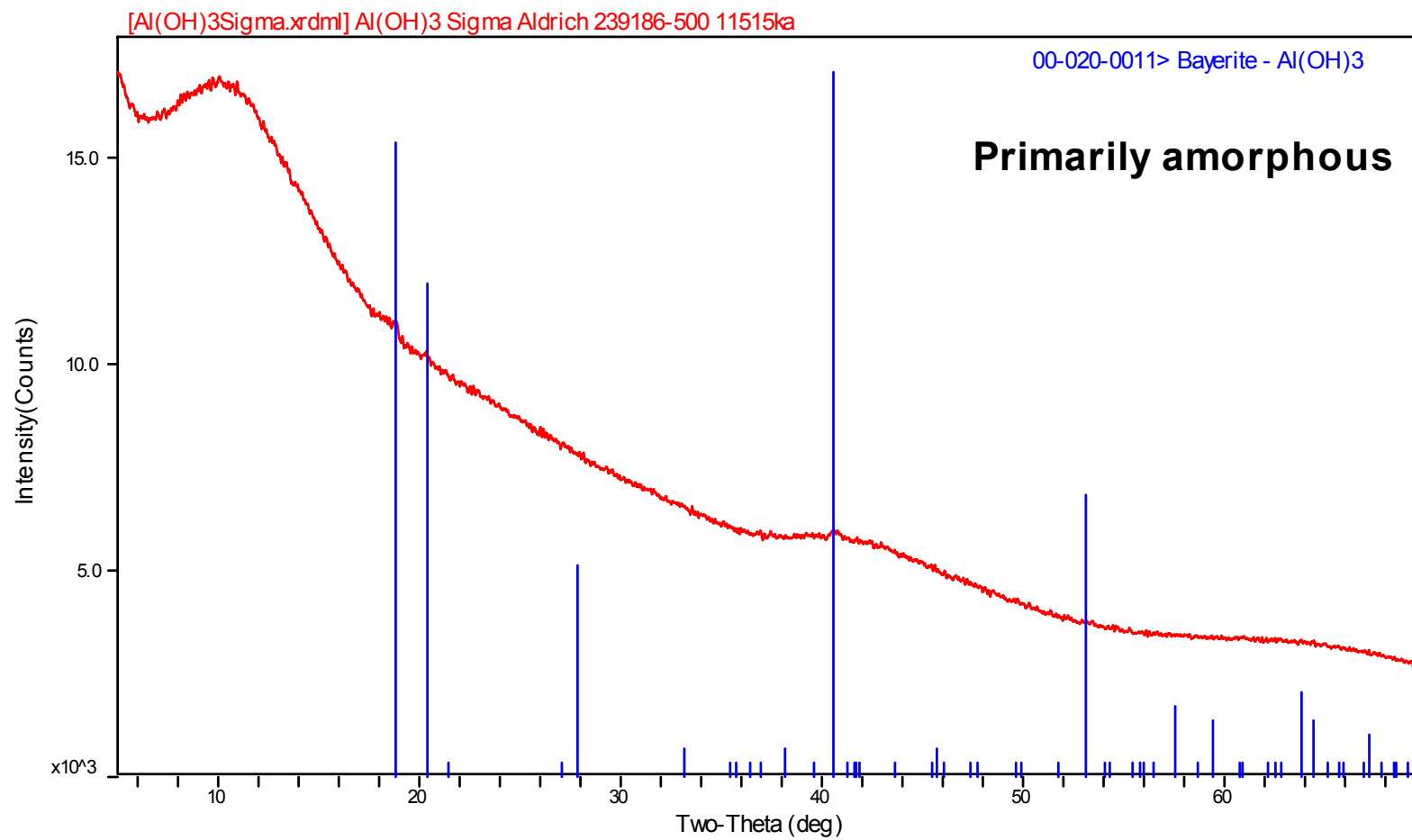


Figure 31. X-ray diffraction pattern of Al(OH)₃ from Sigma Aldrich

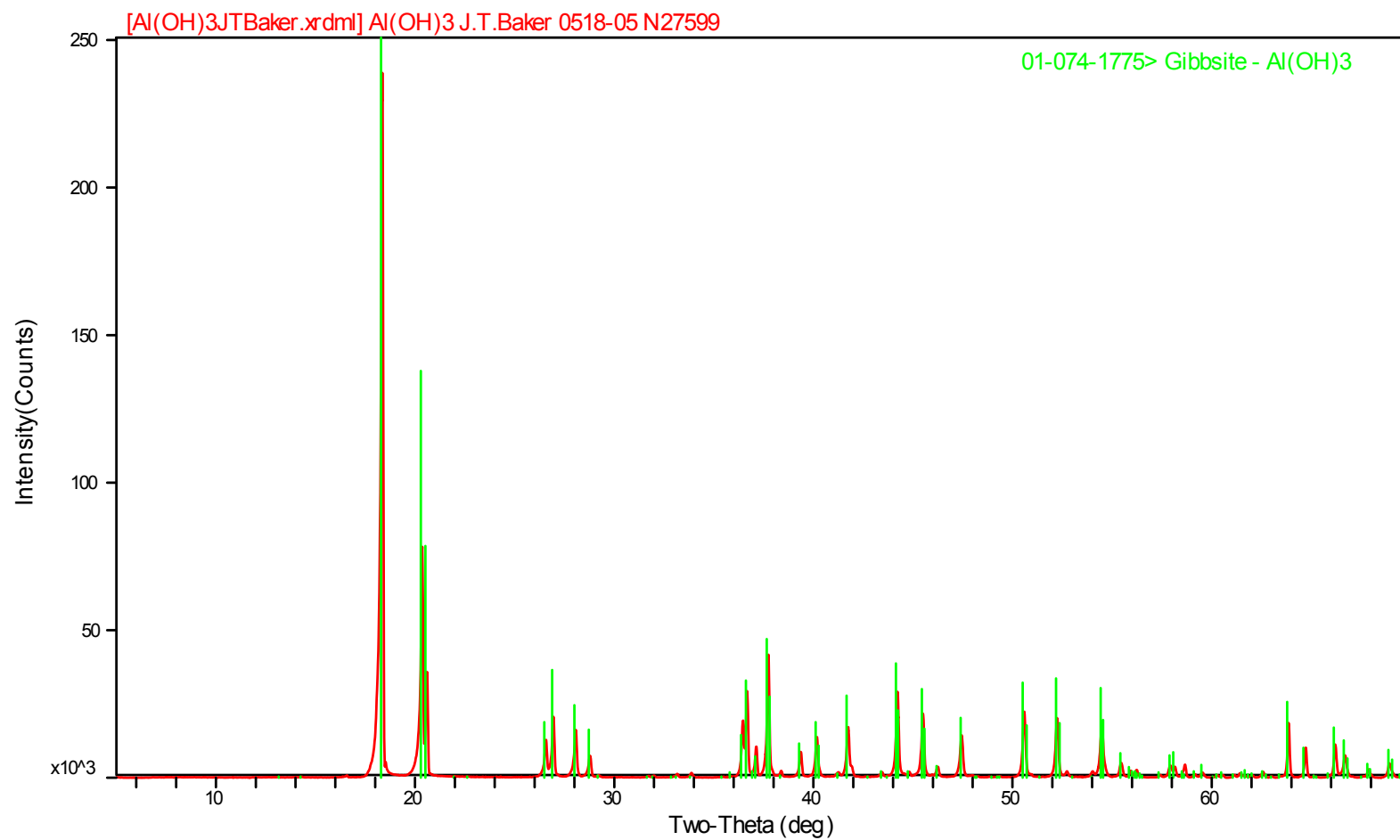


Figure 32. X-ray diffraction pattern of Al(OH)₃ from J. T. Baker

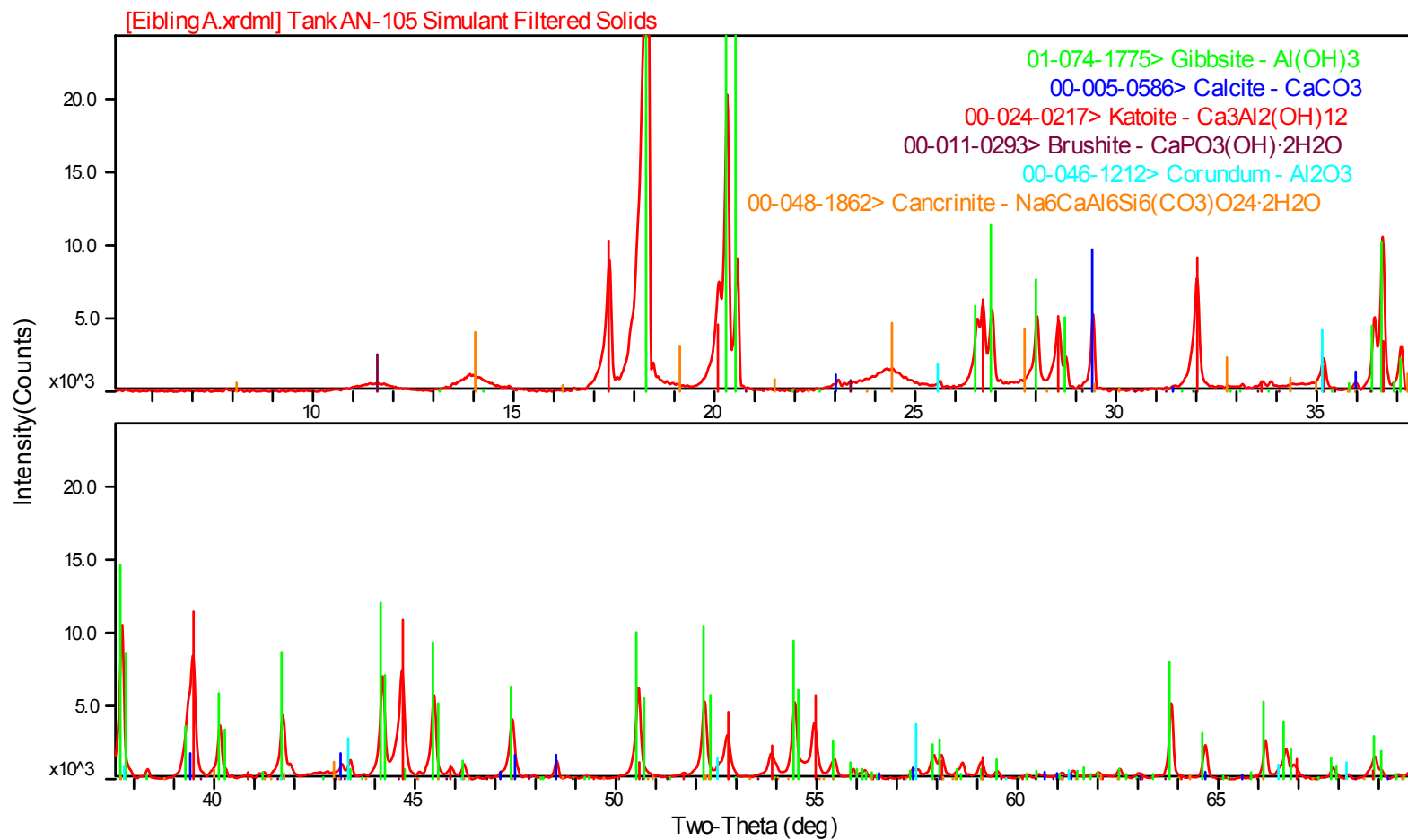


Figure 33. X-ray diffraction pattern of AN-105 filtered residue

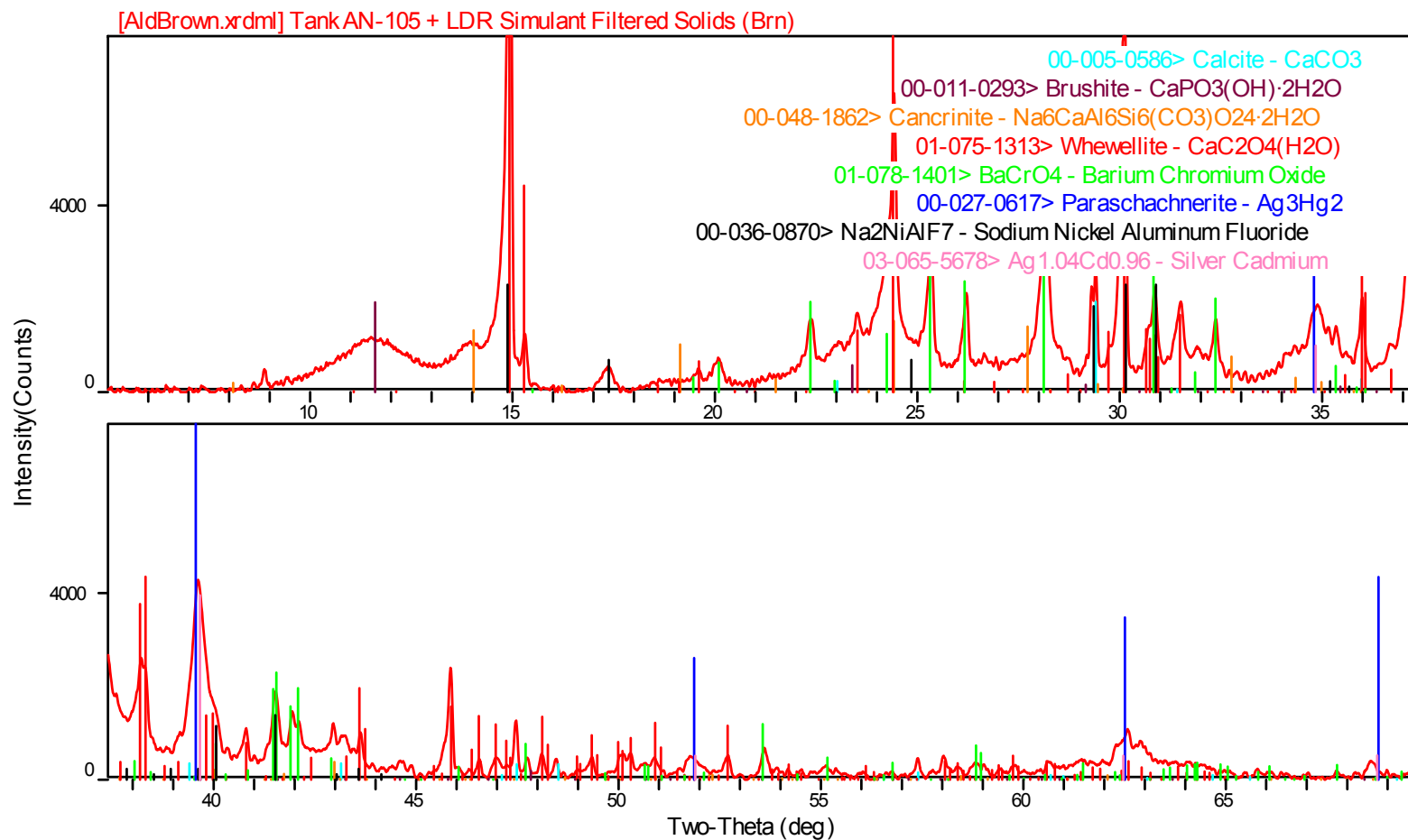


Figure 34. X-ray diffraction pattern of AN-105 spiked with LDR elements filtered brown residue

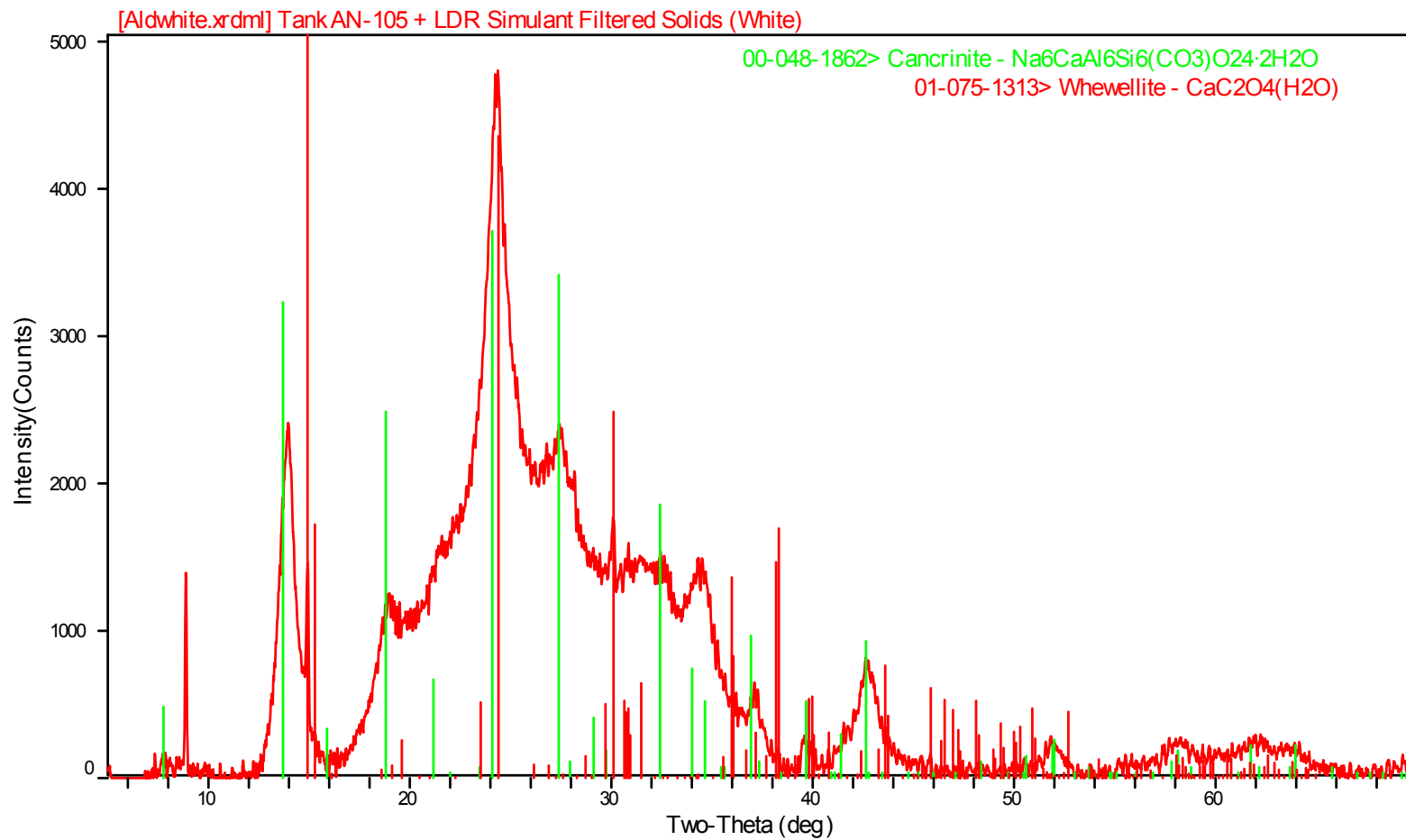


Figure 35. X-ray diffraction pattern of AN-105 spiked with LDR elements filtered white residue

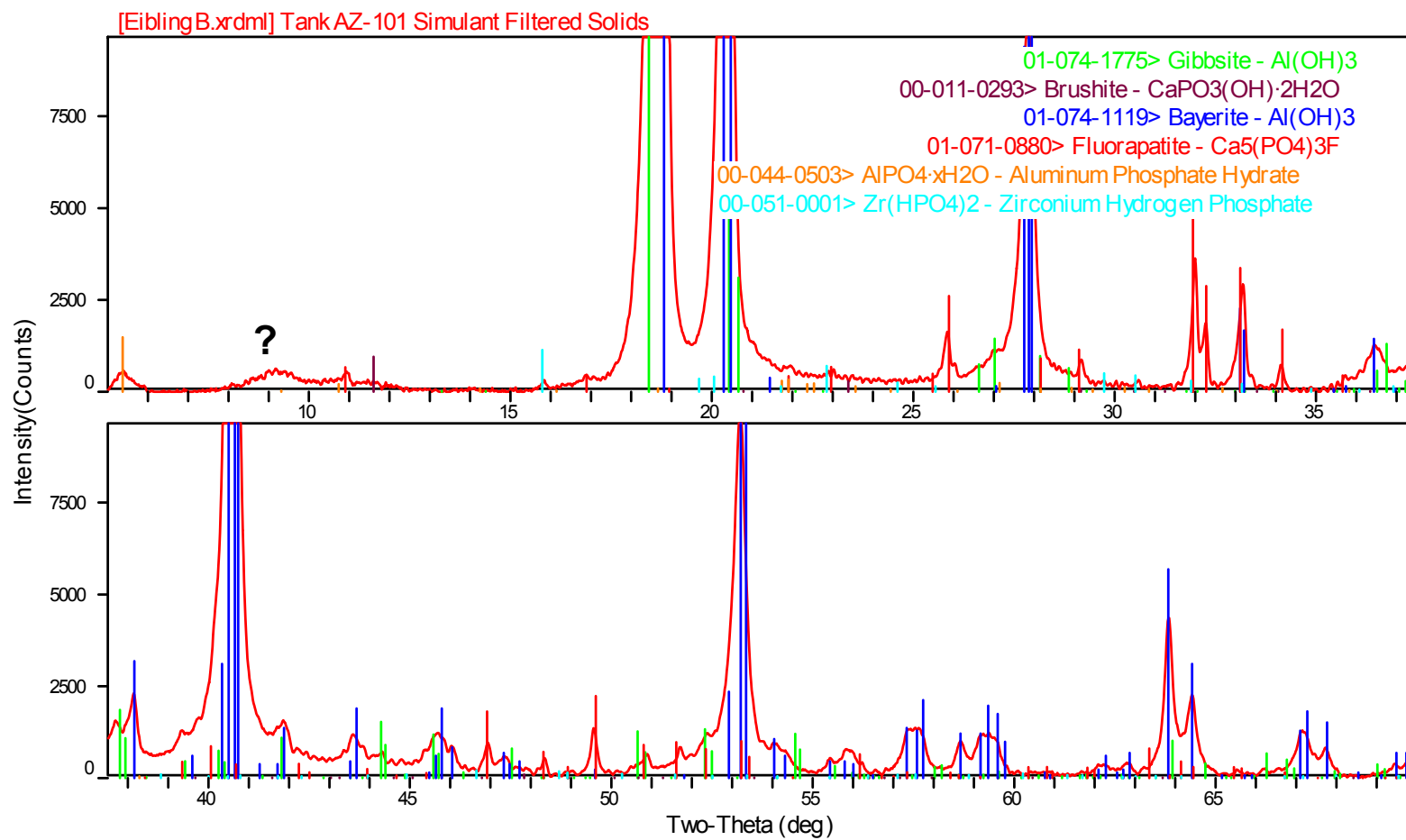


Figure 36. X-ray diffraction pattern of AZ-101 filtered residue

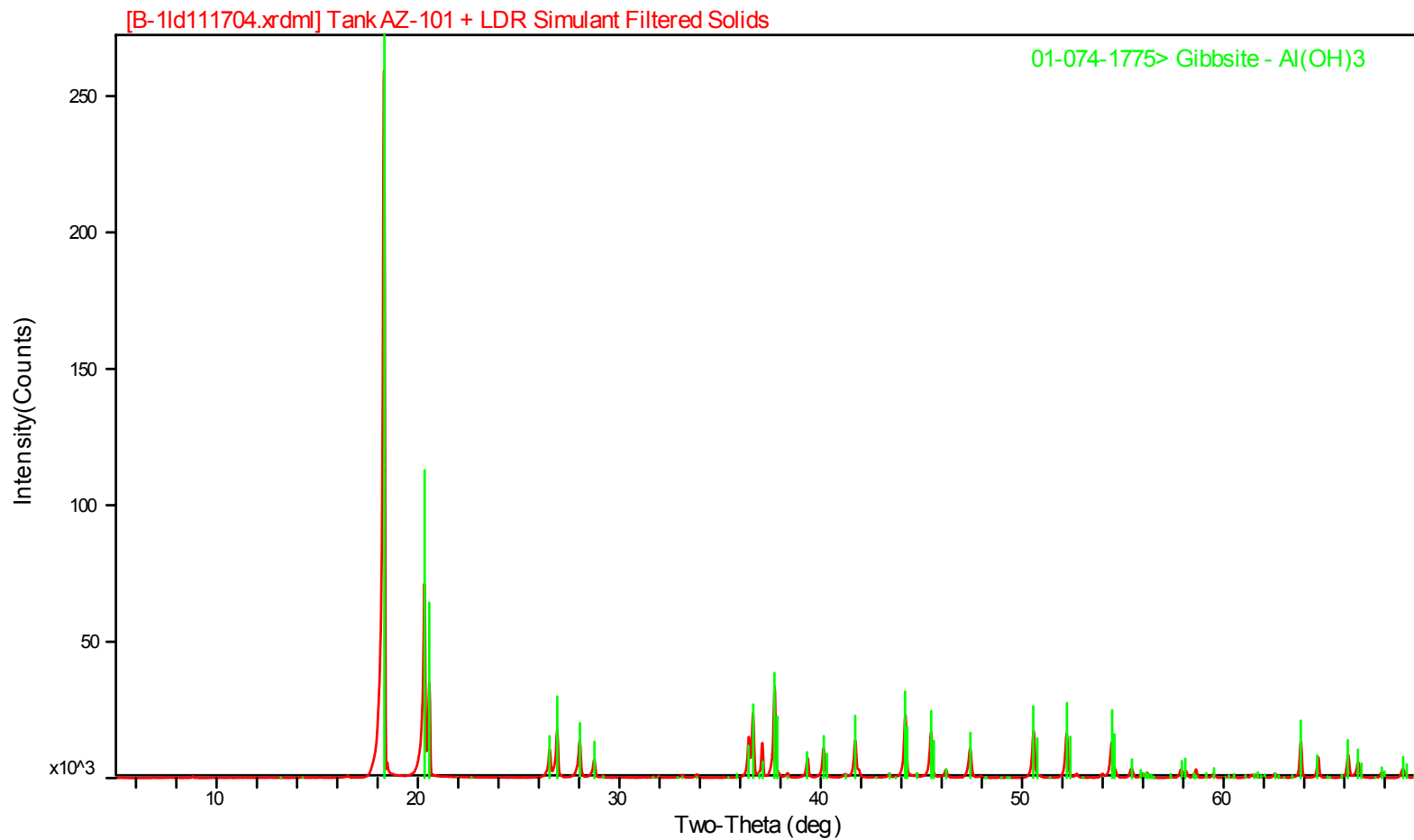


Figure 37. X-ray diffraction pattern of AZ-101 spiked with LDR elements filtered residue

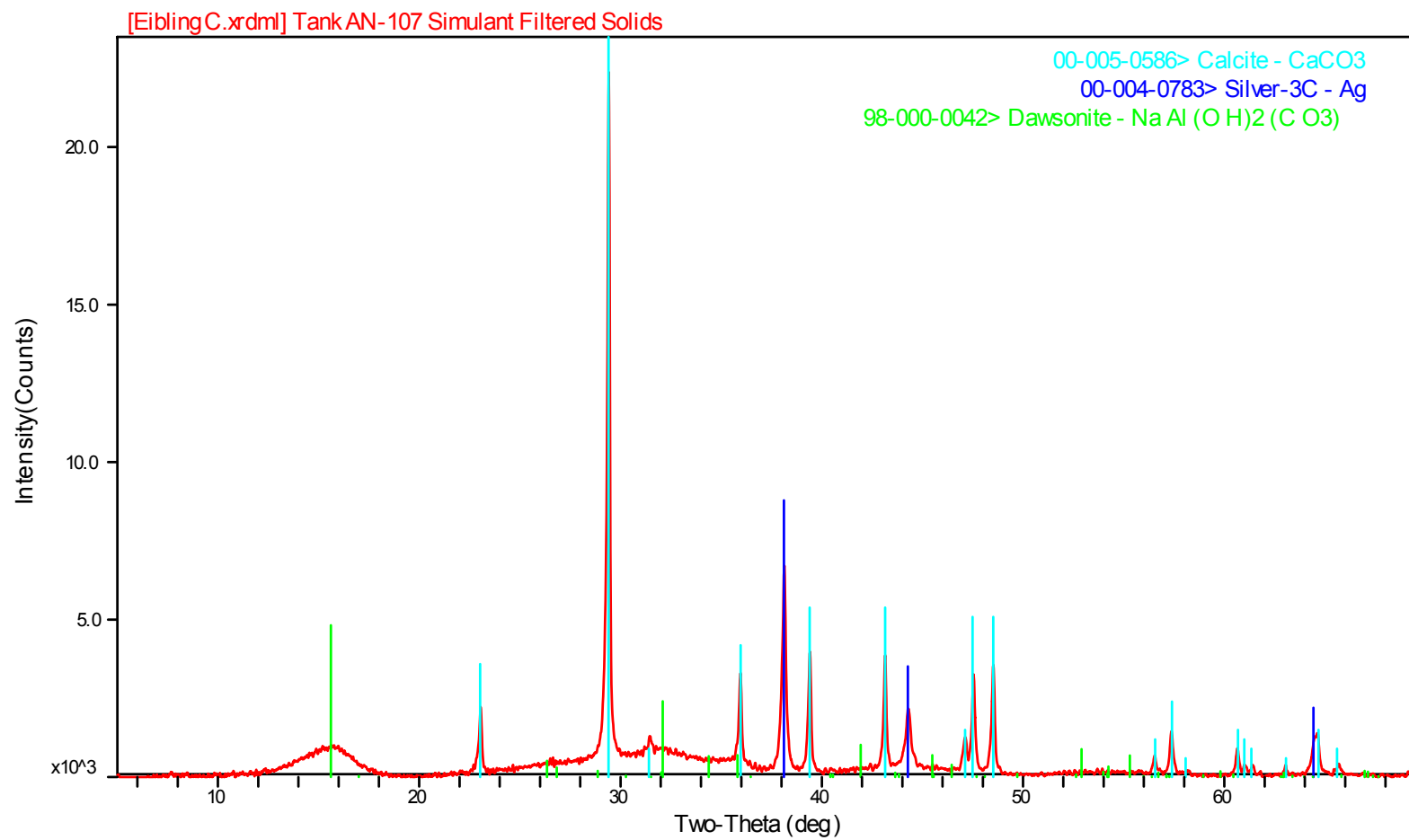


Figure 38. X-ray diffraction pattern of AN-107 filtered residue

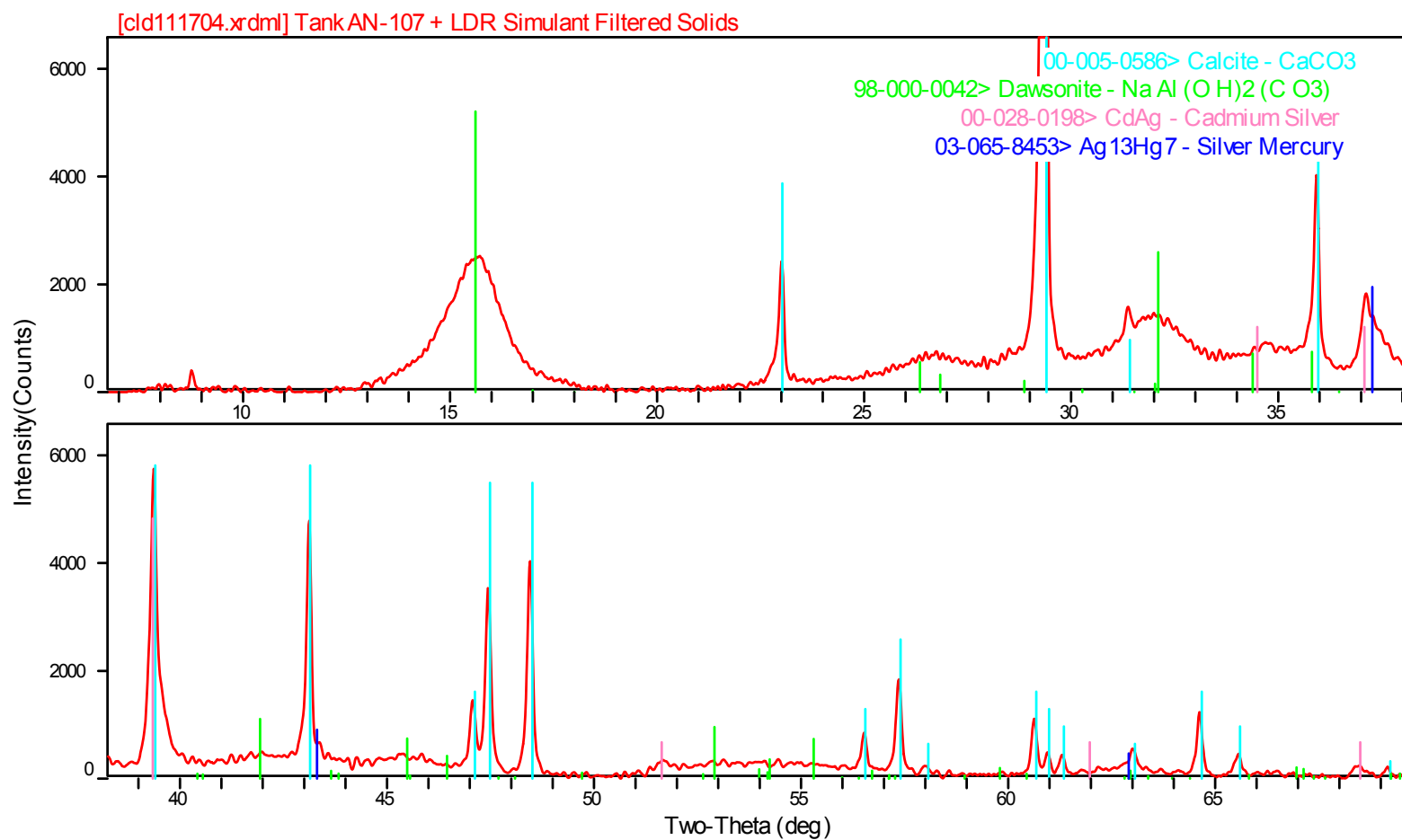


Figure 39. X-ray diffraction pattern of AN-107 spiked with LDR elements filtered residue

7.5 Appendix E: Representative LAW Elemental Scans

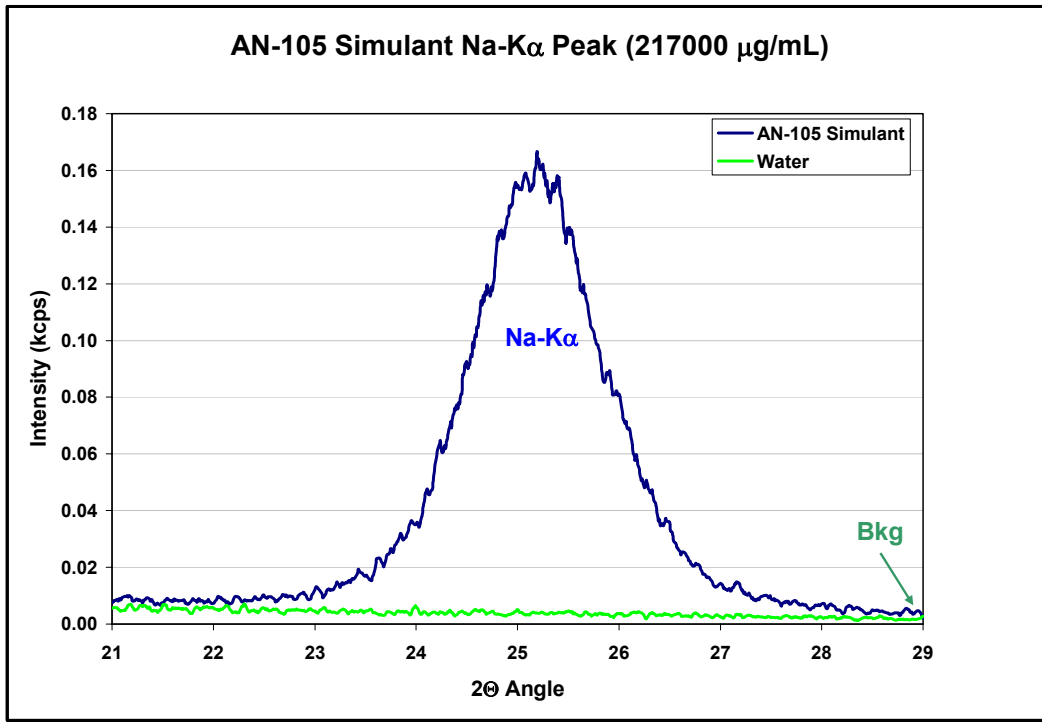


Figure 40. AN-105 simulant Na-K α WD-XRF scan

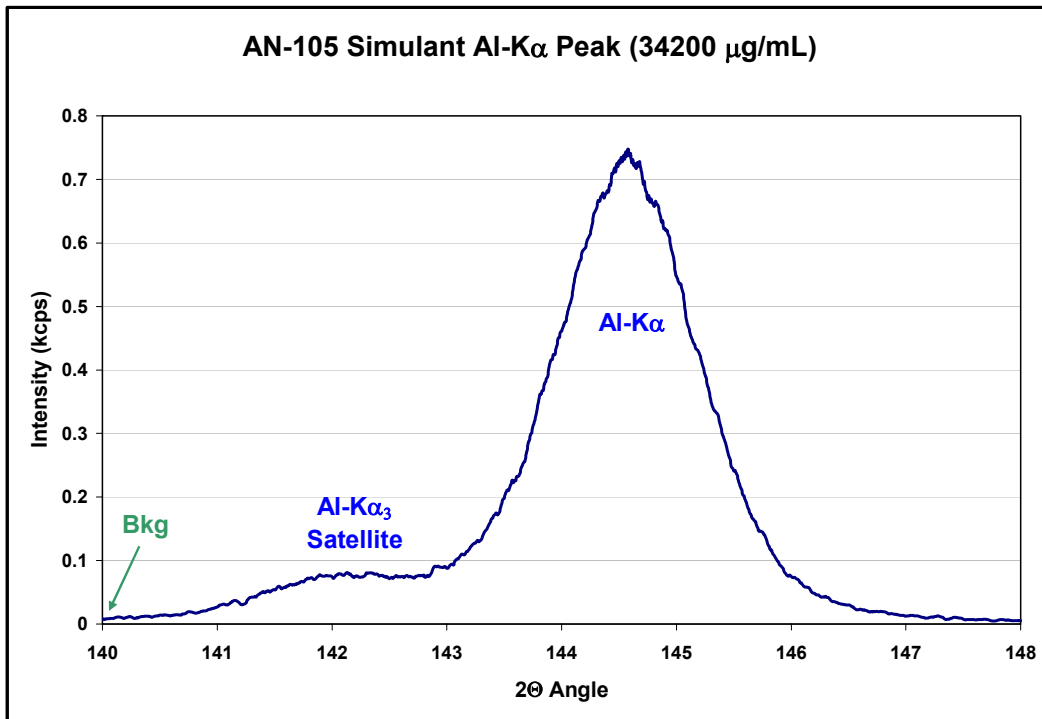


Figure 41. AN-105 simulant Al-K α WD-XRF scan

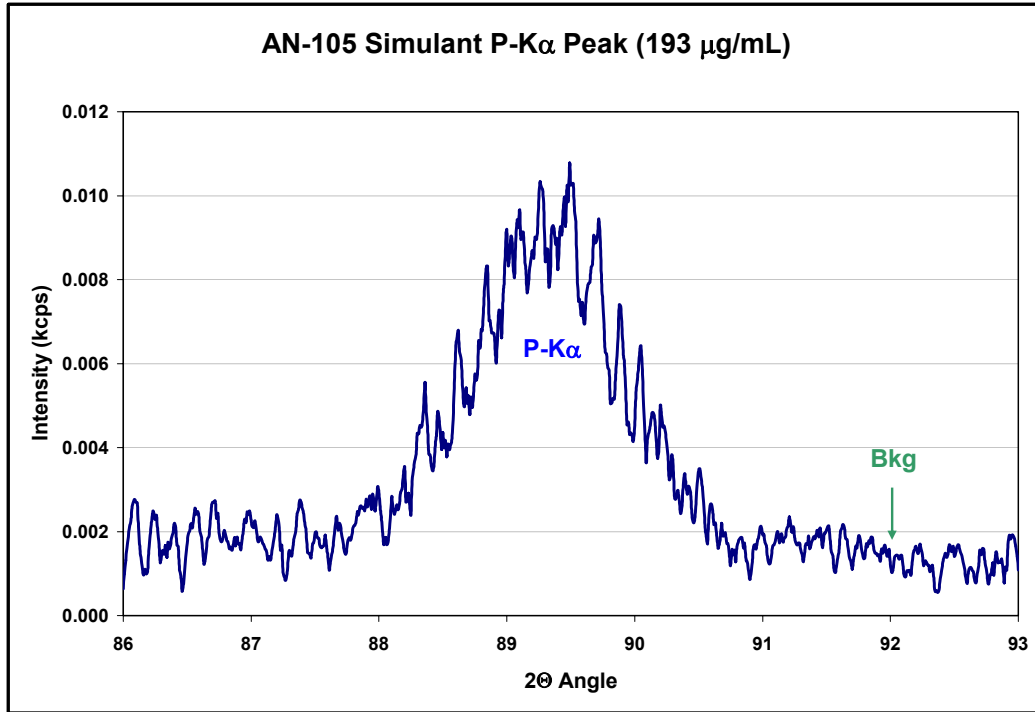


Figure 42. AN-105 simulant P-K α WD-XRF scan

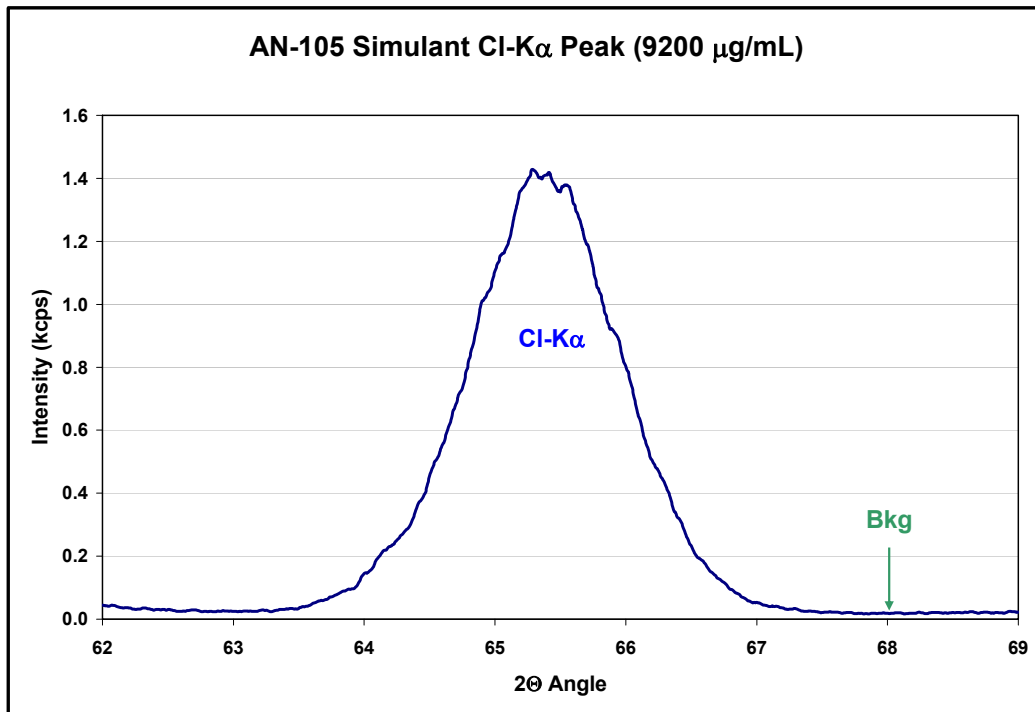


Figure 43. AN-105 simulant Cl-K α WD-XRF scan

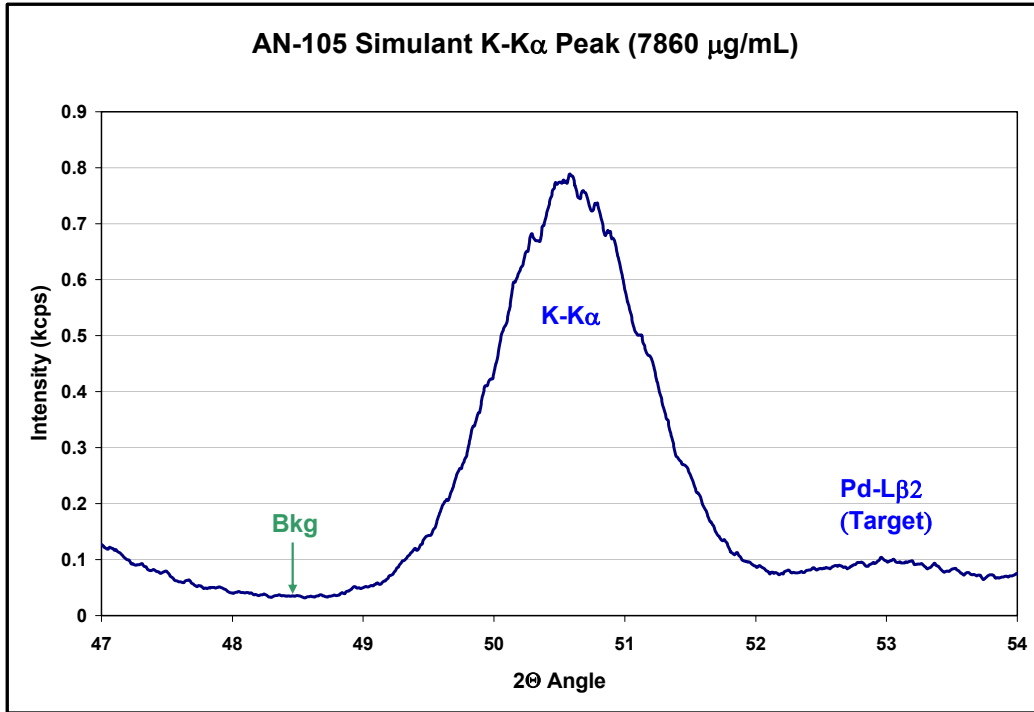


Figure 44. AN-105 simulant K-K α WD-XRF scan

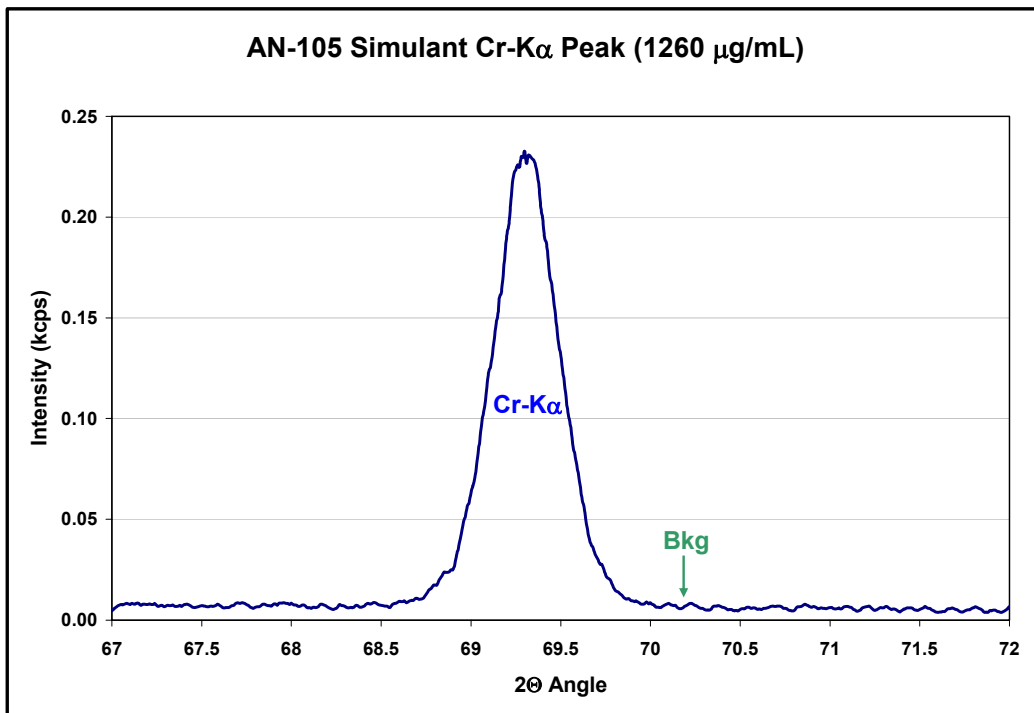


Figure 45. AN-105 simulant Cr-K α WD-XRF scan

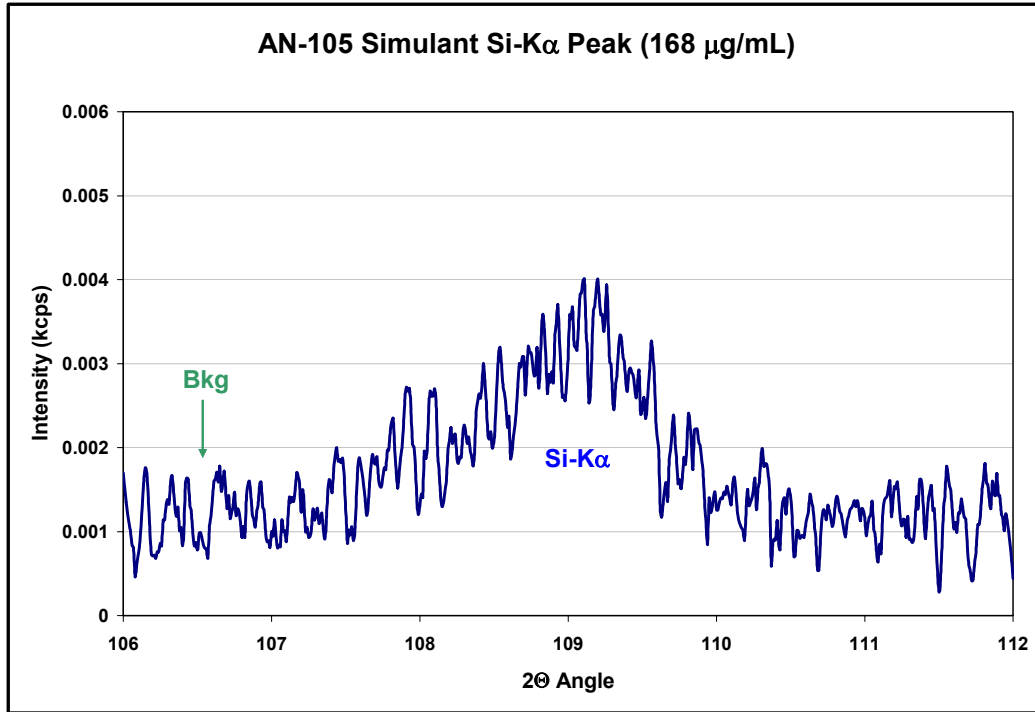


Figure 46. AN-105 simulant Si K α WD-XRF scan

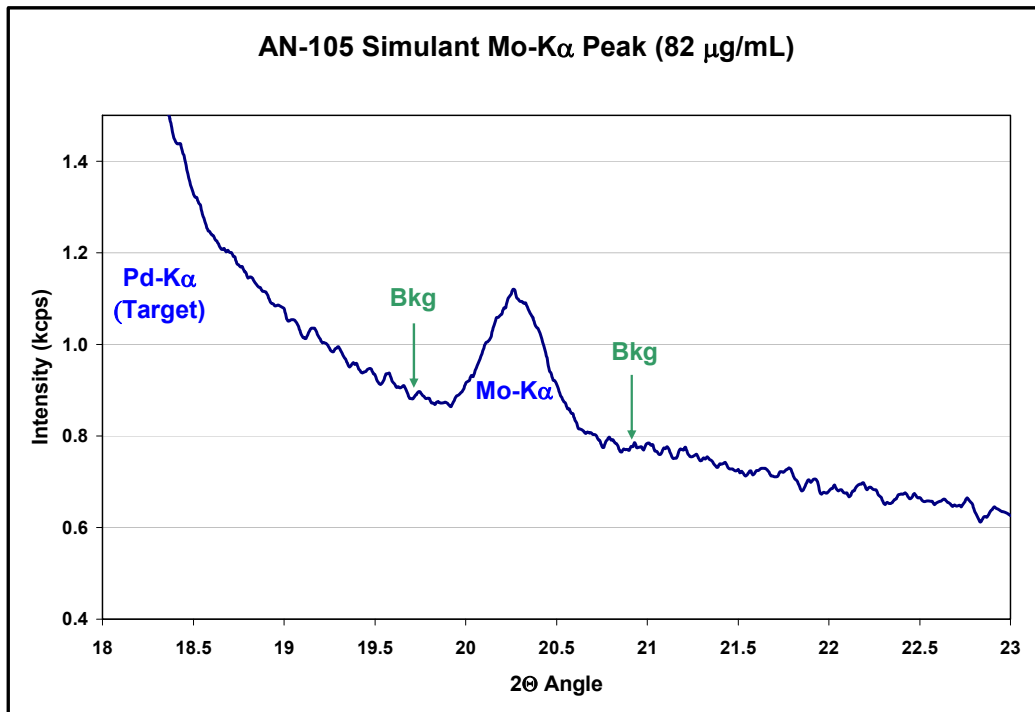


Figure 47. AN-105 simulant Mo-K α WD-XRF scan

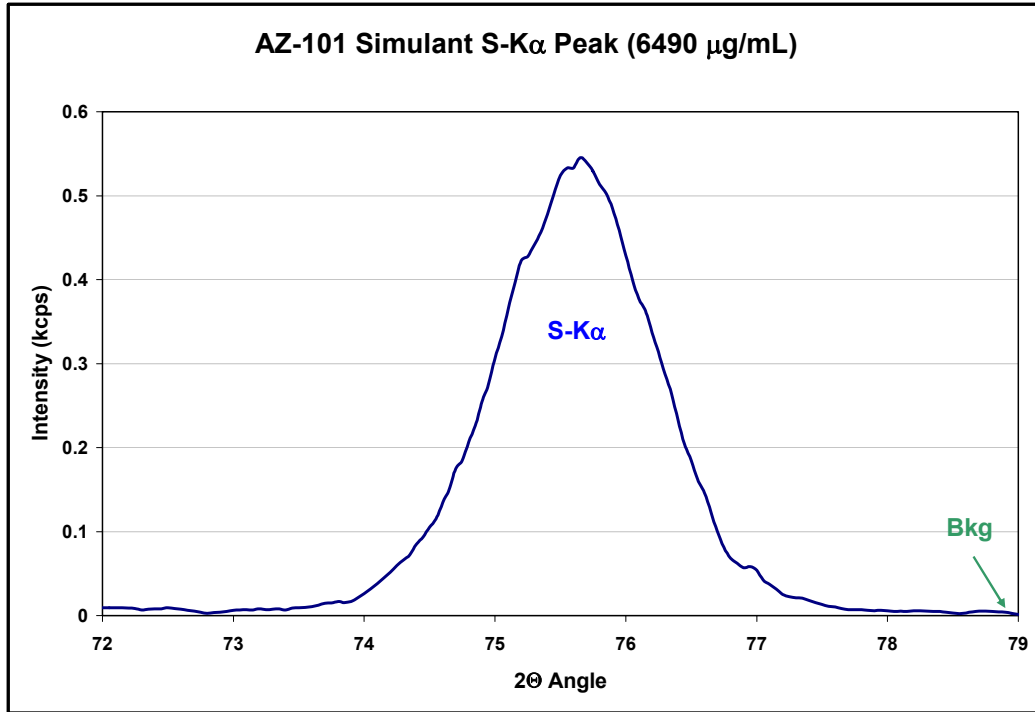


Figure 48. AZ-101 simulant S-K α WD-XRF scan

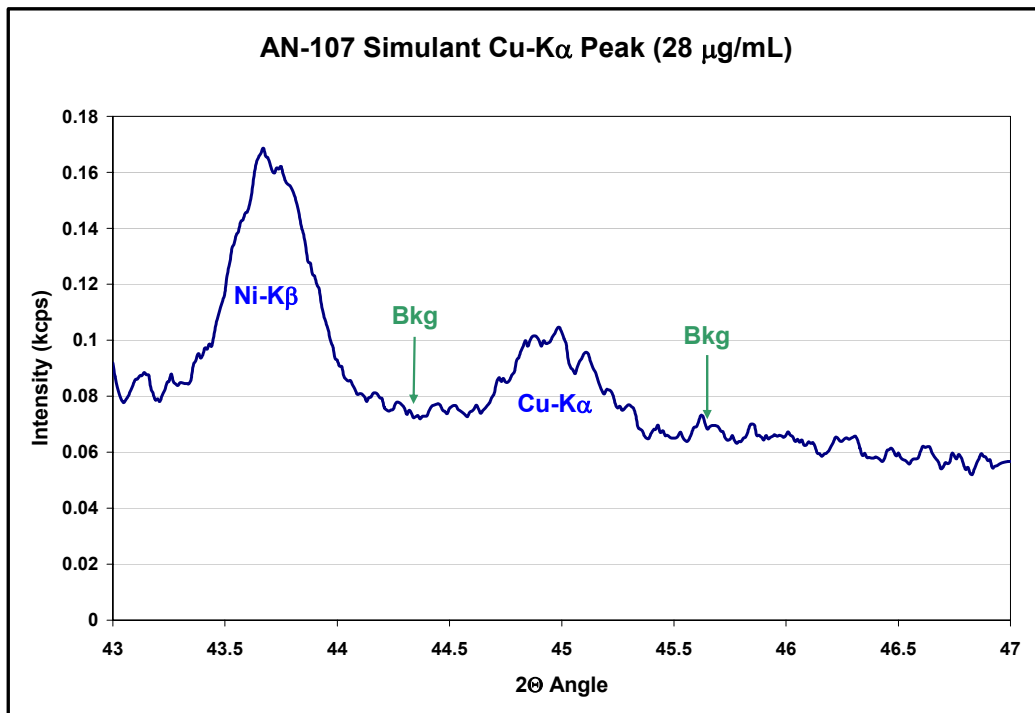


Figure 49. AN-107 simulant Cu-K α WD-XRF scan

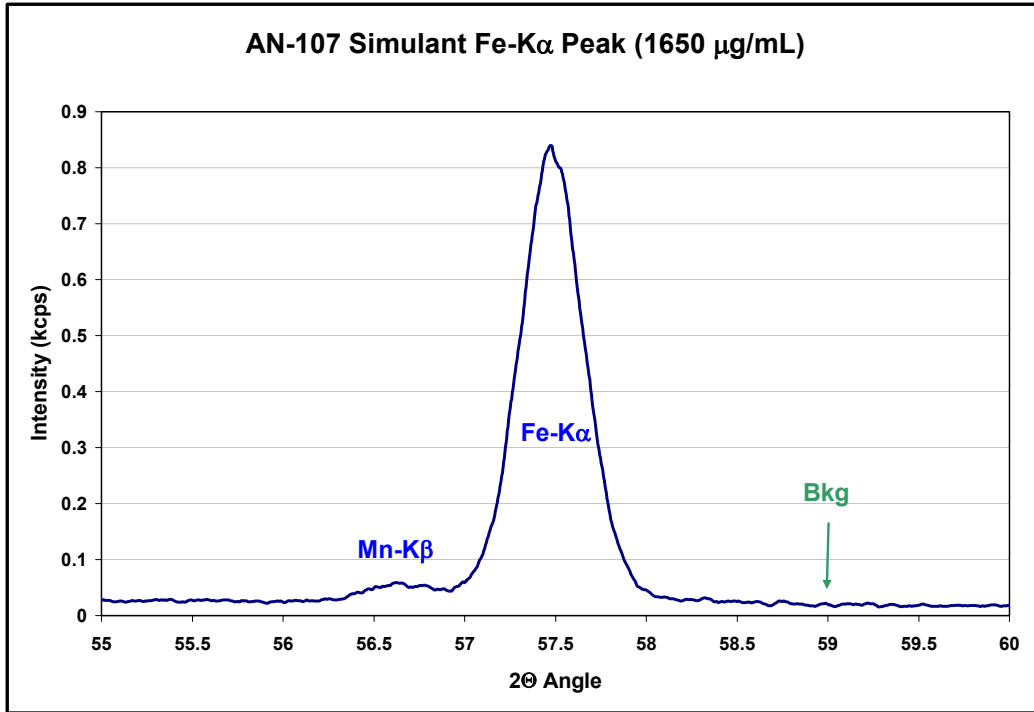


Figure 50. AN-107 simulant Fe-K α WD-XRF scan.

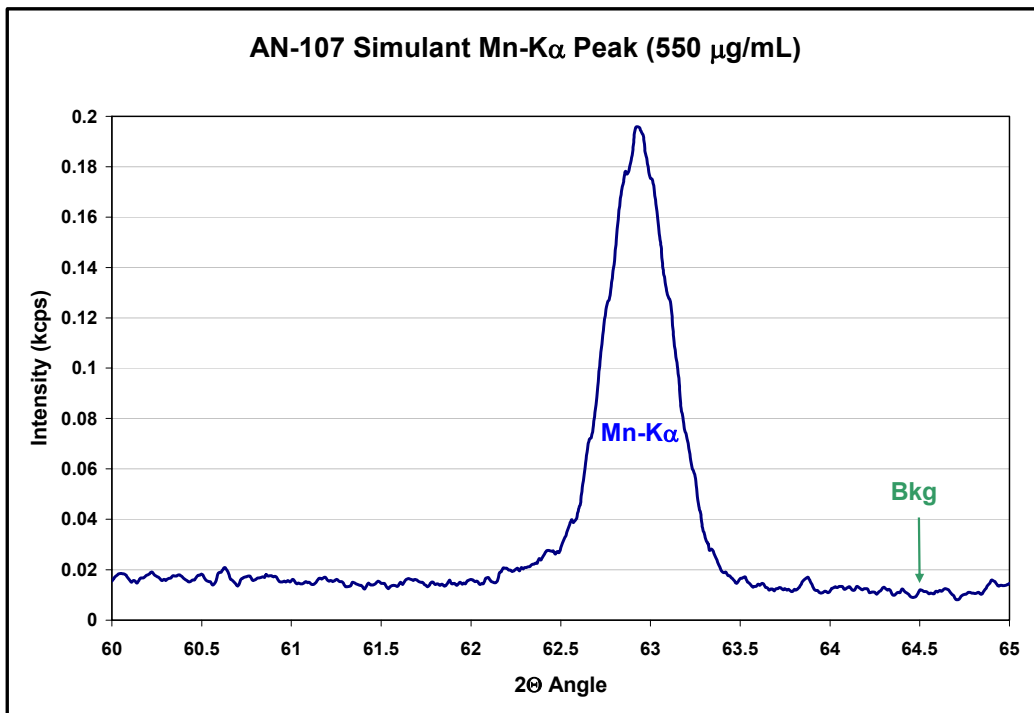


Figure 51. AN-107 simulant Mn-K α WD-XRF scan.

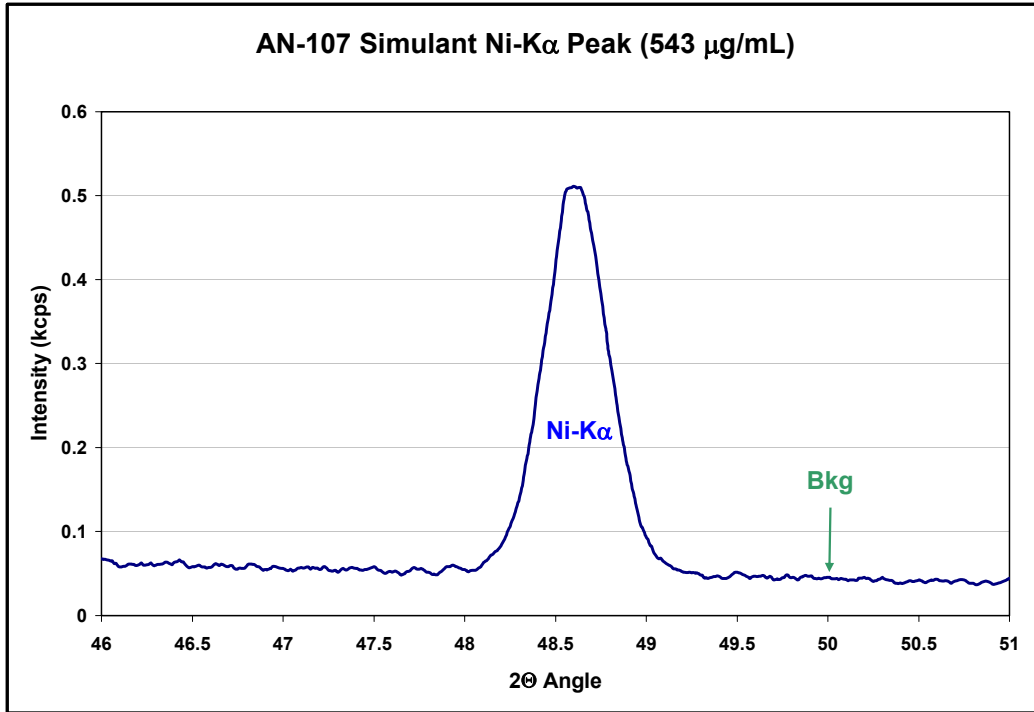


Figure 52. AN-107 simulant Ni-K α WD-XRF scan.

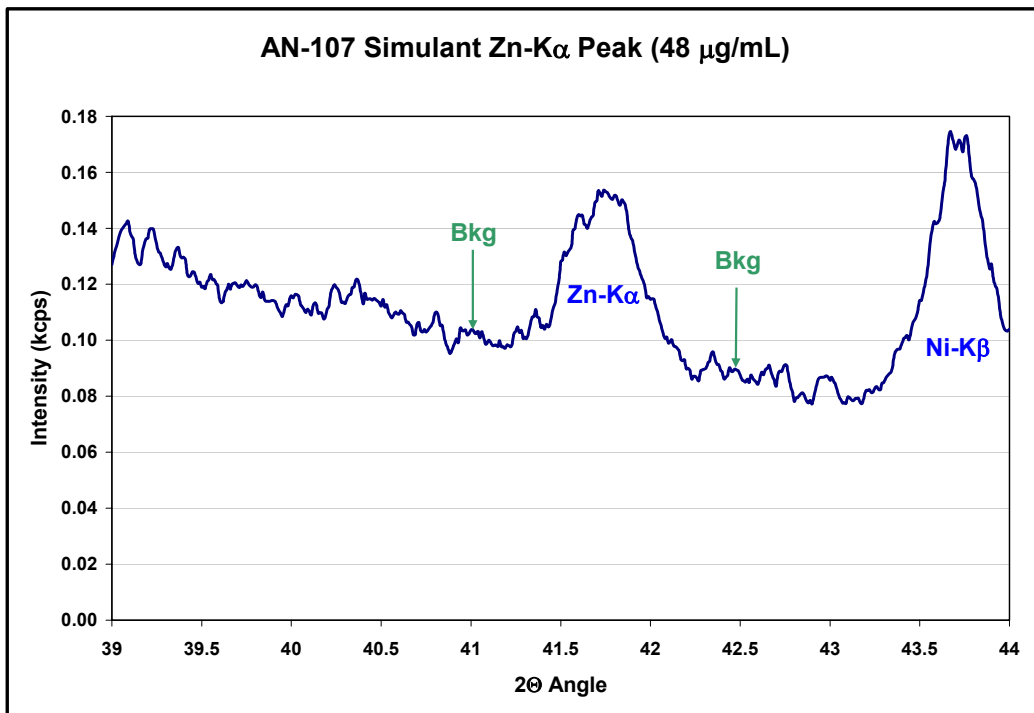


Figure 53. AN-107 simulant Zn-K α WD-XRF scan.

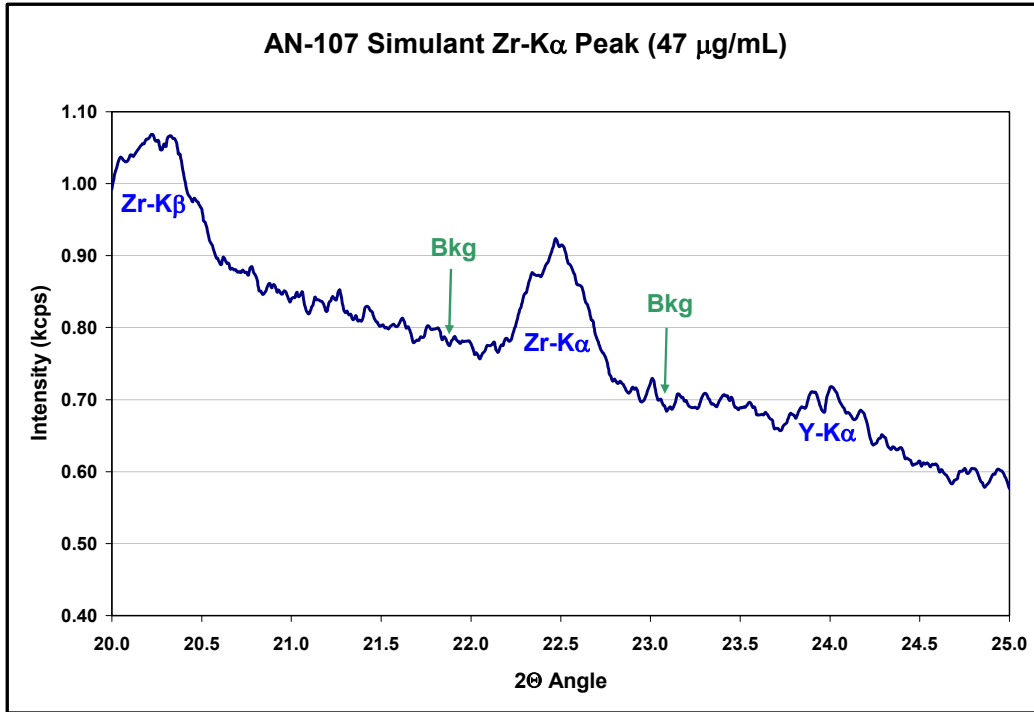


Figure 54. AN-107 simulant Zr-K α WD-XRF scan.

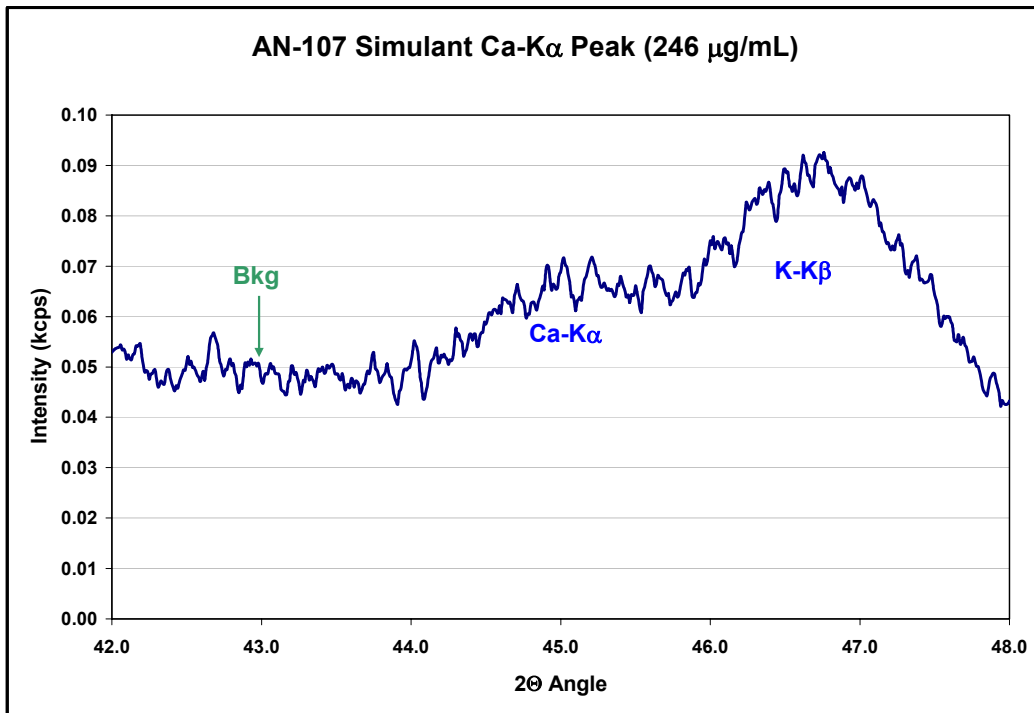


Figure 55. AN-107 simulant Ca-K α WD-XRF scan.

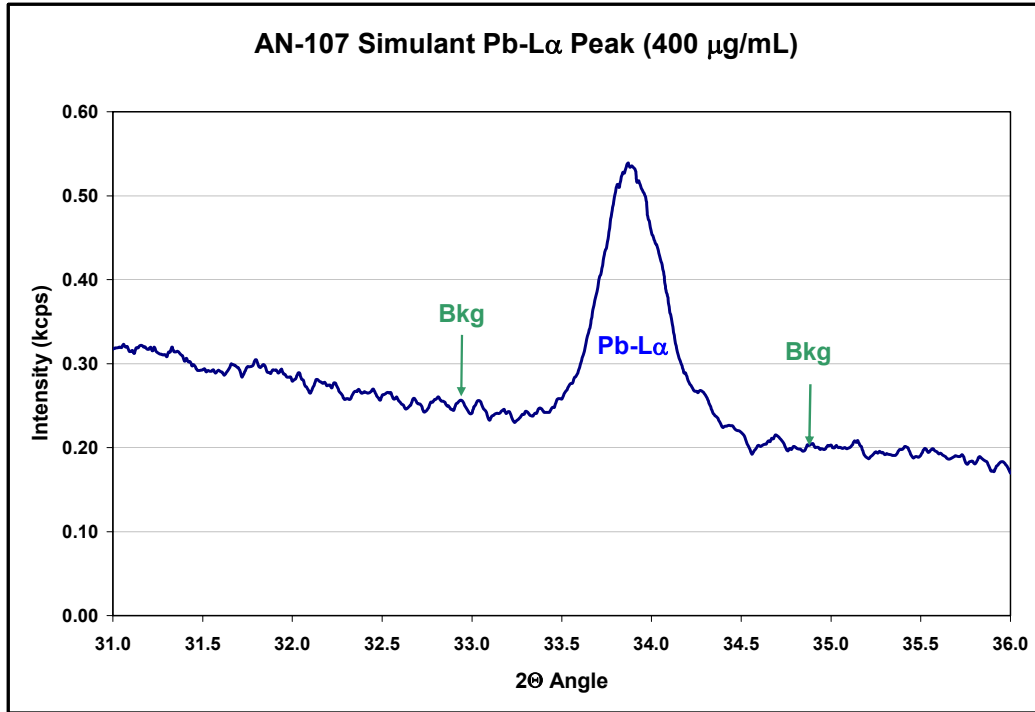


Figure 56. AN-107 simulant Pb-L α WD-XRF scan.

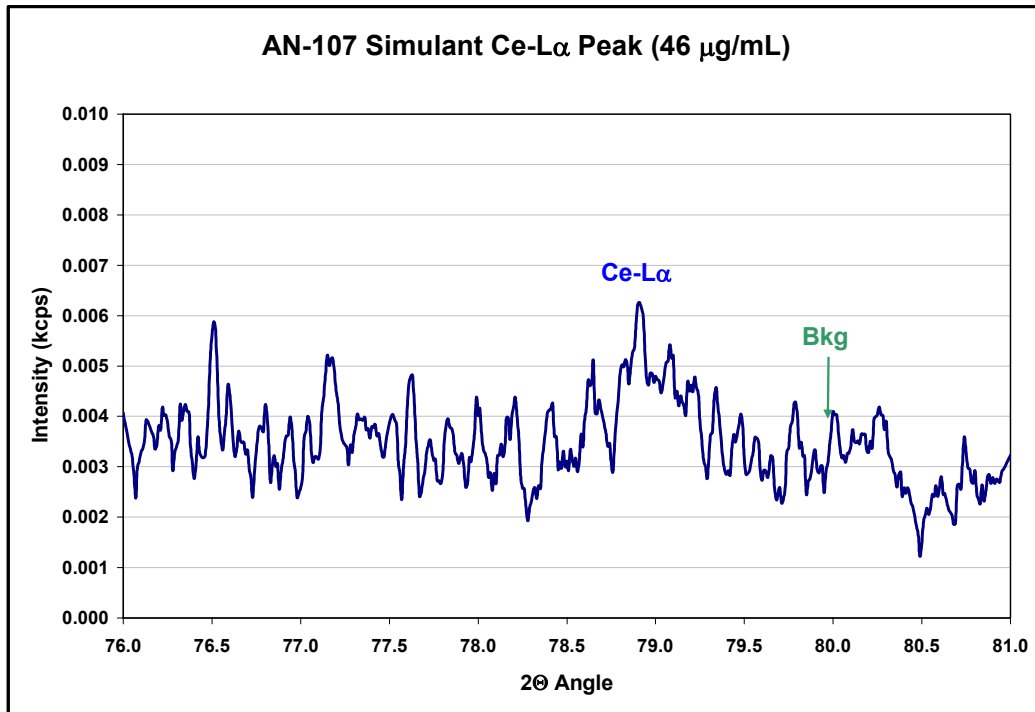


Figure 57. AN-107 simulant Ce-L α WD-XRF scan.

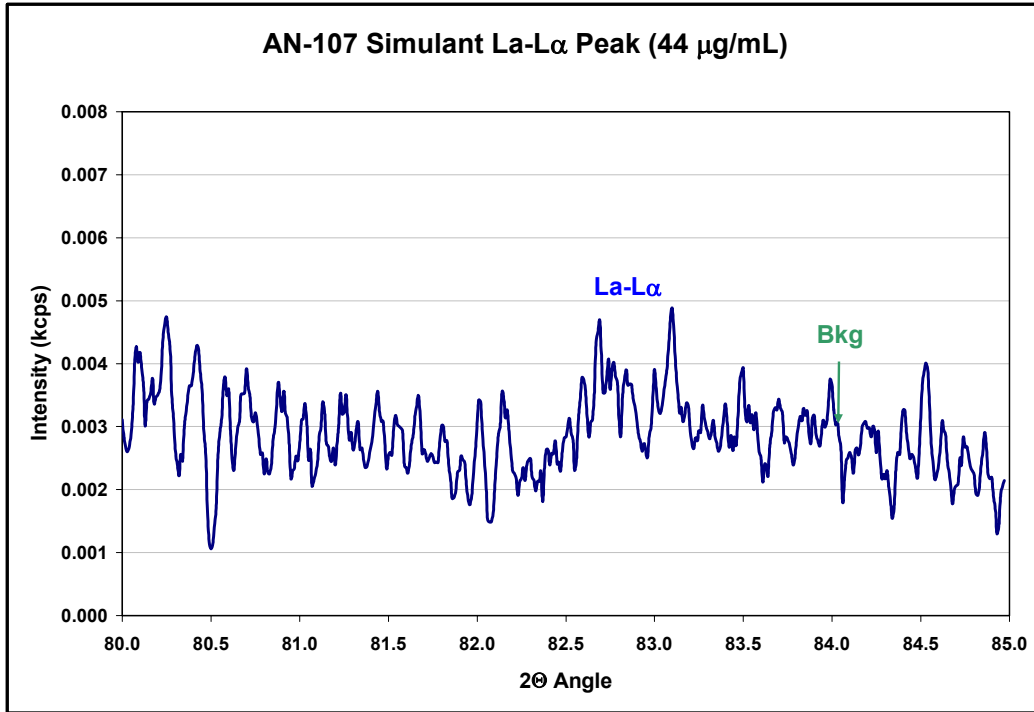


Figure 58. AN-107 simulant La-L α WD-XRF scan.

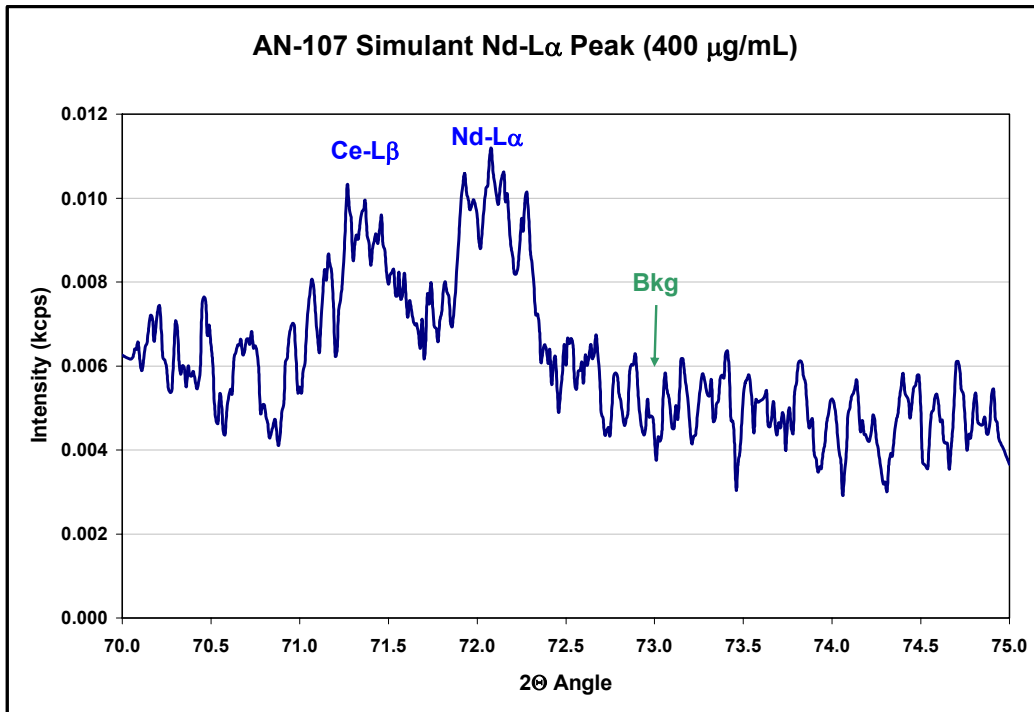


Figure 59. AN-107 simulant Nd-L α WD-XRF scan.

7.6 Appendix F: Dried Deposits

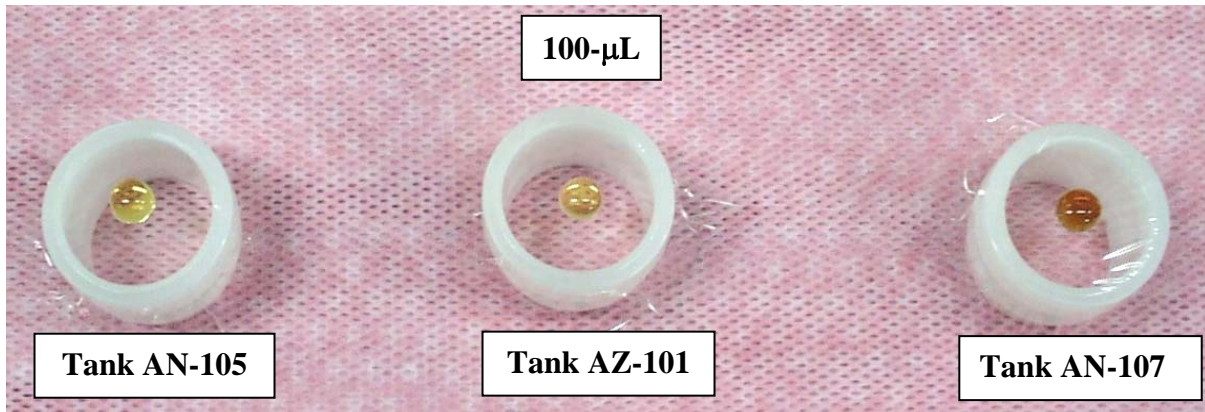


Figure 60. 100- μ L of basic simulant on Ultralene™ film after drying for 6-hr in air.

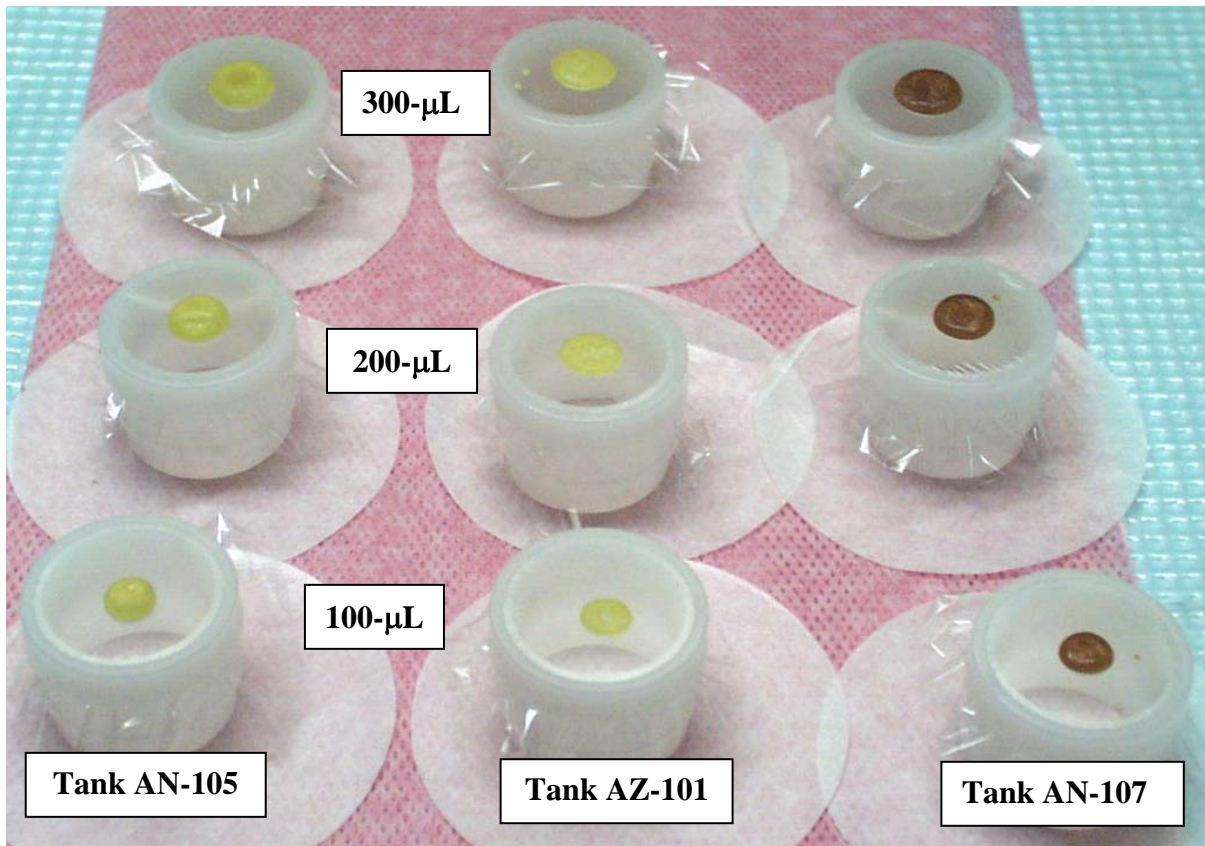


Figure 61. 100-, 200-, & 300- μ L of basic simulant on Ultralene™ film after drying for 24-hr in air.

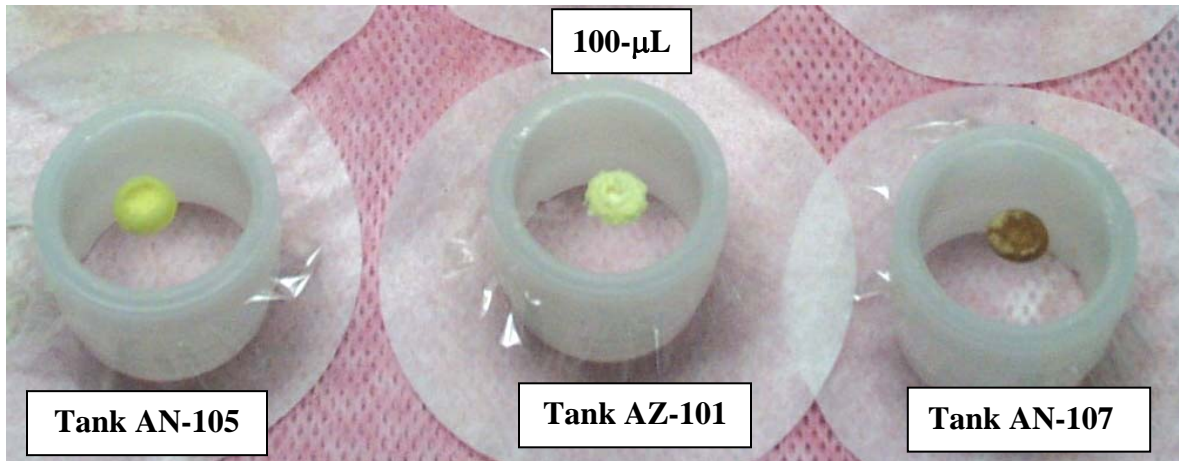


Figure 62. 100- μ l of basic simulant on Ultralene™ film after 10-d in air.

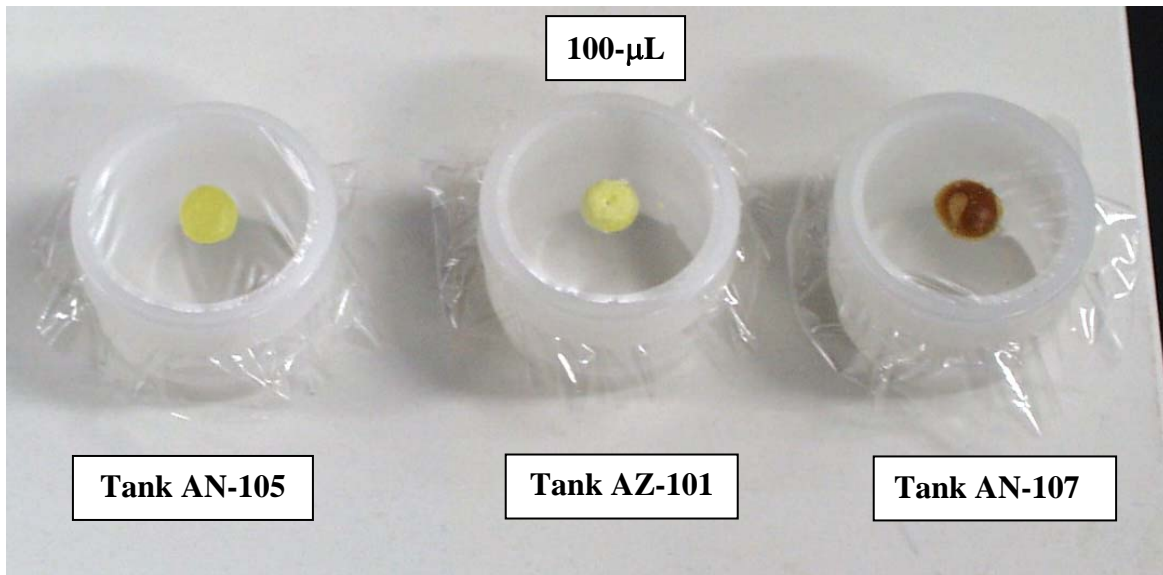


Figure 63. 100- μ l of basic simulant on Ultralene™ film after drying for 1.5-hr in air under an IR lamp.

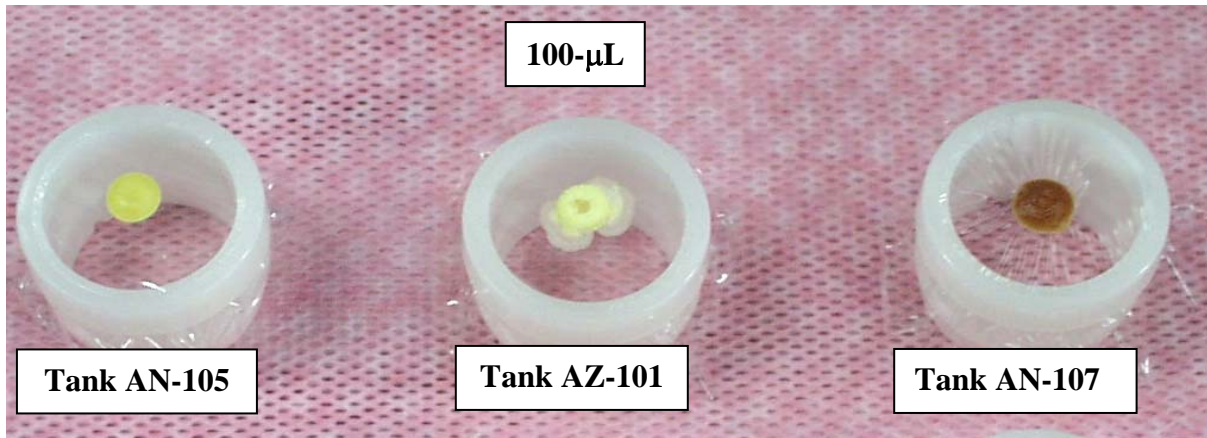


Figure 64. 100- μ l of basic simulant on Ultralene™ film after drying for 6-hr in air under an IR lamp.

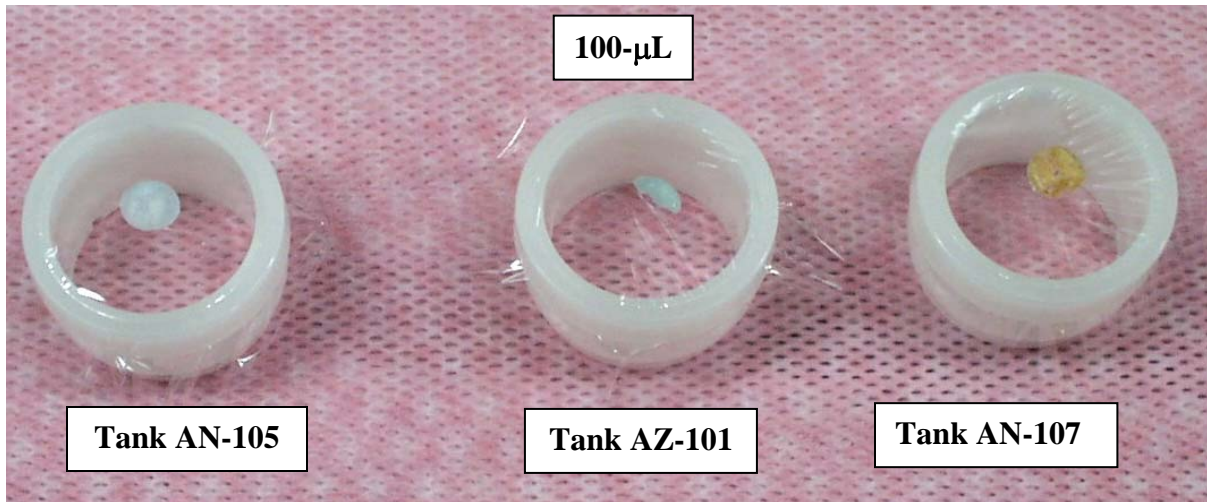


Figure 65. 100- μ l of acidified simulant on Ultralene™ film after drying for 1.5 hr in air under an IR lamp.

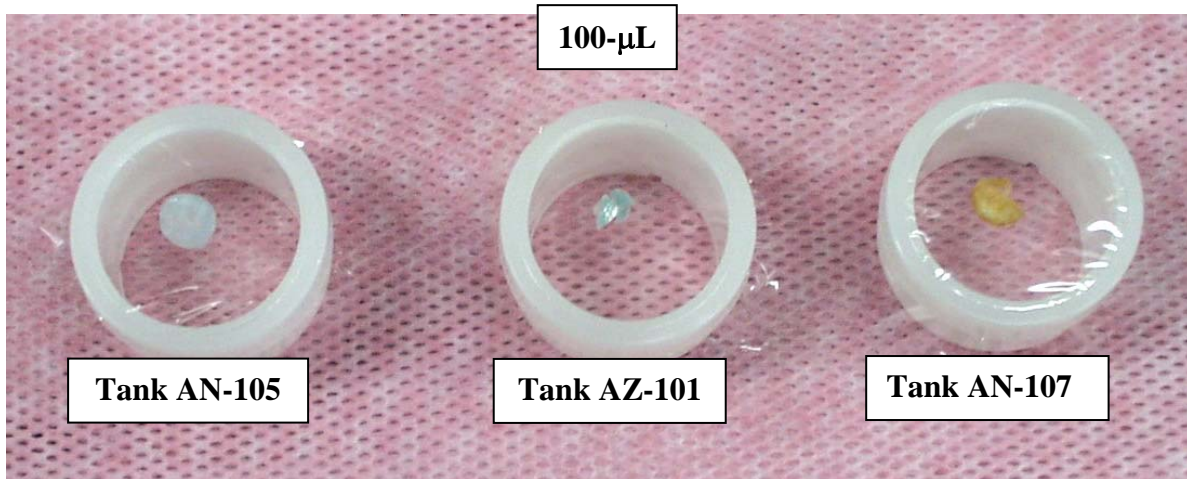


Figure 66. 100- μ L of acidified simulant on polypropylene film after drying for 1.5-hr in air under an IR lamp.

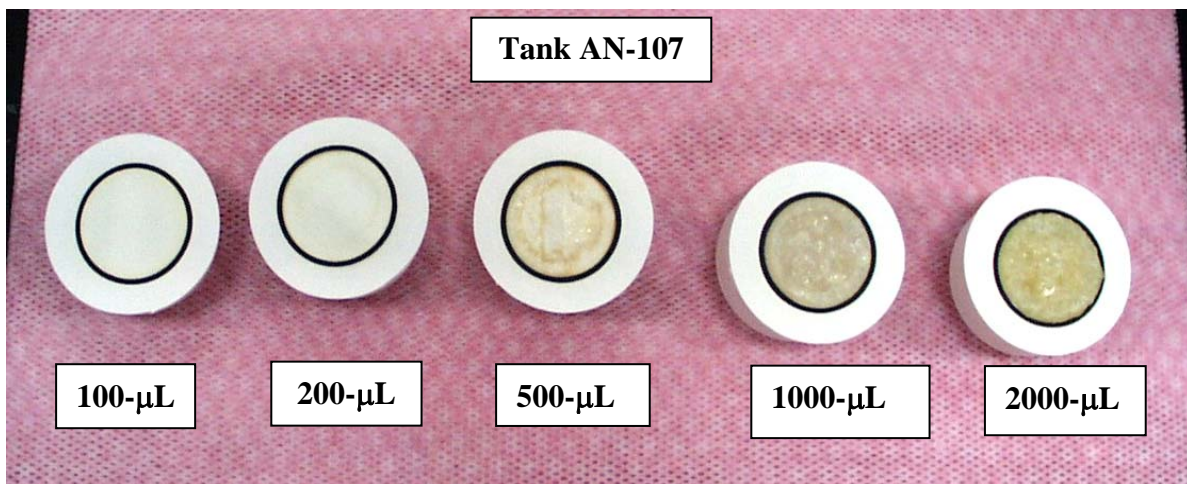


Figure 67. Acidified Tank AN-107 simulant on Bruker cellulose filter paper with a wax retaining ring after drying for 1.5-hr in air under an IR lamp.

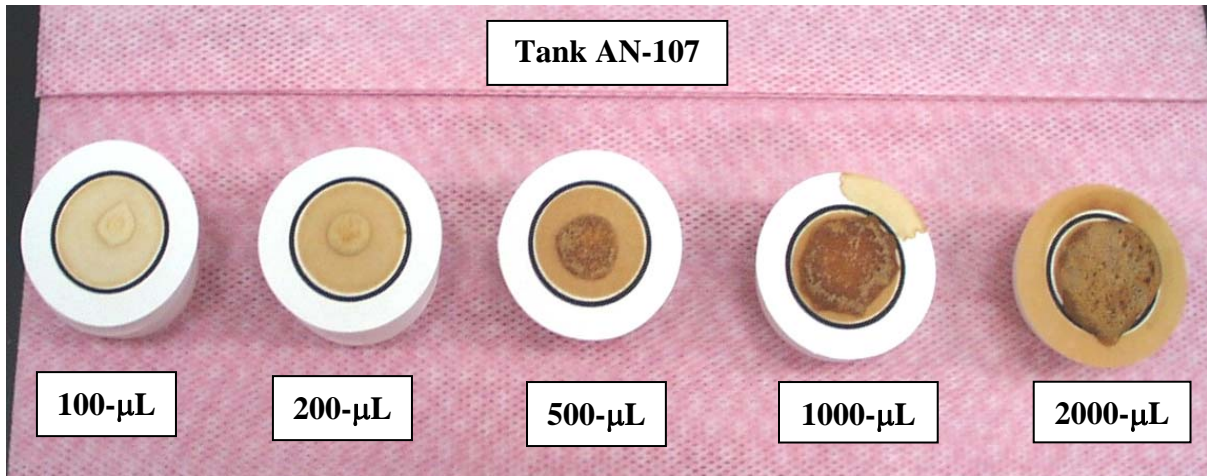


Figure 68. Basic Tank AN-107 simulant on Bruker cellulose filter paper with a wax retaining ring after 8-hr in air under an IR lamp.

7.7 Appendix G: Detection Limits

Table 40. NIST SRM 1411 Borosilicate Glass Limits of Detection

NIST SRM 1411 Soft Borosilicate Glass Limits of Detection

Voltage: 40-kV
Current: 1.2-mA
Atmosphere: Vacuum
Analysis Time: 200-sec on peak; 100-sec (two points) or 200-sec (one point) on each background point
Polished to 1 μm

Sample	SiO ₂ kcps	Na ₂ O kcps	Al ₂ O ₃ kcps	K ₂ O kcps	CaO kcps	Fe ₂ O ₃ kcps
(Pk - Bkg)	17.42472	2.13510	2.48761	1.92094	1.81264	0.07977
Bkg	0.14659	0.13938	0.03846	0.04290	0.04230	0.01105
(Pk - Bkg)	17.41336	2.14354	2.48557	1.92281	1.82128	0.07904
Bkg	0.14775	0.13063	0.03858	0.04294	0.04245	0.01056
(Pk - Bkg)	17.42076	2.15084	2.48042	1.92276	1.81632	0.07740
Bkg	0.14736	0.12756	0.03849	0.04314	0.04259	0.01054
(Pk - Bkg)	17.40673	2.14921	2.48428	1.92721	1.81611	0.07893
Bkg	0.14070	0.12371	0.04004	0.04243	0.04280	0.01095
(Pk - Bkg)	17.36943	2.15045	2.47788	1.91874	1.81531	0.07808
Bkg	0.14974	0.12453	0.03916	0.04242	0.04277	0.01076
(Pk - Bkg)	17.41793	2.16161	2.47852	1.92449	1.81445	0.07904
Bkg	0.14933	0.12159	0.03862	0.04270	0.04329	0.01045
(Pk - Bkg)	17.41085	2.15280	2.47248	1.91967	1.81684	0.07762
Bkg	0.14838	0.12324	0.03782	0.04347	0.04165	0.01098
(Pk - Bkg)	17.41960	2.15739	2.48169	1.92008	1.81569	0.07798
Bkg	0.14770	0.12208	0.03926	0.04245	0.04143	0.01080
(Pk - Bkg)	17.41039	2.16141	2.48238	1.92093	1.82021	0.07797
Bkg	0.15039	0.12085	0.03872	0.04238	0.04070	0.01097
(Pk - Bkg)	17.41029	2.14929	2.48083	1.92207	1.81565	0.07956
Bkg	0.14917	0.12158	0.04026	0.04283	0.04238	0.01047
(Pk - Bkg)	17.42309	2.15503	2.48014	1.92228	1.81315	0.07774
Bkg	0.14886	0.12344	0.03885	0.04398	0.04222	0.01048
(Pk - Bkg)	17.42786	2.15272	2.48486	1.92375	1.38183	0.07811
Bkg	0.14715	0.12136	0.03894	0.04224	0.04240	0.01097
(Pk - Bkg)	17.40956	2.16018	2.47981	1.92092	1.81704	0.07828
Bkg	0.14557	0.12087	0.03846	0.04306	0.04186	0.01099
(Pk - Bkg)	17.41250	2.15426	2.48471	1.92395	1.81084	0.07912
Bkg	0.14863	0.12234	0.03857	0.04289	0.04182	0.01073
(Pk - Bkg)	17.38604	2.14917	2.47861	1.92146	1.81035	0.07844
Bkg	0.14809	0.12234	0.03826	0.04205	0.04234	0.01017
(Pk - Bkg)	17.39251	2.15590	2.48260	1.91807	1.81017	0.07917
Bkg	0.15039	0.12145	0.03802	0.04232	0.04349	0.01111
(Pk - Bkg)	17.41143	2.15227	2.48227	1.92197	1.81308	0.07870
Bkg	0.15035	0.12037	0.03848	0.04328	0.04235	0.01053
(Pk - Bkg)	17.37225	2.15694	2.48301	1.91859	1.81367	0.07886
Bkg	0.14796	0.12054	0.03756	0.04335	0.04167	0.01061
(Pk - Bkg)	17.39780	2.14893	2.48043	1.92526	1.81486	0.07915
Bkg	0.14636	0.12019	0.03779	0.04128	0.04094	0.01036
(Pk - Bkg)	17.40750	2.15843	2.47873	1.91722	1.81453	0.07874
Bkg	0.14754	0.11911	0.03817	0.04337	0.04299	0.01014

Rigaku Mini ZSXII NIST SRM 1411 Limits of Detection (20 measurements)

	SiO ₂ kcps	Na ₂ O kcps	Al ₂ O ₃ kcps	K ₂ O kcps	CaO kcps	Fe ₂ O ₃ kcps
Blank Average	0.14790	0.12336	0.03863	0.04277	0.04222	0.01068
Blank Stdev	0.00217	0.00461	0.00068	0.00060	0.00072	0.00029
Sample Average	17.40723	2.15277	2.48134	1.92166	1.79320	0.07859
Glass Concentration (wt%)	58.04	10.14	5.68	2.97	2.18	0.05
IUPAC LOD in $\mu\text{g/g}$ (3σ)	217	651	47	28	26	6
XRF LOD in $\mu\text{g/g}$ (3σ)	122	157	43	30	24	6
	Si kcps	Na kcps	Al kcps	K kcps	Ca kcps	Fe kcps
IUPAC LOD in $\mu\text{g/g}$ (3σ)	101	483	25	23	19	4
XRF LOD in $\mu\text{g/g}$ (3σ)	57	116	23	25	17	4

Table 41. AN-105 Simulant Solution Limits of Detection

Envelope A (AN-105 simulant) Solution Limits of Detection

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was not replaced)
Cell: 31 mm double open end
Sample film: Ultralene - 4- μ m (film was not replaced before each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec (two points) or 200-sec (one point) on each background point
Volume: 5-mL **filtered** supernate
 3 runs in a row

Sample	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Si kcps	Mo kcps
A (Pk - Bkg)	0.23728	0.71439	0.00751	1.34874	0.73398	0.22743	0.00277	0.26806
Bkg	0.00417	0.00955	0.00146	0.04574	0.03309	0.00658	0.00107	0.84707
B (Pk - Bkg)	0.24810	0.73157	0.00775	1.35593	0.73064	0.22822	0.00251	0.27139
Bkg	0.00402	0.00902	0.00123	0.04593	0.03373	0.00710	0.00120	0.84306
C (Pk - Bkg)	0.24133	0.72545	0.00794	1.35352	0.73695	0.22604	0.00214	0.27276
Bkg	0.00393	0.00948	0.00142	0.04518	0.03308	0.00691	0.00122	0.83192
D (Pk - Bkg)	0.22522	0.70220	0.00698	1.33571	0.72652	0.22515	0.00211	0.26321
Bkg	0.00361	0.00842	0.00148	0.04537	0.03271	0.00700	0.00120	0.82531
E (Pk - Bkg)	0.22971	0.71073	0.00802	1.34874	0.72564	0.22567	0.00243	0.26769
Bkg	0.00411	0.00837	0.00129	0.04609	0.03395	0.00650	0.00116	0.82843
A (Pk - Bkg)	0.23216	0.71121	0.00745	1.35203	0.72869	0.22725	0.00239	0.26660
Bkg	0.00420	0.00937	0.00123	0.04486	0.03198	0.00689	0.00109	0.83361
B (Pk - Bkg)	0.23922	0.72179	0.00737	1.35996	0.72984	0.23045	0.00204	0.26502
Bkg	0.00409	0.00880	0.00145	0.04570	0.03259	0.00658	0.00122	0.83895
C (Pk - Bkg)	0.22879	0.71259	0.00771	1.34998	0.73083	0.22650	0.00230	0.26928
Bkg	0.00419	0.00875	0.00121	0.04704	0.03298	0.00637	0.00129	0.83348
D (Pk - Bkg)	0.21852	0.69257	0.00737	1.33334	0.72567	0.22587	0.00192	0.27363
Bkg	0.00417	0.00890	0.00132	0.04517	0.03351	0.00718	0.00135	0.82265
E (Pk - Bkg)	0.22098	0.69907	0.00749	1.34356	0.72926	0.22895	0.00220	0.25978
Bkg	0.00406	0.00908	0.00137	0.04559	0.03254	0.00666	0.00133	0.83432
A (Pk - Bkg)	0.22130	0.69998	0.00758	1.34101	0.72729	0.22601	0.00238	0.27227
Bkg	0.00413	0.00799	0.00132	0.04615	0.03264	0.00616	0.00117	0.82977
B (Pk - Bkg)	0.21594	0.69907	0.00760	1.35440	0.73069	0.23030	0.00222	0.27490
Bkg	0.00372	0.00864	0.00135	0.04650	0.03256	0.00673	0.00119	0.84675
C (Pk - Bkg)	0.20682	0.68961	0.00766	1.35855	0.71057	0.22911	0.00218	0.27324
Bkg	0.00375	0.00820	0.00132	0.04565	0.03223	0.00669	0.00134	0.85321
D (Pk - Bkg)	0.20189	0.68013	0.00778	1.34789	0.69894	0.22999	0.00228	0.27600
Bkg	0.00359	0.00837	0.00136	0.04670	0.03197	0.00671	0.00140	0.84781
E (Pk - Bkg)	0.19535	0.67267	0.00782	1.34797	0.68527	0.22745	0.00214	0.28177
Bkg	0.00376	0.00852	0.00133	0.04523	0.03121	0.00687	0.00129	0.84043

Rigaku Mini ZSXII AN-105 Simulant Limits of Detection (15 measurements)

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Si kcps	Mo kcps
Blank Average	0.00397	0.00876	0.00134	0.04579	0.03272	0.00673	0.00123	0.83712
Blank Stdev	0.00022	0.00047	0.00008	0.00062	0.00072	0.00027	0.00010	0.00908
Sample Average	0.22417	0.70420	0.00760	1.34876	0.72339	0.22763	0.00227	0.27037
Simulant Concentration (μ g/mL)	217000	34200	193	9200	7860	1260	168	82
IUPAC LOD in μ g/mL (3σ)	641	69	6	13	23	5	21	8
XRF LOD in μ g/mL (3σ)	578	43	9	14	19	4	25	3

Table 42. AZ-101 Simulant Solution Limits of Detection

Envelope B (AZ-101 simulant) Solution Limits of Detection

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was not replaced)
Cell: 31 mm double open end
Sample film: Ultralene - 4- μ m (film was not replaced before each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec (two points) or 200-sec (one point) on each background point
Volume: 5-mL **filtered** supernate
 3 runs in a row

Sample	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	S kcps
A (Pk - Bkg)	0.11057	0.13051	0.02662	0.07307	0.65023	0.17512	0.71551
Bkg	0.00336	0.00232	0.00188	0.01109	0.03658	0.00749	0.00364
B (Pk - Bkg)	0.11136	0.12976	0.02722	0.07111	0.65302	0.17816	0.71732
Bkg	0.00369	0.00238	0.00184	0.01191	0.03704	0.00703	0.00424
C (Pk - Bkg)	0.11386	0.13039	0.02671	0.07282	0.65232	0.17734	0.72050
Bkg	0.00324	0.00270	0.00183	0.01100	0.03566	0.00704	0.00422
D (Pk - Bkg)	0.11181	0.12945	0.02710	0.07146	0.65207	0.17808	0.71874
Bkg	0.00323	0.00270	0.00187	0.01170	0.03676	0.00715	0.00412
E (Pk - Bkg)	0.11519	0.13164	0.02715	0.07406	0.65859	0.17845	0.72258
Bkg	0.00331	0.00250	0.00193	0.01156	0.03563	0.00679	0.00388
A (Pk - Bkg)	0.11077	0.12968	0.02648	0.07444	0.65755	0.17772	0.72245
Bkg	0.00313	0.00246	0.00172	0.01132	0.03576	0.00725	0.00375
B (Pk - Bkg)	0.11058	0.12778	0.02719	0.07346	0.65606	0.17881	0.71826
Bkg	0.00290	0.00275	0.00162	0.01194	0.03680	0.00731	0.00365
C (Pk - Bkg)	0.10958	0.12996	0.02753	0.07319	0.65572	0.17806	0.72193
Bkg	0.00322	0.00257	0.00136	0.01109	0.03656	0.00673	0.00388
D (Pk - Bkg)	0.11207	0.13180	0.02740	0.07476	0.66777	0.17977	0.72886
Bkg	0.00279	0.00234	0.00163	0.01146	0.03800	0.00691	0.00400
E (Pk - Bkg)	0.11071	0.13083	0.02690	0.07262	0.65829	0.17871	0.72618
Bkg	0.00309	0.00217	0.00159	0.01208	0.03617	0.00706	0.00365
A (Pk - Bkg)	0.10251	0.12819	0.02703	0.07487	0.64280	0.17987	0.72721
Bkg	0.00284	0.00251	0.00174	0.01124	0.03574	0.00750	0.00394
B (Pk - Bkg)	0.09974	0.12702	0.02671	0.07558	0.63713	0.18258	0.72939
Bkg	0.00319	0.00254	0.00181	0.01077	0.03558	0.00682	0.00392
C (Pk - Bkg)	0.09768	0.12914	0.02756	0.07477	0.63431	0.18168	0.73763
Bkg	0.00314	0.00252	0.00183	0.01102	0.03372	0.00719	0.00381
D (Pk - Bkg)	0.09541	0.12473	0.02761	0.07578	0.62759	0.18039	0.73435
Bkg	0.00304	0.00256	0.00190	0.01144	0.03296	0.00721	0.00401
E (Pk - Bkg)	0.10010	0.12796	0.02837	0.07742	0.62416	0.18069	0.74635
Bkg	0.00259	0.00251	0.00200	0.01096	0.03281	0.00703	0.00406

Rigaku Mini ZSXII AZ-101 Simulant Limits of Detection (15 measurements)

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	S kcps
Blank Average	0.00312	0.00250	0.00177	0.01137	0.03572	0.00710	0.00392
Blank Stdev	0.00027	0.00015	0.00016	0.00040	0.00149	0.00023	0.00020
Sample Average	0.10746	0.12926	0.02717	0.07396	0.64851	0.17903	0.72582
Simulant Concentration (μ g/mL)	96800	7190	478	460	4530	668	6490
IUPAC LOD in μ g/mL (3σ)	717	26	9	7	31	3	5
XRF LOD in μ g/mL (3σ)	477	26	7	6	13	3	5

Table 43. AN-107 Simulant Solution Limits of Detection

Envelope C (AN-107 simulant) Solution Limits of Detection

Voltage: 40-kV Current: 1.2-mA
 Atmosphere: He (99.99%)
 Instrument Film: Ultralene - 4- μ m (film was not replaced)
 Cell: 31 mm double open end
 Sample film: Ultralene - 4- μ m (film was not replaced before each run)
 Cover film: Micro-porous Teflon (0.2- μ m pores)
 Analysis Time: 200-sec on peak; 100-sec (two points) or 200-sec (one point) on each background point
 Volume: 5-mL **filtered** supernate
 3 runs in a row

Sample	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
A (Pk - Bkg)	0.18803	0.00253	0.01616	0.31853	0.24796	0.03926	0.12932	0.04473	0.79733	0.17644	0.46846	0.05882	0.15637	0.01497	0.27575
Bkg	0.00338	0.00111	0.00142	0.01414	0.03302	0.00657	0.92920	0.05815	0.01975	0.01113	0.04263	0.09565	0.74739	0.05036	0.24516
B (Pk - Bkg)	0.18833	0.00230	0.01685	0.32041	0.24975	0.03890	0.13489	0.04068	0.80177	0.17800	0.47294	0.05705	0.15344	0.01773	0.27661
Bkg	0.00355	0.00122	0.00123	0.01512	0.03377	0.00637	0.92580	0.05976	0.02030	0.01083	0.04395	0.09562	0.74470	0.04851	0.23924
C (Pk - Bkg)	0.18388	0.00264	0.01689	0.32010	0.27898	0.03851	0.13701	0.04274	0.80321	0.17752	0.47410	0.05999	0.15380	0.01734	0.27785
Bkg	0.00342	0.00114	0.00136	0.01477	0.03317	0.00673	0.91937	0.05824	0.02057	0.01071	0.04229	0.09429	0.74132	0.04830	0.24352
D (Pk - Bkg)	0.18185	0.00283	0.01636	0.31936	0.25003	0.03865	0.13760	0.04154	0.80215	0.17858	0.47278	0.05820	0.15770	0.01812	0.27110
Bkg	0.00351	0.00100	0.00148	0.01503	0.03375	0.00677	0.91658	0.05924	0.01948	0.01094	0.04345	0.09524	0.73673	0.04796	0.24313
E (Pk - Bkg)	0.17837	0.00276	0.01616	0.31662	0.25016	0.03988	0.13647	0.04278	0.80362	0.17813	0.47162	0.05853	0.15281	0.01668	0.27472
Bkg	0.00351	0.00104	0.00137	0.01600	0.03284	0.00601	0.91660	0.05865	0.02064	0.01092	0.04305	0.09602	0.74040	0.05020	0.24347
A (Pk - Bkg)	0.17589	0.00292	0.01670	0.31778	0.25053	0.03840	0.13483	0.04171	0.79979	0.17716	0.47429	0.05922	0.15334	0.01891	0.27971
Bkg	0.00330	0.00083	0.00140	0.01566	0.03377	0.00690	0.91423	0.05754	0.02026	0.01071	0.04276	0.09627	0.74114	0.04813	0.24154
B (Pk - Bkg)	0.17377	0.00275	0.01640	0.31801	0.25147	0.03876	0.13122	0.04164	0.81060	0.17897	0.47317	0.05860	0.15179	0.01811	0.27786
Bkg	0.00337	0.00094	0.00131	0.01517	0.03193	0.00686	0.92550	0.05855	0.01999	0.01070	0.04357	0.09560	0.74766	0.04844	0.23932
C (Pk - Bkg)	0.17057	0.00259	0.01625	0.31973	0.24934	0.03875	0.13357	0.04126	0.80728	0.17864	0.47646	0.05905	0.15204	0.01669	0.27809
Bkg	0.00335	0.00108	0.00134	0.01525	0.03481	0.00644	0.91671	0.05915	0.02039	0.01021	0.04315	0.09526	0.74317	0.04964	0.24187
D (Pk - Bkg)	0.16929	0.00273	0.01651	0.31602	0.24849	0.03949	0.13656	0.04195	0.80493	0.17744	0.47431	0.05813	0.16150	0.01831	0.27814
Bkg	0.00329	0.00107	0.00138	0.01550	0.03328	0.00668	0.91629	0.05937	0.01984	0.01095	0.04211	0.09526	0.73537	0.04805	0.24168
E (Pk - Bkg)	0.16763	0.00263	0.01671	0.31759	0.25140	0.03870	0.13098	0.04065	0.80564	0.17825	0.47435	0.05794	0.15245	0.02017	0.27977
Bkg	0.00329	0.00091	0.00136	0.01489	0.03305	0.00632	0.92137	0.05930	0.02035	0.01071	0.04392	0.09629	0.74059	0.04667	0.24072
A (Pk - Bkg)	0.16483	0.00244	0.01608	0.31442	0.24756	0.03834	0.13404	0.04220	0.80534	0.17811	0.47344	0.05791	0.15372	0.01620	0.27550
Bkg	0.00317	0.00102	0.00129	0.01532	0.03376	0.00677	0.91837	0.05795	0.01942	0.01082	0.04395	0.09550	0.74143	0.04946	0.24501
B (Pk - Bkg)	0.16726	0.00240	0.01611	0.31680	0.24992	0.03896	0.13322	0.03991	0.80244	0.18111	0.47796	0.05792	0.15395	0.01803	0.27928
Bkg	0.00325	0.00115	0.00118	0.01496	0.03398	0.00665	0.91983	0.05940	0.02056	0.01031	0.04272	0.09668	0.74173	0.04740	0.23973
C (Pk - Bkg)	0.16459	0.00248	0.01836	0.33354	0.24994	0.03933	0.13483	0.04121	0.82303	0.18239	0.47912	0.05885	0.15850	0.01741	0.27862
Bkg	0.00354	0.00112	0.00123	0.01468	0.03288	0.00639	0.91728	0.05949	0.01990	0.01046	0.04323	0.09555	0.74146	0.04879	0.24013
D (Pk - Bkg)	0.16551	0.00245	0.01897	0.33962	0.24616	0.03939	0.13991	0.04285	0.81982	0.18067	0.48654	0.06001	0.15860	0.01842	0.27591
Bkg	0.00385	0.00113	0.00142	0.01437	0.03139	0.00634	0.93608	0.05774	0.02067	0.01050	0.04213	0.09602	0.75395	0.04794	0.24239
E (Pk - Bkg)	0.16361	0.00270	0.01830	0.34193	0.23877	0.03891	0.14282	0.04108	0.82475	0.18402	0.48738	0.06032	0.16336	0.01697	0.27812
Bkg	0.00332	0.00110	0.00174	0.01473	0.03128	0.00669	0.93353	0.06012	0.01973	0.01000	0.04273	0.09495	0.75063	0.04865	0.24424

Rigaku Mini ZSXII AN-107 Simulant Limits of Detection (15 measurements)

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
Blank Average	0.00341	0.00106	0.00137	0.01504	0.03311	0.00657	0.92178	0.05884	0.02012	0.01066	0.04304	0.09561	0.74318	0.04857	0.24208
Blank Stdev	0.00017	0.00010	0.00013	0.00048	0.00097	0.00025	0.00674	0.00078	0.00042	0.00031	0.00063	0.00059	0.00496	0.00101	0.00199
Sample Average	0.17356	0.00261	0.01685	0.32203	0.25070	0.03895	0.13515	0.04180	0.80745	0.17903	0.47579	0.05870	0.15556	0.01760	0.27714
Simulant Concentration (μ g/mL)	183000	215	379	1830	1900	157	38	28	1650	550	543	48	47	246	400
IUPAC LOD in μ g/mL (3σ)	527	25	9	8	22	3	6	2	3	3	2	1	4	42	9
XRF LOD in μ g/mL (3σ)	584	25	8	7	13	3	3	2	3	3	2	2	2	29	7

Table 44. AN-107 Simulant Filter Paper (100- μ L Sample) Limits of Detection under Helium Purge

Envelope C (AN-107 simulant) Filter Paper Limits of Detection

Voltage: 40-kV Current: 1.2-mA
 Atmosphere: He (99.99%)
 Instrument Film: Ultralene - 4-mm (film was not replaced)
 Cell: None
 Sample Filter: Cellulose - Bruker
 Cover film: None
 Analysis Time: 200-sec on peak; 100-sec (two points) or 200-sec (one point) on each background point
 Volume: 100- μ L of (2.5-mL H₂O/2.5-mL HNO₃/5mL AN-107 solution)
 3 runs in a row

Sample	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
A (Pk - Bkg)	0.40236	0.00550	0.02939	0.06024	0.22287	0.03385	0.00789	0.01165	0.39304	0.09608	0.15924	0.02079	0.00719	0.03184	0.03329
Bkg	0.00379	0.00067	0.00098	0.01315	0.02404	0.00544	0.06104	0.02782	0.01282	0.00751	0.02282	0.03636	0.06406	0.04032	0.05422
B (Pk - Bkg)	0.36001	0.00514	0.02800	0.04960	0.21687	0.03266	0.00741	0.01159	0.38280	0.09204	0.15763	0.01897	0.00656	0.03076	0.03519
Bkg	0.00381	0.00054	0.00087	0.01432	0.02556	0.00553	0.06162	0.02763	0.01320	0.00806	0.02318	0.03648	0.06557	0.03953	0.05483
C (Pk - Bkg)	0.28446	0.00635	0.02648	0.06675	0.20940	0.03214	0.00841	0.01052	0.37000	0.08950	0.14933	0.01689	0.00876	0.03221	0.03234
Bkg	0.00303	0.00070	0.00096	0.01377	0.02560	0.00519	0.06049	0.02882	0.01293	0.00765	0.02322	0.03751	0.06401	0.04058	0.05684
D (Pk - Bkg)	0.32850	0.00521	0.02588	0.05455	0.21026	0.03226	0.00862	0.01168	0.36864	0.08997	0.14860	0.01865	0.00581	0.03240	0.03232
Bkg	0.00360	0.00056	0.00105	0.01390	0.02544	0.00535	0.06098	0.02747	0.01332	0.00770	0.02359	0.03688	0.06580	0.03965	0.05554
E (Pk - Bkg)	0.32324	0.00544	0.02658	0.04852	0.20967	0.03302	0.00708	0.00980	0.36217	0.08795	0.14428	0.01793	0.00777	0.03181	0.02806
Bkg	0.00334	0.00056	0.00091	0.01358	0.02383	0.00496	0.05926	0.02779	0.01301	0.00712	0.02327	0.03575	0.06155	0.04001	0.05418
A (Pk - Bkg)	0.39232	0.00586	0.02849	0.05920	0.22181	0.03369	0.00763	0.01071	0.39291	0.09497	0.15972	0.01824	0.00691	0.03490	0.03420
Bkg	0.00364	0.00057	0.00101	0.01417	0.02492	0.00531	0.06072	0.02849	0.01335	0.00783	0.02233	0.03715	0.06429	0.03888	0.05326
B (Pk - Bkg)	0.33253	0.00552	0.02654	0.05148	0.21702	0.03336	0.00658	0.01077	0.37496	0.09161	0.15356	0.01792	0.00667	0.03355	0.03394
Bkg	0.00324	0.00065	0.00100	0.01398	0.02442	0.00526	0.06157	0.02768	0.01339	0.00764	0.02397	0.03656	0.06338	0.04040	0.05486
C (Pk - Bkg)	0.28958	0.00637	0.02603	0.06934	0.20614	0.03423	0.00761	0.01151	0.36648	0.08871	0.14975	0.01861	0.00741	0.03299	0.03238
Bkg	0.00304	0.00072	0.00103	0.01385	0.02450	0.00495	0.06000	0.02708	0.01274	0.00739	0.02262	0.03593	0.06307	0.03945	0.05470
D (Pk - Bkg)	0.32466	0.00534	0.02605	0.05508	0.20084	0.03368	0.00768	0.01040	0.36567	0.08909	0.14878	0.01842	0.00762	0.03373	0.03178
Bkg	0.00342	0.00047	0.00087	0.01434	0.02351	0.00520	0.05891	0.02697	0.01284	0.00734	0.02254	0.03519	0.06147	0.03895	0.05493
E (Pk - Bkg)	0.31522	0.00531	0.02658	0.04876	0.19680	0.03379	0.00768	0.01006	0.35815	0.08637	0.14502	0.01706	0.00681	0.03120	0.03030
Bkg	0.00306	0.00062	0.00107	0.01429	0.02313	0.00470	0.05722	0.02673	0.01243	0.00755	0.02128	0.03521	0.06048	0.03986	0.05269
A (Pk - Bkg)	0.38876	0.00556	0.02955	0.06043	0.20125	0.03363	0.00779	0.01087	0.38873	0.09467	0.15993	0.01900	0.00792	0.03499	0.03255
Bkg	0.00403	0.00060	0.00109	0.01392	0.02233	0.00524	0.05841	0.02720	0.01229	0.00754	0.02229	0.03495	0.06170	0.03982	0.05538
B (Pk - Bkg)	0.31615	0.00508	0.02707	0.05284	0.19506	0.03267	0.00898	0.01176	0.37557	0.09204	0.15327	0.01830	0.00668	0.03510	0.03525
Bkg	0.00326	0.00069	0.00096	0.01276	0.02197	0.00511	0.05786	0.02605	0.01304	0.00752	0.02174	0.03516	0.06115	0.03968	0.05498
C (Pk - Bkg)	0.25388	0.00638	0.02576	0.06848	0.18320	0.03215	0.00608	0.00999	0.36011	0.08691	0.14441	0.01730	0.00869	0.03214	0.03272
Bkg	0.00283	0.00077	0.00093	0.01296	0.02254	0.00490	0.05906	0.02744	0.01275	0.00717	0.02312	0.03535	0.06106	0.04004	0.05543
D (Pk - Bkg)	0.28915	0.00491	0.02534	0.05571	0.18562	0.03186	0.00713	0.01067	0.36316	0.08709	0.14724	0.01787	0.00722	0.03075	0.02955
Bkg	0.00288	0.00049	0.00084	0.01411	0.02146	0.00518	0.05992	0.02670	0.01201	0.00733	0.02301	0.03579	0.06202	0.03900	0.05398
E (Pk - Bkg)	0.27973	0.00580	0.02625	0.04815	0.18290	0.03220	0.00795	0.00964	0.35533	0.08493	0.14396	0.01927	0.00679	0.03141	0.02972
Bkg	0.00304	0.00047	0.00093	0.01394	0.02176	0.00488	0.05643	0.02586	0.01227	0.00717	0.02105	0.03229	0.05914	0.03877	0.05113

Rigaku Mini ZSXII AN-107 Simulant Limits of Detection (15 measurements)

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
Blank Average	0.00333	0.00061	0.00097	0.01380	0.02367	0.00515	0.05957	0.02732	0.01283	0.00750	0.02267	0.03577	0.06258	0.03966	0.05446
Blank Stdev	0.00037	0.00009	0.00008	0.00049	0.00142	0.00023	0.00159	0.00080	0.00042	0.00026	0.00082	0.00124	0.00191	0.00057	0.00135
Sample Average	0.32537	0.00558	0.02693	0.05661	0.20398	0.03301	0.00763	0.01077	0.37185	0.09013	0.15098	0.01835	0.00725	0.03265	0.03224
Simulant Concentration (μ g/mL)	183000	215	379	1830	1900	157	38	28	1650	550	543	48	47	246	400
IUPAC LOD in μ g/mL (3 σ)	623	11	3	48	40	3	24	6	6	5	9	10	37	13	50
XRF LOD in μ g/mL (3 σ)	308	9	4	36	14	3	12	4	5	5	5	5	15	14	27

Table 45. AN-107 Simulant Filter Paper (200- μ L Sample) Limits of Detection under Helium Purge

Envelope C (AN-107 simulant) Filter Paper Limits of Detection

Voltage: 40-kV Current: 1.2-mA
 Atmosphere: He (99.99%)
 Instrument Film: Ultralene - 4-mm (film was not replaced)
 Cell: None
 Sample Filter: Cellulose - Bruker
 Cover film: None
 Analysis Time: 200-sec on peak; 100-sec (two points) or 200-sec (one point) on each background point
 Volume: 200- μ L of (2.5-mL H₂O/2.5-mL HNO₃/5mL AN-107 solution)
 3 runs in a row

Sample	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
A (Pk - Bkg)	0.46888	0.00707	0.05294	0.04632	0.25407	0.03758	0.01186	0.01745	0.55616	0.12999	0.23971	0.02673	0.01606	0.02436	0.06129
Bkg	0.00465	0.00069	0.00088	0.01141	0.02317	0.00529	0.08174	0.03283	0.01457	0.00844	0.02798	0.04529	0.08518	0.03792	0.07086
B (Pk - Bkg)	0.45803	0.00688	0.04698	0.04591	0.24620	0.03539	0.01221	0.01605	0.50236	0.11921	0.21205	0.02468	0.01275	0.02454	0.05042
Bkg	0.00450	0.00054	0.00087	0.01193	0.02449	0.00556	0.07825	0.03209	0.01408	0.00798	0.02767	0.04349	0.08317	0.03744	0.06809
C (Pk - Bkg)	0.45460	0.00693	0.04669	0.04420	0.24166	0.03584	0.01168	0.01416	0.49197	0.11600	0.20552	0.00229	0.01597	0.02239	0.04896
Bkg	0.00428	0.00054	0.00112	0.01123	0.02490	0.00528	0.07661	0.03314	0.01436	0.00821	0.02759	0.04406	0.07998	0.04001	0.06869
D (Pk - Bkg)	0.46595	0.00646	0.04840	0.04163	0.25448	0.03693	0.01184	0.01646	0.52685	0.12448	0.22455	0.02492	0.01339	0.02518	0.05496
Bkg	0.00435	0.00059	0.00105	0.01273	0.02540	0.00538	0.07985	0.03238	0.01382	0.00776	0.02706	0.04523	0.08354	0.03775	0.06802
E (Pk - Bkg)	0.44284	0.00616	0.04657	0.04154	0.24780	0.03443	0.01131	0.01466	0.49814	0.11750	0.21024	0.02307	0.01400	0.02489	0.05188
Bkg	0.00440	0.00065	0.00083	0.01188	0.02599	0.00585	0.07864	0.03275	0.01497	0.00827	0.02710	0.04373	0.08176	0.03719	0.06757
A (Pk - Bkg)	0.52871	0.00727	0.05406	0.04658	0.25340	0.03866	0.01276	0.01673	0.55343	0.13061	0.23892	0.02807	0.01491	0.02551	0.05951
Bkg	0.00492	0.00057	0.00088	0.01167	0.02383	0.00512	0.08064	0.03307	0.01439	0.00839	0.02857	0.04458	0.08490	0.03836	0.07142
B (Pk - Bkg)	0.45128	0.00684	0.04693	0.04698	0.24301	0.03711	0.01055	0.01475	0.50167	0.11828	0.21292	0.02509	0.01352	0.02472	0.05025
Bkg	0.00423	0.00039	0.00093	0.01164	0.02368	0.00529	0.07599	0.03146	0.01363	0.00764	0.02715	0.04222	0.07920	0.03791	0.06667
C (Pk - Bkg)	0.42380	0.00644	0.04644	0.04223	0.22722	0.03597	0.01276	0.01406	0.49373	0.11473	0.20397	0.02260	0.01458	0.02168	0.04888
Bkg	0.00405	0.00056	0.00104	0.01168	0.02331	0.00557	0.07364	0.03199	0.01317	0.00794	0.02676	0.04263	0.07690	0.03969	0.06728
D (Pk - Bkg)	0.44335	0.00674	0.04800	0.04272	0.23193	0.03636	0.01120	0.01421	0.51948	0.12073	0.21748	0.02590	0.01443	0.02521	0.05208
Bkg	0.00388	0.00058	0.00099	0.01143	0.02310	0.00531	0.07654	0.03201	0.01453	0.00771	0.02703	0.04270	0.07982	0.03772	0.06928
E (Pk - Bkg)	0.40381	0.00590	0.04508	0.03949	0.21964	0.03444	0.01037	0.01407	0.48833	0.11480	0.20921	0.02320	0.01555	0.02466	0.05133
Bkg	0.00393	0.00059	0.00092	0.01222	0.02316	0.00544	0.07530	0.03187	0.01352	0.00753	0.02638	0.04297	0.07861	0.03649	0.06888
A (Pk - Bkg)	0.43608	0.00726	0.05093	0.04500	0.22351	0.03821	0.01375	0.01738	0.54305	0.12852	0.23641	0.02710	0.01480	0.02659	0.06169
Bkg	0.00385	0.00070	0.00115	0.01147	0.02128	0.00500	0.07842	0.03125	0.01345	0.00779	0.02661	0.04322	0.08254	0.03871	0.07063
B (Pk - Bkg)	0.38328	0.00636	0.04475	0.04360	0.21788	0.03496	0.01219	0.01507	0.49063	0.11610	0.21006	0.02379	0.01419	0.02539	0.04964
Bkg	0.00377	0.00059	0.00087	0.01171	0.02143	0.00563	0.07502	0.03118	0.01329	0.00755	0.02606	0.04271	0.07757	0.03705	0.06686
C (Pk - Bkg)	0.37387	0.00640	0.04474	0.04263	0.21333	0.03449	0.01187	0.01524	0.48188	0.11262	0.20425	0.02363	0.01448	0.02172	0.05078
Bkg	0.00354	0.00056	0.00081	0.01145	0.02188	0.00533	0.07360	0.03084	0.01347	0.00776	0.02639	0.04117	0.07810	0.03941	0.06605
D (Pk - Bkg)	0.39567	0.00624	0.04778	0.04261	0.21904	0.03623	0.01272	0.01468	0.51332	0.12041	0.22042	0.02509	0.01548	0.02540	0.05497
Bkg	0.00312	0.00064	0.00115	0.01116	0.02136	0.00480	0.07555	0.03216	0.01324	0.00758	0.02650	0.04370	0.07960	0.03757	0.06737
E (Pk - Bkg)	0.37011	0.00595	0.04468	0.04060	0.21140	0.03536	0.01307	0.01456	0.48789	0.11409	0.20618	0.02350	0.01430	0.02344	0.05226
Bkg	0.00374	0.00061	0.00098	0.01131	0.02235	0.00481	0.07466	0.03127	0.01363	0.00773	0.02735	0.04260	0.07823	0.03488	0.06624

Rigaku Mini ZSXII AN-107 Simulant Limits of Detection (15 measurements)

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
Blank Average	0.00408	0.00059	0.00096	0.01166	0.02329	0.00531	0.07696	0.03202	0.01387	0.00789	0.02708	0.04335	0.08061	0.03787	0.06826
Blank Stdev	0.00046	0.00007	0.00011	0.00041	0.00147	0.00029	0.00252	0.00072	0.00057	0.00031	0.00068	0.00112	0.00271	0.00130	0.00168
Sample Average	0.43335	0.00659	0.04766	0.04347	0.23364	0.03613	0.01201	0.01530	0.50993	0.11987	0.21679	0.02331	0.01456	0.02438	0.05326
Simulant Concentration (μ g/mL)	183000	215	379	1830	1900	157	38	28	1650	550	543	48	47	246	400
IUPAC LOD in μ g/mL (3 σ)	585	7	3	52	36	4	24	4	5	4	5	7	26	39	38
XRF LOD in μ g/mL (3 σ)	256	7	2	43	12	3	8	3	4	4	4	4	9	19	19

Table 46. AN-107 Simulant Filter Paper (100- μ L Sample) Limits of Detection in Vacuum

Envelope C (AN-107 simulant) Filter Paper Limits of Detection

Voltage: 40-kV Current: 1.2-mA
 Atmosphere: Vacuum
 Instrument Film: Ultralene - 4-mm (film was not replaced)
 Cell: None
 Sample Filter: Cellulose - Bruker
 Cover film: None
 Analysis Time: 200-sec on peak; 100-sec on background
 Volume: 100- μ L of (2.5-mL H₂O/2.5-mL HNO₃/5mL AN-107 solution)
 3 runs in a row

Sample	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
A (Pk - Bkg)	2.46305	0.00919	0.03737	0.07517	0.23940	0.03791	0.00648	0.01290	0.40518	0.09633	0.16043	0.01980	0.00827	0.03564	0.03587
Bkg	0.02663	0.00069	0.00101	0.01381	0.02460	0.00486	0.05981	0.02647	0.01227	0.00771	0.02148	0.03577	0.06151	0.03896	0.05106
B (Pk - Bkg)	2.11950	0.00922	0.03826	0.06522	0.23896	0.03938	0.00927	0.01223	0.41078	0.09947	0.16333	0.01938	0.00857	0.03367	0.03674
Bkg	0.02349	0.00067	0.00088	0.01361	0.02596	0.00515	0.06007	0.02767	0.01268	0.00771	0.02305	0.03607	0.06318	0.03980	0.05185
C (Pk - Bkg)	1.70816	0.01018	0.03502	0.08209	0.22643	0.03658	0.00739	0.01031	0.38332	0.09107	0.15331	0.01871	0.00767	0.02962	0.03242
Bkg	0.02023	0.00051	0.00097	0.01401	0.02515	0.00479	0.06027	0.02771	0.01329	0.00747	0.02211	0.03561	0.06192	0.04085	0.05271
D (Pk - Bkg)	1.96263	0.00812	0.03403	0.06878	0.23012	0.03611	0.00792	0.01081	0.38642	0.09140	0.15221	0.01966	0.00783	0.03007	0.03442
Bkg	0.02240	0.00057	0.00071	0.01380	0.02482	0.00516	0.05994	0.02751	0.01343	0.00754	0.02317	0.03520	0.06253	0.04047	0.05239
E (Pk - Bkg)	1.92868	0.00784	0.03446	0.06145	0.22698	0.03702	0.00836	0.01088	0.37658	0.08919	0.14774	0.01721	0.00760	0.03080	0.03223
Bkg	0.02155	0.00051	0.00084	0.01378	0.02580	0.00488	0.05714	0.02587	0.01275	0.00749	0.02223	0.03402	0.05877	0.04014	0.04992
A (Pk - Bkg)	2.47570	0.00884	0.03826	0.07610	0.23925	0.03829	0.00785	0.00991	0.40221	0.09480	0.15976	0.01984	0.00743	0.03483	0.03513
Bkg	0.02640	0.00049	0.00090	0.01339	0.02506	0.00485	0.05881	0.02788	0.01248	0.00712	0.02151	0.03475	0.06169	0.03903	0.05048
B (Pk - Bkg)	2.09276	0.00878	0.03759	0.06428	0.23761	0.03731	0.00711	0.01179	0.40288	0.09457	0.16090	0.01935	0.00937	0.03479	0.03611
Bkg	0.02535	0.00068	0.00087	0.01378	0.02584	0.00532	0.06015	0.02671	0.01217	0.00719	0.02280	0.03556	0.06201	0.03879	0.05117
C (Pk - Bkg)	1.71499	0.01043	0.03527	0.08383	0.22608	0.03635	0.00829	0.01058	0.38403	0.09100	0.15333	0.01954	0.00852	0.03024	0.03254
Bkg	0.02024	0.00061	0.00093	0.01422	0.02513	0.00492	0.05906	0.02748	0.01269	0.00721	0.02174	0.03500	0.06186	0.04031	0.05245
D (Pk - Bkg)	1.96344	0.00820	0.03492	0.06871	0.23054	0.03643	0.00934	0.00996	0.38710	0.09055	0.15522	0.01986	0.00834	0.02985	0.03277
Bkg	0.02273	0.00053	0.00082	0.01408	0.02429	0.00523	0.05914	0.02761	0.01271	0.00785	0.02225	0.03517	0.06146	0.04106	0.05325
E (Pk - Bkg)	1.93679	0.00813	0.03569	0.06128	0.22402	0.03677	0.00608	0.00945	0.37796	0.08830	0.14736	0.01915	0.00582	0.03085	0.03319
Bkg	0.02210	0.00059	0.00081	0.01483	0.02642	0.00548	0.05776	0.02652	0.01267	0.00753	0.02242	0.03311	0.05968	0.04046	0.04952
A (Pk - Bkg)	2.49417	0.00882	0.03897	0.07586	0.24098	0.03774	0.00807	0.01029	0.41180	0.09751	0.16417	0.01863	0.00855	0.03734	0.03525
Bkg	0.02642	0.00048	0.00070	0.01422	0.02517	0.00498	0.05942	0.02706	0.01197	0.00764	0.02159	0.03561	0.06073	0.03918	0.05153
B (Pk - Bkg)	2.44576	0.00874	0.03855	0.06429	0.23977	0.03823	0.00957	0.01155	0.40930	0.09686	0.16391	0.01999	0.00811	0.03251	0.03615
Bkg	0.02420	0.00063	0.00086	0.01373	0.02461	0.00491	0.05934	0.02653	0.01251	0.00713	0.02290	0.03445	0.06269	0.03970	0.05263
C (Pk - Bkg)	1.72274	0.01048	0.03483	0.08274	0.22697	0.03650	0.00676	0.01147	0.38650	0.09110	0.15255	0.01818	0.00775	0.03103	0.03335
Bkg	0.02030	0.00055	0.00088	0.01443	0.02576	0.00535	0.05967	0.02641	0.01274	0.00751	0.02295	0.03635	0.06196	0.03944	0.05231
D (Pk - Bkg)	1.96710	0.00806	0.03389	0.06899	0.23140	0.03733	0.00797	0.01085	0.38766	0.09174	0.15468	0.01848	0.00856	0.03295	0.03364
Bkg	0.02152	0.00055	0.00094	0.01444	0.02472	0.00502	0.06037	0.02694	0.01310	0.00744	0.02180	0.03554	0.06078	0.03935	0.05157
E (Pk - Bkg)	1.94566	0.00811	0.03549	0.06276	0.22767	0.03601	0.00735	0.01109	0.37674	0.08929	0.14721	0.01850	0.00623	0.03255	0.03243
Bkg	0.02285	0.00054	0.00080	0.01410	0.02460	0.00522	0.05694	0.02624	0.01262	0.00735	0.02188	0.03422	0.05905	0.03883	0.04974

Rigaku Mini ZSXII AN-107 Simulant Limits of Detection (15 measurements)

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
Blank Average	0.02309	0.00057	0.00086	0.01400	0.02520	0.00507	0.05919	0.02697	0.01267	0.00746	0.02226	0.03510	0.06132	0.03976	0.05151
Blank Stdev	0.00226	0.00007	0.00009	0.00036	0.00062	0.00021	0.00110	0.00063	0.00039	0.00022	0.00059	0.00086	0.00130	0.00075	0.00117
Sample Average	2.06274	0.00888	0.03617	0.07077	0.23241	0.03720	0.00785	0.01094	0.39256	0.09288	0.15574	0.01909	0.00791	0.03245	0.03415
Simulant Concentration (μ g/mL)	183000	215	379	1830	1900	157	38	28	1650	550	543	48	47	246	400
IUPAC LOD in μ g/mL (3 σ)	602	5	3	28	15	3	16	5	5	4	6	6	23	17	41
XRF LOD in μ g/mL (3 σ)	128	6	3	29	12	3	11	4	4	5	5	4	14	14	25

Table 47. AN-107 Simulant Filter Paper (200- μ L Sample) Limits of Detection in Vacuum

Envelope C (AN-107 simulant) Filter Paper Limits of Detection

Voltage: 40-kV
Current: 1.2-mA
Atmosphere: Vacuum
Instrument Film: Ultralene - 4-mm (film was not replaced)
Cell: None
Sample Filter: Cellulose - Bruker
Cover film: None
Analysis Time: 200-sec on peak; 100-sec (two points) or 200-sec (one point) on each background point
Volume: 200- μ L of (2.5-mL H₂O/2.5-mL HNO₃/5mL AN-107 solution)
3 runs in a row

Sample	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
A (Pk - Bkg)	2.96654	0.01196	0.06910	0.05189	0.27706	0.04183	0.01386	0.01765	0.58942	0.13806	0.24905	0.03017	0.01575	0.02440	0.06533
Bkg	0.03196	0.00073	0.00092	0.01400	0.02393	0.00532	0.08031	0.03304	0.01352	0.00804	0.02676	0.04287	0.08346	0.03972	0.06692
B (Pk - Bkg)	2.59244	0.01090	0.06161	0.05388	0.26931	0.03900	0.01517	0.01520	0.52738	0.12254	0.22242	0.02740	0.01552	0.02447	0.05198
Bkg	0.02924	0.00058	0.00076	0.01214	0.02553	0.00569	0.07313	0.03101	0.01389	0.00815	0.02593	0.04124	0.07699	0.03729	0.06406
C (Pk - Bkg)	2.53802	0.01028	0.06262	0.05158	0.26621	0.03904	0.01242	0.01590	0.51645	0.12097	0.21343	0.02397	0.01434	0.02385	0.05070
Bkg	0.02893	0.00070	0.00091	0.01279	0.02620	0.00560	0.07206	0.03054	0.01381	0.00804	0.02615	0.04116	0.07538	0.03986	0.06168
D (Pk - Bkg)	2.80266	0.01123	0.06714	0.05312	0.27599	0.04021	0.01425	0.01608	0.54732	0.12943	0.22610	0.02672	0.01498	0.02586	0.05474
Bkg	0.03074	0.00060	0.00083	0.01256	0.02723	0.00574	0.07509	0.03171	0.01414	0.00757	0.02666	0.04204	0.07887	0.03880	0.06521
E (Pk - Bkg)	2.68620	0.01026	0.06199	0.05253	0.26821	0.03855	0.01162	0.01601	0.52425	0.12316	0.21771	0.02523	0.01352	0.02323	0.05568
Bkg	0.02984	0.00056	0.00087	0.01393	0.02655	0.00567	0.07724	0.03164	0.01410	0.00809	0.02705	0.04178	0.08041	0.03731	0.06436
A (Pk - Bkg)	2.94330	0.01184	0.06994	0.05129	0.28092	0.04169	0.01388	0.01797	0.58689	0.13736	0.25009	0.02935	0.01521	0.02524	0.06396
Bkg	0.03217	0.00076	0.00092	0.01405	0.02461	0.00565	0.07909	0.03218	0.01369	0.00856	0.02666	0.04415	0.08387	0.03959	0.06796
B (Pk - Bkg)	2.67466	0.01110	0.06148	0.05348	0.27074	0.03861	0.01142	0.01492	0.52548	0.12199	0.21960	0.02524	0.01415	0.02252	0.05272
Bkg	0.02957	0.00058	0.00104	0.01272	0.02541	0.00566	0.07651	0.03197	0.01369	0.00790	0.02622	0.04300	0.08016	0.03806	0.06544
C (Pk - Bkg)	2.54776	0.01060	0.06308	0.05339	0.26609	0.03899	0.01184	0.01474	0.51938	0.12112	0.21189	0.02448	0.01351	0.02339	0.05119
Bkg	0.02845	0.00049	0.00059	0.01236	0.02719	0.00548	0.07264	0.03132	0.01430	0.00798	0.02598	0.04184	0.07653	0.04006	0.06172
D (Pk - Bkg)	2.80851	0.01149	0.06667	0.05392	0.27407	0.04170	0.01337	0.01583	0.55112	0.12784	0.22859	0.02656	0.01650	0.02693	0.05673
Bkg	0.03110	0.00065	0.00082	0.01206	0.02639	0.00505	0.07527	0.03132	0.01339	0.00789	0.02571	0.04250	0.07940	0.03793	0.06496
E (Pk - Bkg)	2.72840	0.01019	0.06218	0.05311	0.26480	0.03922	0.01190	0.01685	0.52424	0.12142	0.22053	0.02541	0.01462	0.02495	0.05430
Bkg	0.02973	0.00064	0.00098	0.01287	0.02672	0.00537	0.07765	0.03069	0.01471	0.00797	0.02654	0.04221	0.08129	0.03677	0.06580
A (Pk - Bkg)	2.99471	0.01192	0.07077	0.05163	0.27702	0.04275	0.01210	0.01774	0.59169	0.13719	0.25189	0.02748	0.01453	0.02392	0.06653
Bkg	0.03203	0.00054	0.00094	0.01398	0.02477	0.00530	0.08028	0.03254	0.01410	0.00868	0.02689	0.04416	0.08365	0.04048	0.06691
B (Pk - Bkg)	2.66794	0.01095	0.06141	0.05319	0.27014	0.04009	0.01114	0.01590	0.52597	0.12338	0.22043	0.02484	0.01464	0.02297	0.05525
Bkg	0.02961	0.00058	0.00091	0.01282	0.02584	0.00575	0.07609	0.03158	0.01422	0.00765	0.02570	0.04265	0.07847	0.03764	0.06380
C (Pk - Bkg)	2.56350	0.01014	0.06360	0.05195	0.27122	0.03942	0.01176	0.01423	0.52483	0.12030	0.21556	0.02337	0.01471	0.02161	0.04913
Bkg	0.02902	0.00074	0.00095	0.01264	0.02637	0.00544	0.07319	0.03244	0.01317	0.00880	0.02533	0.04157	0.07575	0.04160	0.06378
D (Pk - Bkg)	2.79477	0.01135	0.06599	0.05233	0.27640	0.04126	0.01228	0.01570	0.55289	0.12942	0.22643	0.02592	0.01644	0.02572	0.05543
Bkg	0.03052	0.00060	0.00093	0.01310	0.02646	0.00536	0.07620	0.03239	0.01441	0.00745	0.02679	0.04242	0.07834	0.03893	0.06563
E (Pk - Bkg)	2.73103	0.00991	0.06334	0.05324	0.26516	0.03868	0.01259	0.01643	0.52532	0.12343	0.21751	0.02456	0.01451	0.02354	0.05297
Bkg	0.03134	0.00048	0.00088	0.01373	0.02710	0.00564	0.07893	0.03108	0.01350	0.00803	0.02693	0.04266	0.08080	0.03760	0.06646

Rigaku Mini ZSXII AN-107 Simulant Limits of Detection (15 measurements)

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	Mo kcps	Cu kcps	Fe kcps	Mn kcps	Ni kcps	Zn kcps	Zr kcps	Ca kcps	Pb kcps
Blank Average	0.03028	0.00062	0.00088	0.01305	0.02602	0.00551	0.07625	0.03170	0.01391	0.00805	0.02635	0.04242	0.07956	0.03878	0.06498
Blank Stdev	0.00122	0.00009	0.00011	0.00071	0.00099	0.00020	0.00271	0.00073	0.00042	0.00038	0.00053	0.00090	0.00277	0.00140	0.00180
Sample Average	2.73603	0.01094	0.06473	0.05270	0.27156	0.04007	0.01264	0.01608	0.54218	0.12651	0.22608	0.02605	0.01486	0.02417	0.05578
Simulant Concentration (μ g/mL)	183000	215	379	1830	1900	157	38	28	1650	550	543	48	47	246	400
IUPAC LOD in μ g/mL (3σ)	245	5	2	73	21	2	24	4	4	5	4	5	26	43	39
XRF LOD in μ g/mL (3σ)	110	5	2	38	11	3	8	3	3	4	4	4	8	19	17

7.8 Appendix H: Precision

Table 48. Aluminum Block Precision in One Position on Autosampler.

Aluminum Block Precision

Ten consecutive runs with sample in the same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: Vacuum
Instrument Film: None
Cell: None
Analysis Time: 300-sec on peak

Intensities

Al	
kcps	
170.114	
170.159	
170.146	
170.168	
170.082	
170.202	
170.206	
170.096	
170.094	
170.126	
Average	170.139
Stdev	0.044
%RSD (2 hr)	0.03

Table 49. Aluminum Block Precision in Ten Positions on Autosampler.

Aluminum Block Precision

Ten consecutive runs with sample in the ten positions on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: Vacuum
Instrument Film: None
Cell: None
Analysis Time: 300-sec on peak

Intensities

Al	
kcps	
	169.235
	169.239
	169.270
	169.289
	169.207
	169.189
	169.299
	169.396
	169.274
	169.200
Average	169.260
Stdev	0.061
%RSD (8 hr)	0.04

Table 50. NIST SRM 1411 Borosilicate Glass Precision

NIST SRM 1411 Soft Borosilicate Glass Precision

Twenty consecutive runs with sample in the same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: Vacuum
Instrument Film: None
Cell: None
Analysis Time: 200-sec on peak; 100-sec on background

Background Subtracted Intensities

	SiO₂	Na₂O	Al₂O₃	K₂O	CaO	Fe₂O₃
	kcps	kcps	kcps	kcps	kcps	kcps
17.42472	2.13510	2.48761	1.92094	1.81264	0.07977	
17.41336	2.14354	2.48557	1.92281	1.82128	0.07904	
17.42076	2.15084	2.48042	1.92276	1.81632	0.07740	
17.40673	2.14921	2.48428	1.92721	1.81611	0.07893	
17.36943	2.15045	2.47788	1.91874	1.81531	0.07808	
17.41793	2.16161	2.47852	1.92449	1.81445	0.07904	
17.41085	2.15280	2.47248	1.91967	1.81684	0.07762	
17.41960	2.15739	2.48169	1.92008	1.81569	0.07798	
17.41039	2.16141	2.48238	1.92093	1.82021	0.07797	
17.41029	2.14929	2.48083	1.92207	1.81565	0.07956	
17.42309	2.15503	2.48014	1.92228	1.81315	0.07774	
17.42786	2.15272	2.48486	1.92375	1.81826	0.07811	
17.40956	2.16018	2.47981	1.92092	1.81704	0.07828	
17.41250	2.15426	2.48471	1.92395	1.81084	0.07912	
17.38604	2.14917	2.47861	1.92146	1.81035	0.07844	
17.39251	2.15590	2.48260	1.91807	1.81017	0.07917	
17.41143	2.15227	2.48227	1.92197	1.81308	0.07870	
17.37225	2.15694	2.48301	1.91859	1.81367	0.07886	
17.39780	2.14893	2.48043	1.92526	1.81486	0.07915	
17.40750	2.15843	2.47873	1.91722	1.81453	0.07874	
Average	17.40723	2.15277	2.48134	1.92166	1.81502	0.07859
Stdev	0.01616015	0.00630317	0.00335956	0.00254655	0.00295566	0.00066241
%RSD (10 hr)	0.09	0.29	0.14	0.13	0.16	0.84

Table 51. AN-105 Simulant Solution Precision – Three Runs of Ten Unfiltered Samples in Autosampler.

Envelope A (AN-105 simulant) Solution Precision

Three consecutive runs with samples in same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was not replaced)
Cell: 31 mm double open end
Sample film: Ultralene - 4- μ m (same film for each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **unfiltered** supernate

Background Subtracted Intensities						
	Na	Al	P	Cl	K	Cr
	kcps	kcps	kcps	kcps	kcps	kcps
Water Blank	0.00207	0.00115	0.00020	0.00575	0.06540	0.00687
A	0.21402	0.69834	0.00754	1.35601	0.72614	0.20220
B	0.22030	0.70478	0.00756	1.35823	0.72494	0.20549
C	0.22504	0.70910	0.00825	1.35821	0.72675	0.20267
D	0.22473	0.71222	0.00779	1.36375	0.72623	0.20357
E	0.22220	0.70989	0.00756	1.35604	0.72598	0.20419
F	0.21700	0.70519	0.00736	1.34908	0.72342	0.20361
G	0.21541	0.70477	0.00781	1.35341	0.72353	0.20196
H	0.22070	0.70717	0.00807	1.34993	0.72494	0.20109
I	0.21782	0.71222	0.00760	1.35648	0.72684	0.20672
J	0.21042	0.70131	0.00773	1.35219	0.72299	0.20202
A	0.20553	0.69577	0.00766	1.34620	0.72385	0.20296
B	0.20075	0.69388	0.00738	1.34381	0.72518	0.20391
C	0.23418	0.69819	0.00728	1.35050	0.72692	0.20319
D	0.23340	0.71364	0.00725	1.35729	0.70734	0.20347
E	0.22776	0.69974	0.00701	1.34614	0.68725	0.20113
F	0.22246	0.68794	0.00781	1.34501	0.66192	0.20136
G	0.22007	0.68477	0.00755	1.34718	0.65121	0.19978
H	0.22480	0.68866	0.00773	1.34423	0.64023	0.19971
I	0.21899	0.67905	0.00772	1.33961	0.62786	0.20051
J	0.21384	0.67085	0.00771	1.34141	0.61595	0.19798
A	0.21582	0.66828	0.00742	1.33790	0.60098	0.19202
B	0.21039	0.66379	0.00742	1.34099	0.59865	0.19615
C	0.21076	0.66578	0.00757	1.34087	0.59738	0.19651
D	0.21730	0.67429	0.00765	1.35143	0.59514	0.19746
E	0.21350	0.66852	0.00766	1.35399	0.59427	0.19554
F	0.21226	0.66939	0.00703	1.35505	0.59422	0.19663
G	0.21559	0.67453	0.00721	1.35587	0.59320	0.19683
H	0.22122	0.68311	0.00741	1.36541	0.59652	0.19606
I	0.21580	0.67674	0.00754	1.36046	0.59195	0.19906
J	0.21628	0.66949	0.00717	1.35949	0.58568	0.19657
Average	0.21794	0.68971	0.00755	1.35121	0.66558	0.20035

Precision Analysis						
	Na	Al	P	Cl	K	Cr
	kcps	kcps	kcps	kcps	kcps	kcps
Var (Sampling)	0.000012	0.000006	0	0	0.000059	5.63E-07
Var (Replicates)	0.000004	0.000304	1.91E-08	0.000017	0.004288	0.000013
Var (Residual)	0.000040	0.000059	7.43E-08	0.000051	0.000555	0.000003
Var (Total)	0.000056	0.000369	9.344E-08	0.000068	0.004902	1.6563E-05
%RSD (Sampling)	1.6	0.4	0	0	1.2	0.4
%RSD (Replicates)	0.9	2.5	1.8	0.3	9.8	1.8
%RSD (Residual)	2.9	1.1	3.6	0.5	3.5	0.9
%RSD (Total)	3.4	2.8	4.0	0.6	10.5	2.0
Std Error of Mean	0.0018	0.0102	0.0001	0.0026	0.0381	0.0021
% Std Error of Mean	0.8	1.5	1.2	0.2	5.7	1.0

Table 52. AN-105 Simulant Solution Precision – Three Runs of Ten Randomized Unfiltered Samples in Autosampler.

Envelope A (AN-105 simulant) Solution Precision

The order of the samples on the autosampler was randomized between runs.

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was replaced before each run)
Cell: 31-mm double open end
Sample film: Ultralene - 4- μ m (same film for each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **unfiltered** supernate

Background Subtracted Intensities

	Pos	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Water Blank	1	0.00207	0.00091	0.00001	0.00681	0.06429	0.00631
A	2	0.22319	0.77032	0.00733	1.33043	0.72150	0.20127
B	3	0.22492	0.79181	0.00748	1.31780	0.71619	0.20040
C	4	0.22256	0.81986	0.00720	1.31064	0.71344	0.20274
D	5	0.22708	0.84330	0.00760	1.30920	0.71027	0.20124
E	6	0.21555	0.84495	0.00694	1.28574	0.70724	0.20228
F	7	0.22333	0.91468	0.00675	1.28029	0.70146	0.20500
G	8	0.21558	0.94469	0.00735	1.26078	0.69887	0.20016
H	9	0.21894	0.94469	0.00679	1.25306	0.69798	0.20186
I	10	0.21488	0.97118	0.00637	1.24055	0.69309	0.19428
J	11	0.21561	0.98921	0.00705	1.24477	0.69765	0.19935
A	9	0.22362	1.09938	0.00661	1.19477	0.67791	0.19749
B	7	0.22624	1.08340	0.00695	1.20227	0.68043	0.19788
C	10	0.21837	1.08160	0.00637	1.19532	0.67985	0.19657
D	11	0.21913	1.09402	0.00617	1.19127	0.67896	0.19707
E	4	0.22788	1.01702	0.00628	1.23051	0.69433	0.19971
F	2	0.23684	1.02349	0.00666	1.23483	0.69125	0.19984
G	1	0.21911	0.97397	0.00672	1.23233	0.68883	0.19804
H	8	0.22317	1.08279	0.00645	1.20207	0.68511	0.19657
I	6	0.22387	1.08374	0.00676	1.19006	0.68047	0.19628
J	3	0.23211	1.03659	0.00659	1.23597	0.69389	0.19915
A	6	0.22642	1.16699	0.00635	1.16369	0.67555	0.19756
B	11	0.21669	1.16205	0.00651	1.14409	0.66421	0.19545
C	2	0.22076	1.13396	0.00617	1.17497	0.67812	0.19770
D	8	0.22203	1.16589	0.00630	1.16530	0.67097	0.19708
E	3	0.22415	1.14878	0.00599	1.16778	0.67491	0.20143
F	9	0.22125	1.18546	0.00583	1.14741	0.66960	0.20056
G	4	0.22499	1.16254	0.00616	1.17017	0.67189	0.19831
H	1	0.20677	1.08433	0.00598	1.15737	0.66873	0.19877
I	5	0.22483	1.17921	0.00635	1.15294	0.66534	0.19637
J	7	0.22386	1.19670	0.00580	1.16155	0.66875	0.19640
Average		0.2221	1.0332	0.0066	1.2183	0.6872	0.1989

Precision Analysis

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Var (Sampling)	0	0	1.32E-08	0	0	2.00E-06
Var (Replicates)	0.000003	0.019022	2.16E-07	0.003751	0.000304	0.000003
Var (Residual)	0.000032	0.003472	7.27E-08	0.000591	0.000054	0.000002
Var (Total)	0.000035	0.022494	3.0158E-07	0.004342	0.000358	0.000007
%RSD (Sampling)	0.0	0.0	2	0	0.0	0.7
%RSD (Replicates)	0.8	13.4	7.0	5.0	2.5	0.9
%RSD (Residual)	2.6	5.7	4.1	2.0	1.1	0.7
%RSD (Total)	2.7	14.5	8.3	5.4	2.8	1.3
Std Error of Mean	0.0015	0.0800	0.0003	0.0355	0.0101	0.0011
% Std Error of Mean	0.7	7.8	4.2	2.9	1.5	0.6

Table 53. AN-105 Simulant Solution Precision – Three Runs of Ten Filtered Samples in Autosampler.

Envelope A (AN-105 simulant) Solution Precision

Three consecutive runs with samples in same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was not replaced)
Cell: 31 mm double open end
Sample film: Ultralene - 4- μ m (same film for each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **filtered** supernate

Background Subtracted Intensities						
	Na	Al	P	Cl	K	Cr
	kcps	kcps	kcps	kcps	kcps	kcps
Water Blank	0.00235	0.00153	0.00036	0.00597	0.00670	0.00705
A	0.22831	0.71384	0.00773	1.34548	0.72979	0.22710
B	0.22478	0.71537	0.00791	1.34249	0.71728	0.22593
C	0.23014	0.72048	0.00775	1.34521	0.72907	0.22567
D	0.22444	0.71326	0.00787	1.34336	0.72817	0.22347
E	0.22658	0.70966	0.00773	1.33860	0.72807	0.22598
F	0.22809	0.71791	0.00795	1.34695	0.73099	0.22167
G	0.21966	0.70787	0.00802	1.33766	0.72479	0.22414
H	0.22315	0.71309	0.00800	1.34007	0.72684	0.22544
I	0.21513	0.70630	0.00826	1.33663	0.72960	0.22697
J	0.22335	0.71005	0.00807	1.33620	0.72527	0.22454
A	0.22122	0.71206	0.00798	1.33818	0.72903	0.22489
B	0.21555	0.70264	0.00812	1.33631	0.72854	0.22417
C	0.22097	0.70487	0.00789	1.33758	0.72695	0.22608
D	0.21327	0.69891	0.00783	1.33454	0.72699	0.22370
E	0.21228	0.69621	0.00730	1.33640	0.72635	0.22585
F	0.21727	0.70702	0.00781	1.33921	0.72888	0.22306
G	0.21062	0.69190	0.00743	1.33060	0.72653	0.22337
H	0.21147	0.69883	0.00775	1.33554	0.72427	0.22372
I	0.21047	0.69608	0.00760	1.33103	0.72071	0.22936
J	0.21237	0.69644	0.00740	1.33786	0.71417	0.22670
A	0.20232	0.68923	0.00795	1.33452	0.70614	0.22634
B	0.19775	0.67816	0.00807	1.33456	0.69664	0.22446
C	0.19737	0.67925	0.00816	1.33042	0.68878	0.22498
D	0.19759	0.66979	0.00794	1.33621	0.68216	0.22330
E	0.19448	0.66758	0.00804	1.33345	0.67470	0.22342
F	0.19462	0.66729	0.00757	1.33320	0.67512	0.22235
G	0.18969	0.65849	0.00817	1.33125	0.66352	0.22245
H	0.19991	0.67379	0.00774	1.32679	0.65733	0.22325
I	0.20105	0.66725	0.00777	1.33188	0.65306	0.22151
J	0.20243	0.66914	0.00769	1.33343	0.65109	0.22353
Average	0.2122	0.6951	0.0079	1.3365	0.7090	0.2246

Precision Analysis						
	Na	Al	P	Cl	K	Cr
	kcps	kcps	kcps	kcps	kcps	kcps
Var (Sampling)	0.000006	0.000028	0	0.000004	0.000019	8.36E-07
Var (Replicates)	0.000180	0.000436	8.90E-09	0.000019	0.000866	0.000000581
Var (Residual)	0.000012	0.000015	5.68E-08	0.000007	0.000111	0.000002
Var (Total)	0.000198	0.000479	6.57E-08	0.000030	0.000996	3.4166E-06
%RSD (Sampling)	1.2	0.8	0	0.15	0.6	0.4
%RSD (Replicates)	6.3	3.0	1.2	0.3	4.2	0.3
%RSD (Residual)	1.6	0.6	3.0	0.2	1.5	0.6
%RSD (Total)	6.6	3.1	3.3	0.4	4.5	0.8
Std Error of Mean	0.0078	0.0122	0.0001	0.0026	0.0172	0.0006
% Std Error of Mean	3.7	1.8	0.8	0.2	2.4	0.3

Table 54. AZ-101 Simulant Solution Precision – Three Runs of Unfiltered Samples in Autosampler.

Envelope B (AZ-101 simulant) Solution Precision

Three consecutive runs with samples in same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was not replaced)
Cell: 31 mm double open end
Sample film Ultralene - 4- μ m (same film for each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **unfiltered** supernate

Background Subtracted Intensities						
	Na	Al	P	Cl	K	Cr
	kcps	kcps	kcps	kcps	kcps	kcps
Water Blank	0.00190	0.00106	0.00018	0.00571	0.06553	0.00726
A	0.10853	0.27925	0.02689	0.07143	0.64275	0.15747
B	0.11369	0.28726	0.02722	0.07112	0.64454	0.15587
C	0.10919	0.29236	0.02677	0.07217	0.64653	0.15870
D	0.11033	0.29958	0.02754	0.07029	0.64749	0.15850
E	0.11103	0.30056	0.02667	0.07172	0.64240	0.15939
F	0.11132	0.29846	0.02690	0.07232	0.64176	0.15658
G	0.10697	0.29329	0.02655	0.07144	0.64175	0.15789
H	0.10505	0.28913	0.02625	0.07345	0.64238	0.15841
I	0.11002	0.29849	0.02715	0.07221	0.64365	0.15757
J	0.10759	0.29246	0.02738	0.07441	0.64419	0.15702
A	0.09600	0.27486	0.02654	0.07410	0.61990	0.16012
B	0.09529	0.27451	0.02702	0.07269	0.61007	0.16002
C	0.08709	0.27230	0.02708	0.07339	0.59819	0.15862
D	0.08534	0.27393	0.02645	0.07327	0.58769	0.15760
E	0.08744	0.27371	0.02611	0.07328	0.57833	0.15771
F	0.09056	0.27092	0.02629	0.07346	0.57430	0.15890
G	0.08669	0.26911	0.02582	0.07449	0.56709	0.16029
H	0.08758	0.26210	0.02705	0.07391	0.56576	0.15742
I	0.08834	0.27218	0.02630	0.07509	0.56023	0.15679
J	0.08669	0.26620	0.02697	0.07450	0.56134	0.15966
A	0.08947	0.26423	0.02856	0.07513	0.56258	0.16231
B	0.09294	0.26577	0.02784	0.07768	0.56706	0.16242
C	0.08797	0.26928	0.02753	0.07765	0.56926	0.16616
D	0.09021	0.27215	0.02841	0.07764	0.57004	0.16489
E	0.09181	0.27657	0.02849	0.07819	0.57045	0.16575
F	0.09535	0.27553	0.02798	0.07903	0.57233	0.16636
G	0.09186	0.27280	0.02844	0.07927	0.57312	0.16604
H	0.09307	0.27047	0.02922	0.07834	0.57824	0.16642
I	0.09788	0.27938	0.02910	0.07952	0.57817	0.16736
J	0.09614	0.27599	0.02857	0.07950	0.58053	0.16955
Average	0.0970	0.2788	0.0273	0.0747	0.5994	0.1607

Precision Analysis						
	Na	Al	P	Cl	K	Cr
	kcps	kcps	kcps	kcps	kcps	kcps
Var (Sampling)	0.000001	0.000008	0	4.82E-07	0	0
Var (Replicates)	0.000116	0.000152	9.37E-07	0.000010	0.001481	0.000019
Var (Residual)	0.000009	0.00002	2.31E-07	7.35E-07	0.000191	0.000003
Var (Total)	0.000126	0.000180	1.168E-06	1.1217E-05	0.001672	0.000022
%RSD (Sampling)	1.0	1.0	0	1	0.0	0.0
%RSD (Replicates)	11.1	4.4	3.5	4.2	6.4	2.7
%RSD (Residual)	3.1	1.6	1.8	1.2	2.3	1.1
%RSD (Total)	11.6	4.8	4.0	4.5	6.8	2.9
Std Error of Mean	0.0062	0.0072	0.0006	0.0018	0.0223	0.0025
% Std Error of Mean	6.4	2.6	2.1	2.5	3.7	1.6

Table 55. AZ-101 Simulant Solution Precision – Three Runs of Ten Randomized Unfiltered Samples in Autosampler.

Envelope B (AZ-101 simulant) Solution Precision

The order of the samples on the autosampler was randomized between runs.

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was replaced before each run)
Cell: 31-mm double open end
Sample film: Ultralene - 4- μ m (same film for each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **unfiltered** supernate

Background Subtracted Intensities							
	Pos	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Water Blank	1	0.00224	0.00122	0.00026	0.00619	0.06580	0.00704
A	2	0.10385	1.20739	0.02338	0.05816	0.52351	0.14318
B	3	0.10695	1.16213	0.02287	0.05947	0.54191	0.14743
C	4	0.11143	1.18371	0.02325	0.06054	0.53474	0.14407
D	5	0.10834	1.19923	0.02296	0.06192	0.54479	0.14837
E	6	0.10579	1.22351	0.02325	0.06054	0.52213	0.14327
F	7	0.10369	1.16780	0.02327	0.06108	0.54367	0.14630
G	8	0.10441	1.12900	0.02315	0.06145	0.54472	0.14732
H	9	0.10582	1.12532	0.02307	0.06044	0.54750	0.14717
I	10	0.10125	1.08097	0.02316	0.06059	0.54311	0.15108
J	11	0.10371	1.11586	0.02316	0.05992	0.54016	0.14843
A	9	0.10668	1.08173	0.02270	0.05937	0.52588	0.14448
B	7	0.10516	1.07328	0.02338	0.05943	0.53505	0.14610
C	10	0.10606	1.03692	0.02345	0.05972	0.53533	0.14542
D	11	0.10698	1.07463	0.02318	0.06166	0.54281	0.14787
E	4	0.10859	1.09708	0.02342	0.05980	0.52733	0.14421
F	2	0.11026	1.07737	0.02346	0.06027	0.54689	0.14989
G	1	0.10849	1.04956	0.02359	0.06168	0.54724	0.14876
H	8	0.10716	1.00798	0.02352	0.06237	0.54951	0.14891
I	6	0.10628	1.02224	0.02449	0.06208	0.54559	0.15337
J	3	0.11129	1.03864	0.02398	0.06077	0.54263	0.14789
A	6	0.11436	0.97643	0.02482	0.06339	0.56149	0.15194
B	11	0.09616	0.95913	0.02534	0.06369	0.52042	0.15095
C	2	0.12071	1.02456	0.02497	0.06443	0.55513	0.15271
D	8	0.11530	1.06489	0.02475	0.06480	0.56764	0.15352
E	3	0.11229	1.06645	0.02457	0.06353	0.54246	0.14679
F	9	0.10550	0.93581	0.02537	0.06401	0.56502	0.15351
G	4	0.11364	0.99608	0.02524	0.06489	0.56964	0.15586
H	1	0.11958	0.96743	0.02636	0.06349	0.56332	0.15248
I	5	0.11064	0.95934	0.02540	0.06531	0.56251	0.15604
J	7	0.11138	0.94280	0.02565	0.06311	0.55728	0.15115
Average		0.1120	0.9893	0.0252	0.0641	0.5565	0.1525

Precision Analysis						
	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Var (Sampling)	0.000001	0.000997	2.34E-08	5.40E-07	0.000057	0.000005
Var (Replicates)	0.000009	0.007282	1.00E-06	0.000004	0.000093	0.00001
Var (Residual)	0.000019	0.000738	1.47E-07	4.61E-07	0.000067	0.000002
Var (Total)	0.000029	0.009017	1.1706E-06	5.0005E-06	0.000217	0.000017
%RSD (Sampling)	0.9	3.0	1	1	1.4	1.5
%RSD (Replicates)	2.8	8.0	4.2	3.2	1.8	2.1
%RSD (Residual)	4.0	2.5	1.6	1.1	1.5	1.0
%RSD (Total)	4.8	9.6	4.3	3.5	2.6	2.7
Std Error of Mean	0.0019	0.0505	0.0006	0.0012	0.0063	0.0020
% Std Error of Mean	1.8	4.7	2.4	1.9	1.2	1.3

Table 56. AZ-101 Simulant Solution Precision – Three Runs of Ten Filtered Samples in Autosampler.

Envelope B (AZ-101 simulant) Solution Precision

Three consecutive runs with samples in same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4-µm (film was not replaced)
Cell: 31 mm double open end
Sample film: Ultralene - 4-µm (same film for each run)
Cover film: Micro-porous Teflon (0.2-µm pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **filtered** supernate

Background Subtracted Intensities - Run #1

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	S kcps
Water Blank	0.00248	0.00108	0.00017	0.00626	0.06576	0.00910	0.00124
A	0.11451	0.12189	0.02801	0.07441	0.66292	0.17741	0.73194
B	0.12022	0.12407	0.02780	0.07238	0.66211	0.17835	0.74517
C	0.12586	0.12579	0.02790	0.07339	0.67038	0.17779	0.74906
D	0.12412	0.12910	0.02876	0.07487	0.66947	0.17911	0.74405
E	0.12242	0.12727	0.02776	0.07707	0.67261	0.17999	0.74905
F	0.11976	0.12514	0.02794	0.07489	0.66693	0.17630	0.74201
G	0.11868	0.12501	0.02806	0.07615	0.66726	0.17726	0.74519
H	0.12090	0.12525	0.02806	0.07592	0.66356	0.17708	0.74755
I	0.11845	0.12301	0.02832	0.08025	0.66765	0.17908	0.74070
J	0.12480	0.12146	0.02766	0.07449	0.66470	0.17852	0.73527
A	0.12104	0.12491	0.02838	0.07665	0.66541	0.18099	0.74956
B	0.11793	0.12433	0.02871	0.07555	0.65095	0.18000	0.75031
C	0.12003	0.12263	0.02882	0.07556	0.63644	0.17923	0.75136
D	0.11241	0.12355	0.02857	0.07701	0.62700	0.18014	0.75326
E	0.10712	0.11834	0.02823	0.07660	0.61623	0.18143	0.74870
F	0.10449	0.11576	0.02793	0.07706	0.60118	0.17837	0.74891
G	0.09751	0.11341	0.02710	0.07603	0.59847	0.17788	0.74286
H	0.09908	0.11339	0.02807	0.07587	0.59284	0.17841	0.74434
I	0.09330	0.11251	0.02754	0.07880	0.58620	0.17782	0.74040
J	0.09302	0.11229	0.02825	0.07499	0.58067	0.17893	0.74399
A	0.09127	0.11339	0.02986	0.08802	0.61378	0.18548	0.75845
B	0.09273	0.11432	0.02823	0.07639	0.58308	0.18220	0.75677
C	0.09416	0.11379	0.02866	0.07778	0.58426	0.18230	0.77095
D	0.09384	0.11791	0.02819	0.07785	0.58089	0.18476	0.77249
E	0.09278	0.11347	0.02826	0.07980	0.59873	0.18463	0.76229
F	0.08922	0.12945	0.02823	0.08000	0.58335	0.18471	0.77611
G	0.08907	0.11150	0.02846	0.07945	0.58477	0.18579	0.77734
H	0.09209	0.11379	0.02953	0.07954	0.58768	0.18722	0.78605
I	0.08822	0.11350	0.02881	0.07977	0.58453	0.18812	0.78454
J	0.09203	0.11537	0.02851	0.07989	0.58334	0.18373	0.78719
Average	0.1064	0.1195	0.0283	0.0772	0.6236	0.1808	0.7545

Precision Analysis

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps	S kcps
Var (Sampling)	0.000006	0.000001	0	0.000001	0.000043	0	0
Var (Replicates)	0.000213	0.000021	9.19E-08	0.000005	0.001555	0.000013	0.00026
Var (Residual)	0.000039	0.000018	2.48E-07	0.000004	0.000269	0.000002	0.000069
Var (Total)	0.000258	0.000040	3.4031E-07	0.000010	0.001867	0.000015	0.000329
%RSD (Sampling)	2.3	0.8	0	1.3	1.1	0.0	0.0
%RSD (Replicates)	13.7	3.8	1.1	2.9	6.3	2.0	2.1
%RSD (Residual)	5.9	3.6	1.8	2.6	2.6	0.8	1.1
%RSD (Total)	15.1	5.3	2.1	4.1	6.9	2.1	2.4
Std Error of Mean	0.0085	0.0027	0.0002	0.0013	0.0231	0.0021	0.0094
% Std Error of Mean	8.0	2.3	0.7	1.7	3.7	1.2	1.2

Table 57. AN-107 Simulant Solution Precision – Three Runs of Ten Unfiltered Samples in Autosampler.

Envelope C (AN-107 simulant) Solution Precision

Three consecutive runs with samples in same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was not replaced)
Cell: 31 mm double open end
Sample film: Ultralene - 4- μ m (same film for each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **unfiltered** supernate

Background Subtracted Intensities						
	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Water Blank	0.00165	0.00085	0.00000	0.00464	0.05577	0.00612
A	0.18046	0.19664	0.02618	0.28156	0.22841	0.07518
B	0.18721	0.22551	0.02798	0.28421	0.23163	0.07566
C	0.19128	0.23199	0.02742	0.28097	0.22882	0.07712
D	0.18961	0.23755	0.02848	0.28322	0.23244	0.07716
E	0.18804	0.25048	0.02914	0.28003	0.22902	0.07683
F	0.18719	0.25764	0.02948	0.28233	0.23077	0.07816
G	0.18778	0.26082	0.02943	0.28094	0.23060	0.07639
H	0.18541	0.26988	0.03043	0.27716	0.22696	0.07729
I	0.18628	0.28731	0.03057	0.27576	0.22863	0.07706
J	0.18080	0.27600	0.02964	0.27574	0.22437	0.07976
A	0.19668	0.26553	0.02973	0.27731	0.21664	0.08102
B	0.19223	0.26858	0.03018	0.27773	0.21416	0.07894
C	0.19012	0.25787	0.02956	0.27844	0.20735	0.07900
D	0.18945	0.25606	0.02942	0.27824	0.20573	0.07727
E	0.19514	0.26215	0.02926	0.27797	0.20143	0.07631
F	0.20430	0.26371	0.02935	0.27926	0.19654	0.07725
G	0.21009	0.26294	0.02859	0.27970	0.19649	0.07500
H	0.20453	0.26009	0.02847	0.27893	0.19609	0.07656
I	0.20919	0.26600	0.02906	0.27768	0.19492	0.07563
J	0.20328	0.25668	0.02970	0.27899	0.19177	0.07679
A	0.22043	0.24838	0.02978	0.28550	0.19179	0.07721
B	0.21170	0.25007	0.02889	0.28699	0.19231	0.07569
C	0.22013	0.24717	0.02931	0.28761	0.19157	0.07691
D	0.22101	0.23762	0.02880	0.29096	0.19307	0.07632
E	0.21684	0.24415	0.02933	0.28976	0.19232	0.07540
F	0.22906	0.24432	0.02841	0.28976	0.19185	0.07597
G	0.23467	0.24272	0.02922	0.29275	0.19316	0.07347
H	0.23391	0.23728	0.02874	0.29294	0.19392	0.07676
I	0.24440	0.24657	0.02931	0.29226	0.19240	0.07465
J	0.25408	0.23129	0.02844	0.29641	0.19502	0.07563
Average	0.2048	0.2514	0.0291	0.2830	0.2080	0.0767

Precision Analysis						
	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Var (Sampling)	0.000016	0	0	0	0.000000605	1.55E-07
Var (Replicates)	0.000460	0.000065	0.00E+00	0.000042	0.000355	0.00000506
Var (Residual)	0.000067	0.000289	1.00E-06	0.000009	0.000026	0.000002
Var (Total)	0.000543	0.000354	1.00E-06	0.000051	0.0003816	2.661E-06
%RSD (Sampling)	2.0	0.0	0	0	0.4	0.5
%RSD (Replicates)	10.5	3.2	0.0	2.3	9.1	0.9
%RSD (Residual)	4.0	6.8	3.4	1.1	2.5	1.8
%RSD (Total)	11.4	7.5	3.4	2.5	9.4	2.1
Std Error of Mean	0.0125	0.0053		0.0037	0.0109	0.0005
% Std Error of Mean	6.1	2.1		1.3	5.3	0.7

Table 58. AN-107 Simulant Solution Precision – Three Runs of Ten Randomized Unfiltered Samples in Autosampler.

Envelope C (AN-107 simulant) Solution Precision

The order of the samples on the autosampler was randomized between runs.

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was replaced before each run)
Cell: 31-mm double open end
Sample film: Ultralene - 4- μ m (same film for each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **unfiltered** supernate

Background Subtracted Intensities

	Pos	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Water Blank	1	0.00221	0.00148	0.00024	0.00464	0.06732	0.00693
A	2	0.18384	0.19048	0.02637	0.28443	0.22607	0.08033
B	3	0.19339	0.20842	0.02747	0.27986	0.22374	0.08206
C	4	0.19135	0.22135	0.02722	0.27921	0.22476	0.08029
D	5	0.19125	0.22286	0.02796	0.28067	0.22186	0.08016
E	6	0.18249	0.22881	0.02779	0.27384	0.22609	0.08059
F	7	0.19234	0.24982	0.02938	0.27504	0.22706	0.08405
G	8	0.18070	0.26743	0.02970	0.27043	0.22259	0.08344
H	9	0.18526	0.27250	0.02986	0.27262	0.22307	0.08131
I	10	0.17793	0.26800	0.02922	0.27011	0.22664	0.08261
J	11	0.18085	0.25793	0.02862	0.27426	0.22420	0.08364
A	9	0.18325	0.35825	0.03259	0.26214	0.22008	0.08918
B	7	0.19412	0.38142	0.03343	0.26302	0.22098	0.09008
C	10	0.18955	0.36609	0.03307	0.26486	0.22058	0.08628
D	11	0.19063	0.34702	0.03298	0.26712	0.22401	0.08539
E	4	0.19370	0.35664	0.03284	0.26766	0.22440	0.08519
F	2	0.19849	0.33964	0.03197	0.26789	0.22233	0.08562
G	1	0.19223	0.35493	0.03297	0.26716	0.22096	0.08934
H	8	0.18771	0.36635	0.03266	0.26440	0.22362	0.08572
I	6	0.19445	0.34734	0.03159	0.26909	0.22529	0.08489
J ¹	3	0.18489	0.07803	0.01946	0.31126	0.24823	0.03673
A	6	0.19890	0.34991	0.03286	0.26978	0.22481	0.08653
B	11	0.18166	0.32663	0.03184	0.26983	0.21590	0.08653
C	2	0.21734	0.37468	0.03431	0.27481	0.22729	0.08739
D	8	0.19875	0.32899	0.03195	0.27139	0.22587	0.08412
E	3	0.20519	0.34958	0.03167	0.27378	0.22629	0.08437
F	9	0.19794	0.33565	0.03169	0.26844	0.22587	0.08347
G	4	0.20429	0.38615	0.03428	0.26912	0.22181	0.09061
H	1	0.20680	0.35648	0.03291	0.27192	0.22844	0.08515
I	5	0.20013	0.35665	0.03264	0.27000	0.22342	0.08329
J ¹	7	0.19227	0.13994	0.02089	0.31472	0.24999	0.03919
Average		0.1927	0.3132	0.0311	0.2712	0.2239	0.0847

¹ The sample film leaked on original sample J after the first run.

Precision Analysis

	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Var (Sampling)	0	0.00004	0	0	0.000001	0.000001
Var (Replicates)	0.000050	0.004598	0.000006	0.000025	0.000000768	0.0000007
Var (Residual)	0.000055	0.000428	0.000001	0.000014	0.000006	0.000003
Var (Total)	0.000105	0.005066	0.000007	0.000039	7.7684E-06	0.000011
%RSD (Sampling)	0.0	2.0	0	0	0.5	1.2
%RSD (Replicates)	3.7	21.5	7.8	1.8	0.4	3.1
%RSD (Residual)	3.8	6.6	3.2	1.4	1.1	2.0
%RSD (Total)	5.3	22.7	8.5	2.3	1.2	3.9
Std Error of Mean	0.0042	0.0394	0.0015	0.0029	0.0007	0.0017
% Std Error of Mean	2.2	12.5	4.8	1.1	0.3	2.0

Table 59. AN-107 Simulant Solution Precision – Three Runs of Ten Filtered Samples in Autosampler.

Envelope C (AN-107 simulant) Solution Precision

Three consecutive runs with samples in same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: He (99.99%)
Instrument Film: Ultralene - 4- μ m (film was not replaced)
Cell: 31 mm double open end
Sample film Ultralene - 4- μ m (same film for each run)
Cover film: Micro-porous Teflon (0.2- μ m pores)
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 5-mL **filtered** supernate

Background Subtracted Intensities						
	Na	Al	P	Cl	K	Cr
	kcps	kcps	kcps	kcps	kcps	kcps
Water Blank	0.00180	0.00101	0.00011	0.00000	0.06701	0.00696
A	0.17996	0.00211	0.01613	0.31064	0.24541	0.03911
B	0.17848	0.00231	0.01540	0.31162	0.24717	0.04045
C	0.18647	0.00264	0.01640	0.31226	0.24653	0.03941
D	0.17350	0.00252	0.01622	0.30845	0.24249	0.03894
E	0.18656	0.00228	0.01642	0.31832	0.24584	0.03818
F	0.18378	0.00282	0.01625	0.31267	0.24742	0.03833
G	0.18193	0.00269	0.01683	0.31035	0.24726	0.03853
H	0.17846	0.00266	0.01661	0.31067	0.24592	0.03939
I	0.18180	0.00255	0.01598	0.31406	0.24922	0.03986
J	0.18354	0.00250	0.01595	0.31477	0.24469	0.03944
A	0.17475	0.00297	0.01619	0.31213	0.24634	0.03803
B	0.17234	0.00282	0.01611	0.31115	0.24344	0.03935
C	0.18112	0.00264	0.01663	0.31069	0.24835	0.03895
D	0.16709	0.00296	0.01615	0.30851	0.24539	0.03758
E	0.17534	0.00258	0.01623	0.31881	0.24799	0.03823
F	0.18048	0.00281	0.01664	0.31342	0.24461	0.03933
G	0.18651	0.00242	0.01576	0.31292	0.24259	0.03932
H	0.19444	0.00263	0.01626	0.31656	0.24000	0.03902
I	0.19900	0.00282	0.01606	0.31404	0.23615	0.03888
J	0.20527	0.00289	0.01559	0.31411	0.23324	0.04053
A	0.20205	0.00301	0.01600	0.31349	0.23039	0.03926
B	0.19551	0.00312	0.01627	0.31295	0.22610	0.03866
C	0.20039	0.00275	0.01623	0.31356	0.22526	0.03756
D	0.20500	0.00279	0.01622	0.31324	0.22241	0.03764
E	0.20547	0.00291	0.01624	0.32113	0.22450	0.03897
F	0.20299	0.00262	0.01651	0.31775	0.22611	0.03966
G	0.20496	0.00275	0.01685	0.32041	0.22217	0.03983
H	0.20823	0.00283	0.01616	0.32007	0.22321	0.03887
I	0.20759	0.00296	0.01685	0.32293	0.22053	0.03856
J	0.20942	0.00285	0.01599	0.32259	0.22016	0.04079
Average	0.1897	0.0027	0.0162	0.3145	0.2377	0.0390

Precision Analysis						
	Na	Al	P	Cl	K	Cr
	kcps	kcps	kcps	kcps	kcps	kcps
Var (Sampling)	0.000016	4.70E-08	1.57E-07	0.000008	0.000003	4.94E-07
Var (Replicates)	0	6.27E-40	2.57E-36	0	7.42E-34	0
Var (Residual)	6.84E-18	0	0	1.14E-16	0	6.71E-19
Var (Total)	1.6E-05	4.695E-08	1.565E-07	8.0E-06	0.000003	4.939E-07
%RSD (Sampling)	2.2	8.6	2	1	0.7	1.8
%RSD (Replicates)	0.000	0.000	0.000	0.000	0.000	0.000
%RSD (Residual)	0.000	0.000	0.000	0.000	0.000	0.000
%RSD (Total)	2.1	8.0	2.4	0.9	0.7	1.8
Std Error of Mean	0.0013	0.0001	0.0001	0.0008	0.0006	0.0002
% Std Error of Mean	0.7	2.7	0.8	0.3	0.2	0.6

Table 60. AN-107 Simulant Filter Paper Precision – Three Runs of Ten 100 µL Samples in Autosampler.

Envelope C (AN-107 simulant) Precision - Filter Paper

Three consecutive runs with samples in same position on autosampler

Voltage: 40-kV **Current:** 1.2-mA
Atmosphere: Vacuum
Instrument Film: Ultralene - 4-µm (film was not replaced)
Cell: None
Sample Filter: Cellulose - Bruker
Cover film: None
Analysis Time: 200-sec on peak; 100-sec on background
Volume: 100-µL of (2.5-mL H₂O/2.5-mL HNO₃/5mL AN-107 solution)

Background Subtracted Intensities						
	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Filter Blank	0.00433	0.00107	0.00027	0.03908	0.04180	0.01564
A	2.08635	0.00925	0.04013	0.07684	0.24854	0.03271
B	2.41377	0.00884	0.03927	0.09165	0.25471	0.03165
C	1.99642	0.00860	0.03695	0.08012	0.24698	0.03002
D	1.70005	0.00787	0.03435	0.07061	0.23081	0.03053
E	1.86473	0.00789	0.03564	0.06903	0.23629	0.02981
F	1.78109	0.00769	0.03337	0.06596	0.23164	0.02987
G	1.88866	0.00784	0.03443	0.07467	0.23644	0.03123
H	1.63338	0.00993	0.03510	0.07003	0.23539	0.03528
I	1.70853	0.00739	0.03194	0.06564	0.22965	0.03331
J	2.06121	0.00832	0.05966	0.08314	0.24191	0.03506
A	2.09670	0.00954	0.04068	0.06840	0.24916	0.03154
B	2.41979	0.00887	0.03813	0.08111	0.25449	0.03077
C	2.06248	0.00912	0.03852	0.07344	0.24982	0.03174
D	1.70388	0.00781	0.03440	0.06018	0.23407	0.03003
E	1.86674	0.00766	0.03581	0.06126	0.23564	0.03053
F	1.79286	0.00732	0.03338	0.05776	0.23058	0.02893
G	1.88908	0.00788	0.03455	0.06628	0.23850	0.03042
H	1.63991	0.01046	0.03529	0.06815	0.23729	0.02951
I	1.74138	0.00713	0.03308	0.05930	0.22961	0.02825
J	2.07171	0.00869	0.05918	0.06770	0.24274	0.03055
A	2.07490	0.00938	0.03997	0.06795	0.24781	0.03241
B	2.42947	0.00934	0.04024	0.08086	0.25625	0.03201
C	2.03249	0.00894	0.03794	0.07203	0.24590	0.03198
D	1.70045	0.00793	0.03360	0.05979	0.23263	0.03037
E	1.87717	0.00775	0.03594	0.06133	0.23807	0.03028
F	1.80630	0.00740	0.03366	0.06049	0.23336	0.02905
G	1.87952	0.00789	0.03331	0.06765	0.24139	0.02991
H	1.65002	0.01038	0.03595	0.06913	0.23592	0.02962
I	1.73615	0.00737	0.03212	0.06055	0.23031	0.02842
J	2.07309	0.00880	0.05967	0.06992	0.24363	0.03028
Average	1.9260	0.0085	0.0382	0.0670	0.2405	0.0304

Precision Analysis						
	Na kcps	Al kcps	P kcps	Cl kcps	K kcps	Cr kcps
Var (Sampling)	0.054917	8.89E-07	6.20E-05	0.000051	0.000068	1.40E-07
Var (Replicates)	0	2.44E-09	0	0.000022	2.79E-07	6.56E-07
Var (Residual)	1.43E-04	3.67E-08	3.48E-07	0.000004	0.000002	0.000002
Var (Total)	0.055111	9.2829E-07	6.2348E-05	0.000077	7.0279E-05	2.7964E-06
%RSD (Sampling)	12.2	11.1	20.6	10.3	3.4	1.2
%RSD (Replicates)	0.4	0.6	0.0	6.8	0.2	2.6
%RSD (Residual)	0.6	2.3	1.5	2.9	0.6	4.6
%RSD (Total)	12.2	11.3	20.6	13.1	3.5	5.5
Std Error of Mean	0.0743	0.0003	0.0025	0.0035	0.0025	0.0006
% Std Error of Mean	3.9	3.6	6.6	5.1	1.1	1.8

7.9 Appendix I: Calibration Standards

Table 61. AY-102 and AP-101 Concentrations.

Component	AY-102		Reference 2	AP-101	
	Reference 1			Reference 3	Reference 4
	Undiluted Supernate 3.2 M Na mg/L	Concentrated to 5.0M Na mg/L		Undiluted Supernate 5.6 M Na mg/L	Pretreated Supernate 4.85 M Na mg/L
Aluminum	4370	6747	6940	6314	7300
Arsenic	<1	a	a	a	1.3
Barium	<2	a	0.33	a	0.3
Boron	<7	a	15	86	9.6
Cadmium	<1	a	2	a	1.9
Calcium	<6	a	8	a	0.8
Cesium	1	2		a	0.0
Cerium	<7	a		a	0.1
Chromium	83	128	143	130	172
Cobalt		a	<1	a	0.4
Copper	<1.3	a	2	a	1.6
Iron	<21	a	3	a	3.7
Lanthanum	<2	a	<1	a	0.0
Lead	<8	a	15	a	12.2
Magnesium	<1	a	<3	a	2.5
Manganese		a	<1	a	1.3
Molybdenum	50	77	11	a	14.8
Neodymium		a	<3	a	2.5
Nickel	<3	a	8	a	6.2
Potassium	410	633	31200	25755	33894
Selenium	<1	a	a	a	0.5
Silicon	62	96	137		99.8
Silver	4	6	<0.6		0.6
Sodium	74500	115028	129300	111500	129415
Tin		a		a	0.0
Tungsten	101	156		a	28.7
Uranium	39	60		a	54.5
Vanadium	<2	a		a	0.7
Zinc	<1	a	6	a	5.6
Zirconium	<6	a	1	a	1.4
Chloride	140	216	1980	1364	1583
Phosphate	4420	6824	1020	883	1259
Sulfate	2080	3212	4030	2975	3840

- 1) C. J. Coleman, M. S. Hay, and K. B. Martin *Composting and Characterization of Samples from Hanford Tank 241-AY-102/C-106*, WSRC-TR-2003-00205, Rev 0, Savannah River Site, Aiken, SC 29808 (October, 2003)
 - 2) S. K. Fiskum et al, *Inorganic, Radioisotopic, and Organic Analysis of 241-AP-101 Tank Waste*, PNWD-3046, Rev. 0, Pacific Northwest National Laboratory, Richland, WA 99352 (August 2000).
 - 3) H. D. Smith, R. J. Bates, P. R. Bredt, L. R. Greenwood, M. J. Schweiger, M. W. Urie, and D. R. Weier, *Vitrification and Product Testing AP-101 Pretreated LAW Envelope A Glass*, PNWD-3470, Rev. 0, Pacific Northwest National Laboratory, Richland, WA 99352 (June 2004).
 - 4) Best Basis Inventory, Tank 241-AP-101, FY05, Q02
- a) Not reported

Table 62. AZ-101 Concentrations.

Component	Reference 5	Reference 6	Reference 7	Reference 8
	Undiluted Supernate 4.7 M Na	Undiluted Supernate 4.8 M Na	Pretreated Supernate 4.3 M Na	Pretreated Supernate 4.3 M Na
	mg/L	mg/L	mg/L	mg/L
Aluminum	10670	6050	5300	5280
Arsenic	a	9.9	14	14
Barium	a	0.3	<0.2	<0.2
Boron	a	77	8	8
Cadmium	a	0.8	<0.3	a
Calcium	a	9.3	<5	a
Cesium	37	52	a	a
Cerium	a	5	<4	a
Chromium	730	686	570	570
Cobalt	a	a	a	a
Copper	a	0.6	<0.5	a
Iron	a	1.5	<0.5	a
Lanthanum	a	a	a	a
Lead	a	3.3	7	7
Magnesium	a	3	<2	a
Manganese	a	a	a	a
Molybdenum	a	89	85	85
Neodymium	a	3	<2	a
Nickel	a	1	<0.6	a
Potassium	4624	4460	3800	3800
Selenium	a	a	a	a
Silicon	a	206	52	52
Silver	a	0.6	<0.5	a
Sodium	108990	111000	99000	99000
Tin	a	a	44	44
Tungsten	a	58	51	51
Uranium	a	a	a	a
Vanadium	a	a	a	a
Zinc	a	1	1.6	1.6
Zirconium	3.1	1	1.9	1.9
Chloride	200	240	<130	a
Phosphate	1503	1545	1600	1600
Sulfate	17670	16200	16000	16500

- 5) K. M. Hodgson, *Tank Characterization Report for Double-Shell Tank 241-AZ-101*, WHC-SD-WM-ER-410, Rev 0, Westinghouse Hanford Company, Richland, WA 99352 (July 26, 1995).
- 6) M. W. Urie et al, *Chemical Analysis and Physical Property Testing of 241-AZ-101 Tank Waste – Supernatant and Centrifuged Solids*, PNWD-3215, WTP-RPT-048, Rev 0, Pacific Northwest National Laboratory, Richland, WA 99352 (November, 2002).
- 7) A. P. Poloski et al, *Rheological and Physical Properties of AZ-101 LAW Pretreated Waste and Melter Feed* PNWD-3367, WTP-RPT-095, Rev 0, Pacific Northwest National Laboratory, Richland, WA 99352 (November, 2003).
- 8) H. D. Smith et al, *Vitrification and Product Testing of AZ-101 Pretreated LAW Envelope B Glass*, PNWD-3464, WTP-RPT-106, Rev 0, Pacific Northwest National Laboratory, Richland, WA 99352 (June, 2004).
- a) Not reported

Table 63. AZ-102 and AP-103 Concentrations.

Component	AZ-102			AP-103
	Reference 9	Reference 10	Reference 11	Reference 12
	Undiluted Supernate 2.6 M Na mg/L	Pretreated	Pretreated	Undiluted Supernate 7.7 M Na mg/L
		Crucible Test 2.2 M Na mg/L	Crucible Test 4.1 M Na mg/L	
Aluminum	755	402	798	18316
Arsenic	a	a	a	35
Barium	0.8	1	a	22
Boron	8.4	1.1	4.6	43
Cadmium	1.9	0.1	a	10
Calcium	108	1	67	76
Cesium	a	a	a	0
Cerium	a	a	a	43
Chromium	1010	533	1018	588
Cobalt	a	a	a	9
Copper	3.1	<1	a	5
Iron	11.2	<1	5.5	22
Lanthanum	1.8	<1	a	6
Lead	6	1.2	a	45
Magnesium	0.9	<1	3	43
Manganese	0.8	<1	0.9	4
Molybdenum	58	43	a	60
Neodymium	5.5	a	a	34
Nickel	2.2	<1	6	78
Potassium	3167	2584	4555	6470
Selenium	a	a	a	36
Silicon	559	56	56	106
Silver	6.9	a	a	7
Sodium	60900	50888	95039	178139
Tin	a	a	a	a
Tungsten	a	a	a	a
Uranium	a	a	a	14
Vanadium	a	a	a	a
Zinc	0.3	0.4	2.7	a
Zirconium	4.3	<1	40	a
Chloride	248	67	200	4284
Phosphate	a	246	704	2381
Sulfate	a	13287	26300	4756

9) M. S. Hay, M. G. Bronikowski, *Chemical Characterization of an Envelope B/D Sample from Hanford Tank 241-AZ-102*, BNF-003-98-0249, Savannah River Site, Aiken, SC 29808 (August 2000).

10) W. J. Gray, M. E. Peterson, R. D. Scheele, J. M. Tingey, *Characterization of the First Core Sample of Neutralized Current Acid Waste From Double-Shell Tank AZ-102*, Pacific Northwest Laboratory, Richland WA 99352 (January 1993).

11) C. L. Crawford, R. F. Schumacher, and N. E. Bibler, *Final Report for Crucible-Scale Radioactive Vitrification and Product Testing of Waste envelope B (AZ-102) Low- Activity Waste Glass*, WSRC-TR-2003-00536, Rev 0, Savannah River Site, Aiken, SC 29808 (April, 2004).

12) Best Basis Inventory, Tank 241-AP-103, FY05, Q01

a) Not reported

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