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Development of TRU Waste Mobile Analysis Methods for RCRA-Regulated Metals

Cynthia A. Mahan*, Robert Villarreal, Lawrence Drake,
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Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). Glow-discharge mass spectrometry (GD-MS), laser-induced breakdown spectroscopy (LIBS), dc-arc atomic-emission spectroscopy (DC-ARC-AES), laser-ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS), and energy-dispersive x-ray fluorescence (EDXRF) were identified as potential solid-sample analytical techniques for mobile characterization of TRU waste. Each technology developer was provided with surrogate TRU waste samples in order to develop an analytical method. Following successful development of the analytical method, five performance evaluation samples were distributed to each of the researchers in a blind round-robin format. Results of the round robin were compared to known values and Transuranic Waste Characterization Program (TWCP) data quality objectives. Only two techniques, DC-ARC-AES and EDXRF, were able to complete the entire project. Methods development for GD-MS and LA-ICP-MS was halted due to the stand-down at the CMR facility. Results of the round-robin analysis are given for the EDXRF and DCARC-AES techniques. While DC-ARC-AES met several of the data quality objectives, the performance of the EDXRF technique by far surpassed the DC-ARC-AES technique. EDXRF is a simple, rugged, field portable instrument that appears to hold great promise for mobile characterization of TRU waste. The performance of this technique needs to be tested on real TRU samples in order to assess interferences from actinide constituents. In addition, mercury and beryllium analysis will require another analytical technique because the EDXRF method failed to meet the TWCP data quality objectives. Mercury analysis is easily accomplished on solid samples by cold vapor atomic fluorescence (CVAFS). Beryllium can be analyzed by any of a variety of emission techniques.

Background and Research Objectives

Transuranic (TRU) waste characterization is imminent and a critical compliance activity required for all TRU waste destined for treatment and/or disposal. There is an immediate need for mobile laboratory analytical methods to characterize TRU waste for

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RCRA-listed metals (i.e., Sb, As, Ba, Be, Cd, Cr, Hg, Pb, Ni, Se, Ag, Tl, V, and Zn). Current methods of analysis used in the TRU Waste Characterization Program (TWCP) are laboratory-based, costly, have low sample throughput, and require considerable analytical resources to implement the associated Quality Assurance (QA) program. In addition, these methods are not readily amenable for mobile deployment.

Glow-discharge mass spectrometry (GD-MS), laser-induced breakdown spectroscopy (LIBS), dc-arc atomic-emission spectroscopy (DC-ARC-AES) using solid-state integrating detectors, laser-ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS), and energy-dispersive x-ray fluorescence (EDXRF) are all direct chemical analysis techniques and were targeted by this research for evaluation as potential analytical methodologies for TRU waste characterization. All these technologies are suitable for mobile deployment. Furthermore, a major benefit of most of the technologies is the potential to analyze the entire suite of target analytes. This would reduce the current protocol requiring three separate analytical methods to a single instrumental technique. Hence, sample throughput is increased and analytical costs are lowered.

The objective of this research was to identify and demonstrate the existence of rugged, field-laboratory-based analytical techniques that can meet the TWCP quality assurance objectives and provide full TRU waste analyses at reduced cost.

Importance to LANL's Science and Technology Base and National R&D Needs

DOE plans to dispose of approximately 175,600 cubic meters of TRU waste at the Waste Isolation Pilot Plant (WIPP) site. This waste is located at various DOE sites throughout the nation and, generally speaking, the required analytical capabilities for characterization do not exist at the majority of storage sites. Thus, the waste will require transport to a facility with the requisite capabilities. Transportation of TRU waste is tightly regulated, difficult, and costly. By developing mobile analytical laboratories, these problems are obviated. In addition, if a single technique can replace the current suite of laboratory-based instrumental techniques (ICP-MS, ICP-AES, CVAFS), then approximately $150K can be saved for every 40 drums analyzed. The estimated savings extrapolated to include the anticipated analysis of TRU waste stored throughout the DOE complex could result in a cost reduction of nearly one hundred million dollars.

Scientific Approach and Accomplishments

Each technology developer was provided with surrogate Portland-cemented waste samples to use in the analytical method development process. These surrogates, obtained from Idaho National Engineering and Environmental Laboratory (INEEL), are actual samples used in the Performance Demonstration Program (PDP). This program is designed to evaluate the participating laboratories' analytical performance for TRU waste characterization. The analytical results are subjected to an evaluation and the laboratory scored. The results of the scoring determine whether the laboratory qualifies its TRU analytical characterization methods.

The method development phase of this study involved the development of sample preparation procedures, instrument parameter optimization (e.g., analyte wavelength selection and laser power settings) and determination of analytical figures of merit. Following successful development of the analytical method, another set of performance evaluation samples was distributed to each of the researchers in a blind round-robin format. Thus the results of this test also indicate whether the technology meets the performance specification on real evaluation samples. Results of the round robin were compared to known values and TWCP data quality objectives. The data quality objectives are discussed below. Final results of the study, plus estimates of sample throughput, ease of use, and cost were evaluated for the technologies that were able to complete the project goals.

DC-ARC-AES and EDXRF were able to complete the project goals. The results are described below. The method development phase for the techniques LA-ICP-MS and GD-ICP-MS were progressing on schedule but were abruptly halted due to the stand-down in the Chemistry and Materials Research (CMR) facility.

Quality Assurance Program for TRU Waste Disposal

The Quality Assurance Program Plan (QAPP) for the TWCP describes the performance requirements for TRU waste characterization. The data quality objectives (DQOs) are shown in Table 1. Analytical results for PDP samples with concentrations greater than the Program Required Quantitation Limit (PRQL) must result in precisions of less than or equal to 30% and recoveries must be within the range 80-120%. In addition, Table 1 shows the Program Required Detection Limits (PRDL) for each of the target analytes. PDP sample analysis results are scored on these major criteria to determine whether the analytical technique passes or fails, and the laboratory demonstratives effective performance. Additional scoring criteria are made on the "blank" surrogate results. If the laboratory identifies the presence of a target analyte above 50% of the PRQL, then points are subtracted from the overall score. It should also be noted that there

are several run-time quality control (QC) criteria that also must be satisfied for this program. The criteria generally follow SW846 requirements, but are not evaluated in this project.

Table 1. Data Quality Objectives for the Transuranic Waste Characterization Program

Element (ppm)	Precision[a] (%RSD or RPD)	Accuracy[b] (%R)	PRDL[c] (ppm)	PRQL[d] (ppm)
Sb	≤ 30	80-120	10	100
As	≤ 30	80-120	10	100
Ba	≤ 30	80-120	200	2000
Be	≤ 30	80-120	10	100
Cd	≤ 30	80-120	2	20
Cr	≤ 30	80-120	10	100
Pb	≤ 30	80-120	10	100
Hg	≤ 30	80-120	0. 4	4
Ni	≤ 30	80-120	10	100
Se	≤ 30	80-120	2	20
Ag	≤ 30	80-120	10	100
Tl	≤ 30	80-120	10	100
V	≤ 30	80-120	10	100
Zn	≤ 30	80-120	10	100

a ≤ 30% when sample and duplicate conc are ≥ 10 X IDL for ICPAES and ≥ 100 x IDL for ICPMS
b Based on known concentrations
c Program required detection limits 10X below the PRQL
d Program required quantitation limit

Energy Dispersive Xray Project

Background: EDXRF is one of several methods of direct solid analysis that can potentially provide improvements in analytical performance (i.e. cost, turnaround time, field-based characterization) over traditional wet chemical methods of analysis. Recent developments in field-transportable EDXRF have greatly improved the sensitivity and accuracy of this method for elemental analysis of complex matrices (e.g., Pella et al., 1986; Leyden, 1988; Bilbrey et al., 1988; de Boer, et al., 1993). Our recent work with EDXRF for soil characterization indicated that it was relatively accurate and sensitive for most RCRA metals, with typical biases of less than ±10% and detection limits as low as a few ppm (Goldstein et al., 1996). Hence, a major objective was to develop and evaluate an analogous EDXRF method for analysis of Portland-cement waste samples over a range of elements and concentrations suitable for RCRA metal analysis.

Method: The methodology for sample preparation and analysis in EDXRF is relatively straightforward, largely following methods previously developed for soil analysis (Watson et al., 1989; Goldstein et al., 1996). Samples are dried under a heat lamp overnight, mixed and milled in a Spex ball-mill for 5 minutes, sieved to <100 micron size, and then ~0.5 g placed as a powder in a microcell for analysis. This simple method of sample preparation takes <20 minutes per sample, but provides a physically homogeneous sample needed for reproducible XRF analysis. It is also simple and fast enough to be amenable to completion in a mobile analytical laboratory. Sample size is reduced by a factor of 10-20 relative to conventional powder XRF through use of a sample microcell and beam collimator.

All analyses were performed using a commercial EDXRF spectrometer, a Spectrace 5000. This instrument has an x-ray tube source with variable source current and voltage up to 1 mA and 50 kV, which permits optimization of excitation conditions for the element of interest. It also uses a high-resolution, electrically cooled Si(Li) detector, which permits simultaneous collection of x-rays of variable energy with minimal spectral interference. The instrument has a fundamental-parameter data-reduction package available for rapid multi-element standardization and quantification of the acquired spectra. A nearly identical field-transportable instrument is also available, and so performance of this method should be similar under field conditions.

Analytical conditions were optimized to increase method sensitivity by adjusting the excitation x-ray tube voltage and current. Filters of various thickness and composition were also used to remove low-energy noise from the acquired spectra. Based on tests with standards, four separate excitation conditions were used: 1) lowest –Z elements Ca, V, Cr using 12-kV tube voltage and 0.13-mm-thick Al filter, 2) Fe, Ni, Cu, and Zn using 20-kV tube voltage and 0.05-mm-thick Pd filter, 3) As, Se, Hg, Tl, Pb, U, and Th using 35-kV tube voltage and 0.127-mm-thick Pd filter, and 4) Ag, Cd, Sb, and Ba using 50-kV tube voltage and 0.63-mm-thick Cu filter. Acquisition time (livetime) was 800 s per condition, hence analysis takes approximately 90 minutes per sample. This long acquisition time was needed to achieve detection limits at the desired levels utilizing the relatively small sample configuration of the microcell geometry. Samples were analyzed utilizing an auto-sampling turret in automated mode overnight, so throughput is presently ~10-15 samples/day. Spectral interferences are generally absent under the conditions above.

Standardization of the major elements was accomplished by cement standards spanning a range in composition obtained from the National Institute of Standards and Technology (NIST). A dual approach was used to standardize the trace metals. Trace

element standards containing the metals of interest were obtained from prior TRU intercomparison studies. Because these standards spanned a limited range in concentration, additional standards were prepared at LANL by pipetting NIST-traceable multi-element solution standards onto a "blank" cement matrix, followed by drying and homogenization. A total of 6 multi-element standards typically ranging from 10-2000 ppm were used for standardization.

Results: Detection limits for the conditions above are compared to the TRU waste program required detection limits in Table 2. The EDXRF technique meets detection limit requirements for 11 of the 14 metals. Exceptions are V, Hg, and Be, the latter of which is not detected by EDXRF. The detection limit for vanadium is only a factor of two above the required limit, and so it is likely that the required limit could be met by increasing data acquisition time by a factor of 4 or by increasing sample size. However, the required detection limit for mercury is a factor of 40 too low and apparently unattainable by direct EDXRF techniques. Additional field-based techniques, which can more sensitively measure both mercury and beryllium, are required for waste characterization of RCRA metals.

Table 2. EDXRF and Program Required Detection Limits (3σ)

Element	EDXRF Detection Limit (ppm)	Program Required Detection Limit (ppm)
Antimony	3	10
Arsenic	4	10
Barium	10	200
Beryllium	---	10
Cadmium	2	2
Chromium	8	10
Lead	5	10
Mercury	9	0.4
Nickel	5	10
Selenium	2	2
Silver	2	10
Thallium	6	10
Vanadium	20	10
Zinc	2	10

Results of the blind round-robin analysis are shown in Tables 3 and 4. Cells that are shaded show results that would have failed the TWCP criteria, and therefore reduce the analytical scoring, if the results would have been submitted to INEEL under the PDP cycle 4 round-robin test. Beryllium cannot be detected by EDXRF. The majority of results

meet the TWCP data quality objectives for percent recovery and relative percent difference (RPD). Only chromium and mercury deviated slightly from the required recovery for the TRU4 and TRU5 blind samples, with recoveries of 78% and 79%, respectively. While V recoveries for samples TRU2, 4 and 5 were low, the expected values were less than the PRQL (100 ppm), therefore the low recovery does not reduce the analytical score. TRU3 was the performance demonstration 'blank' sample, that is the sample is comprised of just the Portland cement matrix and is not spiked with any of the RCRA elements. Two false positives were found for Ba and Cr. However, it should be noted that a T-test is applied by the scorer using all submitted analysis from the participating laboratories and often times the laboratories indicate the presence of contamination.

Table 3. Results of Blind PDP Samples (Results are µg/g or %Recovery)

TRU1				TRU2			TRU3	
Element	Expected	Found	Recovery	Expected	Found	Recovery	Expected	Found
Sb	263	237 ± 21	90.1	154	136 ± 9	88.3	0	< 3
As	284	282 ± 8	99.3	173	172 ± 6	99.4	2.32	< 4
Ba	3200	2975 ± 300	105.4	1660	1517 ± 60	91.4	71.4	130
Be	407	-		444	-		0	-
Cd	107	95 ± 9	88.8	100	83.3 ± 4.5	83.3	0	< 2
Cr	561	444 ± 8	79.1	202	208 ± 8	103.0	38.3	109 ± 12
Pb	192	190 ± 15	99.0	247	230 ± 10	93.1	4.5	< 5
Hg	22.6	23.5 ± 5.0	104.0	15.9	13.0 ± 2.7	81.8	0	< 9
Ni	581	531 ± 32	91.4	104	119 ± 9	114.4	0	36.2 ± 2.7
Se	98.1	91.8 ± 3.7	93.6	27.7	27.7 ± 2.4	100.0	0.382	2.5 + .1
Ag	229	220 ± 17	96.1	229	217 ± 6	94.8	0	2.6 + 1.0
Tl	509	459 +27	90.2	547	473 ± 21	86.5	0	< 6
V	433	363 ± 18	83.8	81	52.8 ± 5.6	65.2	29.7	54.9 ± 8.6
Zn	385	361 ± 20	93.8	238	230 ± 1	96.6	22.4	51.6 ± 4.8

Table 4. Results of Blind PDP Samples (Results are μg/g)
TRU4/TRU5

Element	Expected	Found 1	Found 2	Recovery	Recovery	RPD
		90.4 ± 2.1	91.2 + 4.1	92.1	92.9	0.9
As	490	471 ± 19	484 ± 4	96.1	98.8	2.7
Ba	5770	5160 ± 344	5212 ± 201	89.4	90.3	1.0
Be	244	-	-			
Cd	88.7	81.7 ± 3.7	81.1 ± 2.0	92.1	91.4	0.7
Cr	550	440 ± 18	431 ± 10	80.0	78.4	2.1
Pb	277	263 ± 6	269 ± 11	94.9	97.1	2.3
Hg	22.3	18.4 ± 2.0	17.7 ± 4.2	82.5	79.4	3.9
Ni	192	200 ± 3	190 ± 3	104.2	99.0	5.1
Se	72	70.1 ± 2.2	68.3 ± 3.2	97.4	94.9	2.6
Ag	198	188 ± 17	196 ± 6	94.9	99.0	4.2
Tl	242	228 ± 6	229 ± 16	94.2	94.6	0.4
V	86	< 20	< 20			
Zn	264	258 ± 10	257 ± 4	97.7	97.3	0.4

Relative standardization uncertainties (%RSD), based on agreement of the six trace-element standards, are given in Table 5. The uncertainty due to standardization is 10% or less for 10 of the 13 detected metals. Exceptions are Hg, Ag, and Ba, which have significantly poorer precision. The higher standardization uncertainties for barium and silver seem to reflect some small bias in the expected values for either the LANL or externally prepared trace-element standards for these elements. It should be noted that when comparing element concentrations between national laboratory PDP results, there is often a higher correlation between the laboratories than to the PDP program 'expected' values. This has been shown in several instances. The high uncertainty for mercury reflects its low concentration, ranging from 7 to 54 ppm in the standards measured.

External precision and accuracy are evaluated from results for three blind quality control samples, given in Table 5. The typical external precision is based on reproducibility of analyses of three replicate aliquots of three different QC samples. For all elements with the exception of Hg, this relative uncertainty is less than 7%. Again, mercury has poorer reproducibility due to its lower concentration in the analyzed samples. Based on these results for samples above the quantitation level, a typical external precision of a few percent can be obtained with this EDXRF method.

Table 5 also shows that average accuracy ranges from 85% for Cr to 102% for Ni. Results for vanadium are relatively poor due to its high detection limit and are not included. Given the total propagated uncertainties based on standardization and external

precision in Table 5, none of the other elements show a significant bias at the 95% confidence interval.

Table 5. EDXRF Method Precision and Accuracy

Element	Concentration Range (ppm)[a]	Standardization Uncertainty [a] (% RSD)	External Precision (% RSD)	Total Propagated Uncertainty (% RSD)	Average Accuracy (%)
Antimony	98-263	8	6	10	91
Arsenic	173-490	5	3	6	98
Barium	1660-5770	20	6	21	94
Cadmium	89-107	8	5	9	89
Chromium	202-561	7	3	8	85
Lead	192-277	4	5	6	96
Mercury	16-23	46	19	50	87
Nickel	104-581	5	4	6	102
Selenium	28-98	7	5	9	97
Silver	198-229	17	6	18	96
Thallium	242-547	7	5	9	91
Vanadium	81-433	10	7	12	---
Zinc	238-385	6	3	7	96

[a] Concentration range for quality control samples used to determine external precision and accuracy.

[a] Standardization uncertainty based on six known standards typically ranging from 10-2000 ppm.

Conclusions: These results indicate that field-based EDXRF techniques can meet requirements for analyses of a large majority of the RCRA-metals in TRU waste samples. While EDXRF appears to be suitable for analyses of 11 of the 14 RCRA-metals, a few metals including mercury, vanadium, and beryllium have detection limits that are significantly above the program requirements. As a result, additional techniques should be investigated for characterization of those metals. In addition, effects of inherent radiation of the samples and matrix variability on method performance also need to be investigated, although these effects are expected to be relatively minor in most cases.

DC-ARC-AES Project

Background: DC-ARC-AES is a bulk-solids analytical technique that uses a solid-state integrating detector to measure the spectral emission intensities produced when a sample is vaporized and excited by a dc arc. The solid-state integrating detector represents relatively new technology, which has the potential to improve analytical performance over the traditional dc arc and conventional spectroscopic techniques. Samples are pulverized, mixed with graphite powder, and burned in the lower of two vertically mounted graphite electrodes. The detector chip is similar to a photographic plate

in that it provides for continuous wavelength coverage and hence most elements in the periodic table can be determined if present in sufficient quantity. Potential analytical benefits over conventional spectroscopic methods include full elemental fingerprinting of the sample, the ability to detect weak spectral lines in the midst of strong matrix signals, improved sample throughput, simultaneous background correction, minimal sample preparation, and instrumental ruggedness.

Method: Method development was a multivariate process involving optimization of the graphite-diluent weight to sample weight, wavelength selection, element integration times, calibration strategies, electrode gap distance, gas flow rates, and applied current. Portland cement surrogate samples with known concentrations of RCRA elements were used to investigate and optimize these parameters. Analysis parameters are shown in Tables 6 and 7. Round-robin samples were diluted with graphite powder in a 1-to-5 ratio. Calibration standards were prepared using graphite powdered SPEX G7 standards diluted with a Portland cement 'blank' for matrix matching purposes.

Table 6. Instrumental Parameters

Analytical Gap:	4mm
Excitation:	15 amps
Gas Flow Rate:	5 LPM

Table 7. Element Channels

Element	λ(nm){order}	Element	λ(nm){order}
Antimony	217.581 {121}	Mercury	253.652 {104}
Arsenic	234.984 {112}	Nickel	305.082 { 86}
Barium	455.403 { 58}	Selenium	196.090 {134}
Beryllium	313.042 { 84}	Silver	328.068 { 80}
Cadmium	228.802 {115}	Thallium	535.046 { 49}
Chromium	283.563 { 93}	Vanadium	310.230 { 85}
Lead	405.783 { 65}	Zinc	206.200 {127}

Results: Detection limits for the dc arc technique, determined from a Portland-cement-matrix blank sample, are compared to the TWCP PRDLs in Table 8. Only 3 elements (Ba, Be and Ag) were able to meet the stated requirements. Sb, Cd, Cr, Pb, and Tl were off by approximately a factor of two, and we believe can be improved by fine-tuning the method. The low detection criteria of Hg preclude analysis by dc arc as well as any other emission technique. The reason for the high detection limits is the interfering

concomitants, especially Fe, which show background interference on most of the elements. Fe is present in these samples at relatively high concentrations (> 6000 ppm).

Table 8. DC-ARC and Program Required Detection Limits (3σ)

Element	DCARC Detection Limit (ppm)	Program Required Detection Limit (ppm)
Antimony	12	10
Arsenic	52	10
Barium	35	200
Beryllium	1	10
Cadmium	5	2
Chromium	23	10
Lead	27	10
Mercury	21	0.4
Nickel	30	10
Selenium	40	2
Silver	1	10
Thallium	12	10
Vanadium	85	10
Zinc	34	10

Results of the 5 round-robin performance demonstration samples are shown in Tables 9 and 10. The shaded cells indicate results that do not comply with the TWCP DQOs. The recoveries range from 72-133%, except for the 47% recovery for V on the TRU4 sample. Of those elements that failed, the majority failed by less than 10%.

Table 9. Results of Blind PDP Samples
(Results are μg/g or % Recovery)

TRU1				TRU2			TRU3	
	Expected	Found	Recovery	Expected	Found	Recovery	Expected	Found
Antimony	263	191 ± 17	73	154	147 + 37	96	0	< 12
Arsenic	284	261 ± 24	92	173	230 + 54	133	2.32	< 52
		± 185	69	1660	1104 + 600	67	71.4	< 35
Beryllium	407	338 ± 30	83	444	442 + 39	100	0	< 1
Cadmium	107	103 + 9	96	100	109 + 26	109	0	< 5
Chromium	561	412 + 71	73	202	179 + 66	89	38.3	< 22
Lead	192	138 + 16	72	247	241 + 80	98	4.5	< 27
Mercury	22.6	< 21		15.9	< 21		0	< 21
Nickel	581	491 + 54	84	104	123 + 36	118	0	< 30
Selenium	98.1	< 40		27.7	< 40		0.38	< 40
Silver	229	183 + 19	80	229	231 + 66	101	0	< 1
Thallium	509	376 + 58	74	547	519 + 139	95	0	< 12
Vanadium	433	382 + 70	88	81	74 +50	92	29.7	< 85
Zinc	385	380 + 31	99	238	249 + 66	105	22.4	< 34

Table 10. Results of Blind PDP Samples (Results are μg/g)

Element	Expected	Found 1	Found 2	Recovery	Recovery	RPD
Sb	98	72	87	73	89	20
As	490	437	540	89	110	21
Ba	5770	*	*			
Be	244	219	266	90	109	20
Cd	89	101	119	114	134	16
Cr	550	317	502	58	91	45
Pb	277	200	242	72	87	19
Hg	22	< 21	< 21			
Ni	192	152	222	79	115	37
Se	72	< 40	< 40			
Ag	198	145	198	73	100	31
Tl	242	182	203	75	84	11
V	86	40	78	47	91	64
Zn	264	264	271	100	103	3

Conclusions: The dc arc technique did not perform as well as expected on the round-robin test. Two major problems exist that may improve the results. First, background correction must be more precise. The 5-fold dilution of the matrix results in concomitant concentrations of interfering elements at very high levels. Over- or under-correction of these interferences result in biases. Secondly, the technique has poor precision. It is believed this is due to a nonhomogenous sample with varying particle sizes. Better sampling, grinding, and sieving processes could result in improved precision and accuracies. Furthermore, an alternate method with a greater dilution of the sample with graphite powder has been tested and the preliminary results show improvements in the detection limits and recoveries for several of the elements.

LA-ICP-MS Participation

We worked on the LA-ICP-MS method for the analysis of cement samples. This involved varying different parameters such as laser wavelength, irradiance, raster speed, and shots per spot. A preliminary method has been developed based upon the results of these experiments. The parameters chosen were those that gave the best short-term signal precision. The figures of merit for the method were in the process of being determined when the laser system failed. Subsequent to restoring the instrument, the CMR building was put in stand-by mode and work could not resume.

Issues: During the preliminary work some problems with the standards were noted. The performance demonstration samples that were used for method development

are not well characterized, and in some cases there are inconsistencies in the "known" concentrations as determined from the two methods: 1) the amount of analyte added to the cement and 2) the concentration of each analyte as determined from traditional wet chemical analyses. In some cases the calibration curves derived from the different values were considerably different. Some of these problems relate to the fact that the blank contains some of the target analytes (Ba, Cr, V, Zn), which makes determining the method detection limits problematic.

Method: The following preliminary method was devised. The sample is ground using a boron-carbide mortar and pestle. A sample pellet (1-cm diameter) is prepared from a 0.25-g sample. No binder is required. The following conditions are used for sample analysis:

- Laser conditions: third harmonic of a Nd:YAG laser, 355-nm, Q-switched
- Irradiances at ~ 10^{10} W/cm^2
- Scan across the sample using a 2 x 2-mm raster pattern of 100-μm step sizes at a rate of 2 mm per 7 sec
- Complete one full raster prior to starting MS acquisition

After sample acquisition, argon gas is allowed to flow through the laser cell and transfer tubing until signals return to blank levels (~ 3 minutes). The MS acquisition time is optimized at 60 s with 3 integrations.

Results: Preliminary results indicate a short-term precision of ~ 5% in most cases, without the use of an internal standard. Detection limits are in the low-ppm range.

Publications

Journal Publications for both DC-ARC and EDXRF are currently being written and will be submitted to refereed journals in F 19Y98.

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