

Evaluation of Inductively Coupled Plasma - Time-of-Flight Mass Spectrometry for Laser Ablation Analyses,

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Purpose

The purpose of this trip to LECO Corporation was to test the non-matrix matched calibration method and the principal component analysis (PCA) method on a laser ablation-inductively coupled plasma-time of flight mass spectrometry (LA-ICP-TOFMS) system. An LA-ICP-TOFMS system allows for multielement single-shot analysis as well as spatial analysis on small samples, because the TOFMS acquires an entire mass spectrum for all ions extracted simultaneously from the ICP. The TOFMS system differs from the double-focusing mass spectrometer, on which the above methods were developed, by having lower sensitivity and lower mass resolution.

Experimental

The experiments were performed on a LECO Renaissance® TOF-ICP-MS at the LECO Corporation World Headquarters in St. Joseph, MI.

Calibration experiments Solutions for calibration additions were prepared by LECO personnel by appropriate dilution of standard stock solutions. All monitored elements were present in the same prepared calibration solution. Standard reference materials, NIST 612 glass and NIST 1648 urban dust, were used for analysis. The experimental set-up, procedure, and data handling are described in Aeschliman, D. B., Bajic, S. J., Baldwin, D. P., Houk, R. S., J. Anal. At. Spectrom. 2003, 18(8), 872-877. The response of the laser ablation system was calibrated by use of a micro-concentric nebulizer (Model PFA-20, Elemental Scientific). Because of the lower sensitivity of the TOFMS, the mass transport of ablated particles was measured off-line with the piezoelectric microbalance (Model 8510, TSI Inc.).

Twenty-one elements were quantitatively determined in the NIST 612 glass. A CETAC LSX-200 (266 nm) laser-ablation system was used for sampling. The LSX-200 was operated at 10 Hz with 4.5 mJ/pulse and 200 μm spot size during the glass analysis. Five replicates were acquired for analysis, with each replicate consisting of 30 laser shots per localized spot on the sample.

Eighteen elements were quantitatively determined in the NIST 1648 urban dust sample. The CETAC LSX-200 (266 nm) laser-ablation system was again used for sampling. The LSX-200 was operated at 10 Hz with 2.2 mJ/pulse and 400 μm spot size during the urban dust analysis. Five replicates were acquired for analysis with each replicate consisting of only 3 laser shots per localized spot on the sample. The urban dust ablation samples were generated by spreading a uniformed layer of sample over one side of double-sided adhesive tape, which was mounted on a plastic pedestal.

PCA experiments Testing of the PCA protocols was accomplished by analysis of glass fragments with indistinguishable refractive indices, obtained from the Illinois State Police Forensic Laboratory, and NIST standard reference material steel samples. The steel samples were filings that were pressed into clay affixed on a teflon pedestal for insertion into the ablation cell. A CETAC

LSX-200 (266 nm) laser ablation system was used for sampling. The LSX-200 was operated at 10 Hz with 4.5 mJ/pulse and 100 μm spot size during the analyses. Five replicates were acquired for analysis with each replicate consisting of 20 laser shots per localized spot on the sample.

PCA was performed using PLS Toolbox v3.03a from Eigenvector Research, Inc. (Manson, WA).

Results

The results for the non-matrix matched calibration experiments on glass and urban dust are summarized in Tables I and II, respectively. The accuracy for the quantitative analysis of the NIST 612 glass is within 16% of the reported certified values, except for gold (Au) which was near the limit of detection (LOD). This is somewhat higher than that reported accuracies on the more sensitive double-focusing instrument (within 3% for 18 elements). The relative error for the elements are consistently positive and roughly of the same value, indicative of a systematic error in the experiment. The possible source of this error is unknown at this time but could be from one or more sources (e.g, off-line microbalance reading lower than actual or improper dilution of standard solutions).

The accuracy for the quantitative analysis of the SRM 1648 urban dust range is within 32% of the reported certified values, except for silver (Ag) and chromium (Cr) which are at -9% to 50% respectively, for the 18 analyzed elements. The relative differences for the urban dust sample are consistently positive and higher than those for the 612 glass sample, again indicative of a systematic error in the experiment.

Figure 1 summarizes the PCA of six glass fragments that are indistinguishable from one another based on their refractive indices but are differentiated based on a PCA of their mass spectral data. A model for each sample is generated and the other samples are compared to the model. An average Q-residual (i.e., measure of the difference between a sample, including all replicates, and the model to which it is compared) is calculated. If the average Q-residual lies below the 95% confidence level, the compared samples are said to be indistinguishable. Similarly, if the average Q-residual lies above the 95% confidence level, the samples are said to be discernable based on their mass spectra. From the figure the majority of the fragments are differentiated at the 95% confidence level, except for S-4 when compared to the S-1029 model. Not being able to discern S-4 from the S-1029 model is probably due to the observed scatter in the signal levels in the replicates for both samples.

A similar experiment conducted on a more sensitive double-focusing mass spectrometer produced a comparable comparison where each of the six samples were readily differentiated from the remaining five at the 95% confidence level. With the more sensitive mass spectrometer, 38 elements were observable (compared to 18 for the TOF mass spectrometer) leading to greater differentiability.

The summarized PCA for steel fillings is shown in Figure 2. The seven steel SRM's are very similar in composition, except for seven elements. As with the glass samples, the majority of the SRMs are distinguishable from one another except for SRM 12h compared to model 14e and SRMs 11f, 12h, and 14e compared to the model of SRM 152. As with the glass fragment data above the lack of discernability of these samples is most likely due to the scatter of the signal levels in the replicate set. The scatter is further evidenced by the relatively high confidence levels for the 14e and 152 models compared to the others.

Conclusion

LA-ICP-TOFMS is useful for multielemental analysis in cases where sample size and/or analysis time prohibit the use of the more sensitive and stable double-focusing instrument because a complete mass spectrum can be acquired from a few laser pulses in under 50 μsec . Additionally LA-ICP-TOFMS may reveal spatial correlations among elements in the sample that would be more difficult to discern with the slower scanning double-focusing mass spectrometer.

To obtain best limits of detection and minimize spectroscopic interferences, the double-focusing MS remains the instrument of choice, as we concluded during our initial survey of commercially-available equipment. In order to make the TOFMS a more attractive choice for LA-ICP-MS, new systems must be developed that address current limitations in sensitivity and noise levels, peak-shape and resolution, and background drift. Given the potential advantages for analysis of extremely small samples and isotopic analyses, and the importance of these characteristics to LA-ICP-MS development, these improvements in ICP-TOFMS are worth pursuing in future work.

Table I: NIST 612 Glass (21 elements, 5 replicates)

		Concentration (ppm)		
		<u>Measured</u>	<u>Certified</u> ¹	<u>Rel. Diff. (%)</u>
Mn	(⁵⁵ Mn ⁺)	44.1 • 4.9	(39.6)	11
Co	(⁵⁹ Co ⁺)	38.5 • 3.9	(35.5)	8
Ni	(⁶⁰ Ni ⁺)	44.0 • 4.1	38.8	13
Cu	(⁶³ Cu ⁺)	39.8 • 2.5	(37.7)	5
Rb	(⁸⁵ Rb ⁺)	35.5 • 3.6	31.4	13
Sr	(⁸⁸ Sr ⁺)	89.8 • 10.6	78.4	15
Ag	(¹⁰⁷ Ag ⁺)	24.0 • 1.2	22.0	9
Ba	(¹³⁸ Ba ⁺)	45.9 • 5.2	(41)	12
La	(¹³⁹ La ⁺)	41.1 • 4.6	(36)	14
Ce	(¹⁴⁰ Ce ⁺)	43.2 • 4.4	(39)	11
Nd	(¹⁴⁶ Nd ⁺)	40.3 • 4.5	(36)	12
Sm	(¹⁵² Sm ⁺)	44.0 • 5.3	(39)	13
Eu	(¹⁵³ Eu ⁺)	39.7 • 4.9	(36)	10
Gd	(¹⁵⁸ Gd ⁺)	45.4 • 5.1	(39)	14
Dy	(¹⁶⁴ Dy ⁺)	39.7 • 4.8	(35)	13
Er	(¹⁶⁶ Er ⁺)	45.4 • 5.1	(39)	16
Yb	(¹⁷⁴ Yb ⁺)	48.5 • 5.5	(42)	15
Au	(¹⁹⁷ Au ⁺)	16.9 • 1.9	(5)	237 ²
Tl	(²⁰⁵ Tl ⁺)	16.7 • 0.9	(15.7)	6
Pb	(²⁰⁸ Pb ⁺)	40.7 • 2.5	38.57	6
U	(²³⁸ U ⁺)	39.2 • 3.2	37.38	5

1. Non-certified values given in parentheses.
2. Note: Near LOD, baseline drift

Table II: NIST Urban Dust (18 elements, 5 replicates)

		Concentration (ppm)		
		<u>Measured</u>	<u>Certified</u> ¹	<u>Rel. Diff. (%)</u>
Mg	(²⁴ Mg ⁺)	970 • •260	(800)	21
Ti	(⁴⁸ Ti ⁺)	520 • •120	(400)	31
V	(⁵¹ V ⁺)	162 • •42	127 • •7	28
Cr	(⁵³ Cr ⁺)	604 • •234	403 • •12	50
Mn	(⁵⁵ Mn ⁺)	976 • •271	786 • •17	24
Fe	(⁵⁷ Fe ⁺)	4900 • •1400	3910 • •100	25
Co	(⁵⁹ Co ⁺)	22 • •6	(18)	24
Ni	(⁶⁰ Ni ⁺)	100 • •25	82 • •3	22
Cu	(⁶³ Cu ⁺)	727 • •218	609 • •27	19
Zn	(⁶⁶ Zn ⁺)	600 • •190	476 • •14	25
As	(⁷⁵ As ⁺)	151 • •42	115 • •10	32
Ag	(¹⁰⁷ Ag ⁺)	5.5 • •2.0	(6)	-9
Cd	(¹¹² Cd ⁺)	99 • •29	75 • •7	32
Sb	(¹²¹ Sb ⁺)	56 • •15	(45)	24
Ba	(¹³⁸ Ba ⁺)	958 • •251	(737)	30
La	(¹³⁹ La ⁺)	50 • •12	(42)	19
Ce	(¹⁴⁰ Ce ⁺)	69 • •19	(55)	26
Pb	(²⁰⁸ Pb ⁺)	800 • •240	655 • •8	22

1. Non-certified values given in parentheses.

Figure 1. PCA of glass fragments.

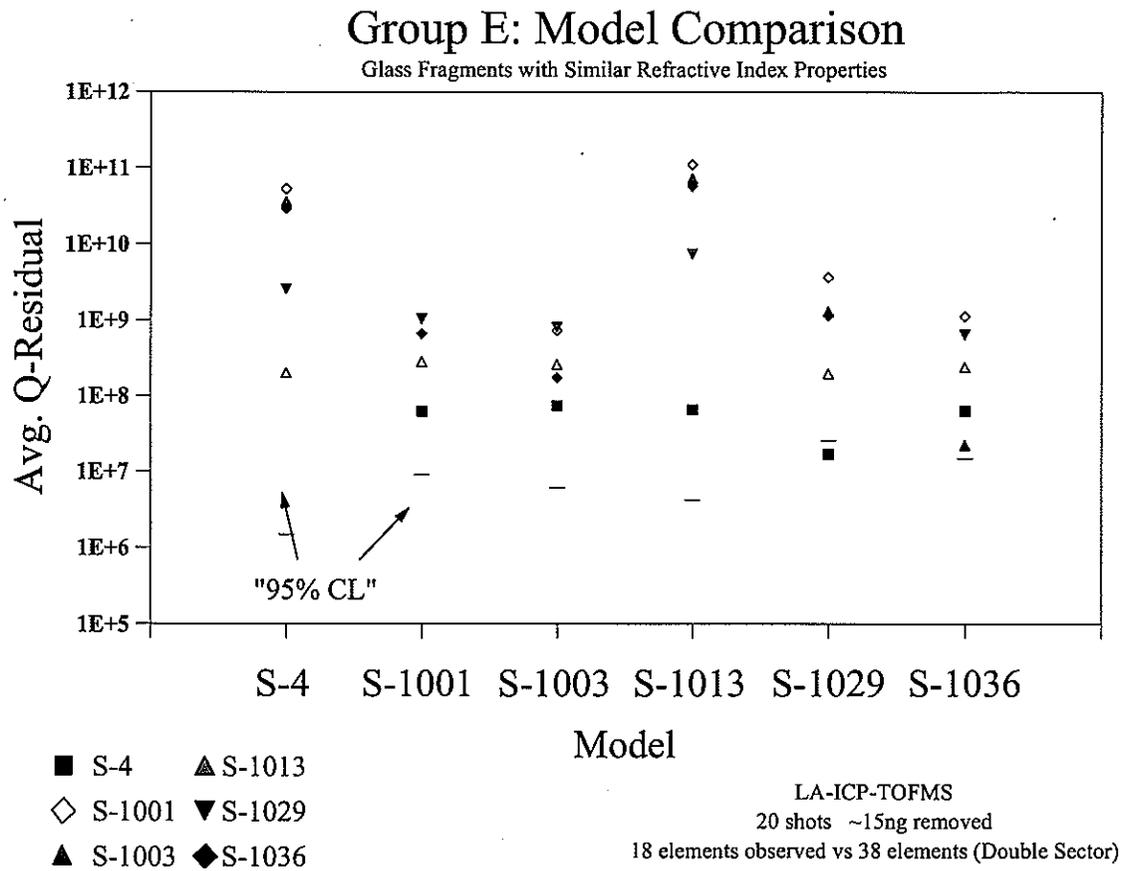


Figure 2. PCA of steel filings.

