DOCTORAL THESIS

Argon fluoride laser induced plume fluorescence for multi-element analysis: sensitivity and universality

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Argon Fluoride Laser Induced Plume Fluorescence for Multi-Element Analysis: Sensitivity and Universality

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Abstract

In 2005, our group first reported a two-pulse multi-element analysis technique that was both sensitive and minimally destructive. The first laser pulse ablated a thin layer of the sample over a hundred μm spot; the second laser pulse at 193 nm induced multi-analytes in the desorbed plume to fluoresce. Since then, this technique of laser-excited atomic fluorescence (LEAF) of ablated plumes, or PLEAF for short, had been applied to the analysis of aqueous lead colloids and metals. Sub ng/g and tens of atto-mole detection limits were demonstrated.

The non-selective photoexcitation in PLEAF was believed to be due to smeared energy levels of species in dense plumes. Smearing was especially severe for highly excited states such as those reached by 193 nm excitation. As the plumes subsequently expanded, the electronic structure of the plume species evolved adiabatically from a dense gas to that of an isolated atom with the electrons still in the excited states. Signature fluorescence from multi-analytes was therefore possible.

The suggested mechanism implied that ArF laser-induced PLEAF should be applicable to any sample matrix and any analyte as long as the species were imbedded in dense plumes and whose excited states could be reached by 193 nm photoexcitation. We therefore investigated the universality of PLEAF in this study by extending the analysis to ceramics, polymers, and their composites. We showed that these matrices could be successfully sampled and emissions from practically all analyte elements were observed. The detection sensitivity was orders of magnitude better than alternative laser spectrochemical probes such as laser-induced breakdown spectroscopy

(LIBS). Under minimally destructive conditions, emissions from Al, Ca, Co, Cr, Cu, Fe, In, Mg, Mn, Na, Pb, Sn, and Si were observed.

We also applied the technique to four practical problems: The analysis of dried paint for trace lead when μg/g detection limits were achieved; the analysis of valuable potteries when two look-alike specimens were differentiated based on practically non-destructive single-shot analysis; the elemental analysis of ink when lines written with different pens could be discriminated yet without discernable sample destruction even under the microscope; and the analysis of electrode-plastic interfaces when the detection sensitivity was comparable to SIMS. In some of these applications, we found that the fluorescence intensity varied with the fluence and the timing of the ArF laser pulse in ways suggestive of particulates in the plume.

Because nearly all analyte elements were excited in PLEAF, multi-analyte spectra were generated even in single-shot analysis. We showed that the rich spectral information contents could be fully exploited by chemometric techniques such as principal component analysis, SIMCA and K-means clustering.

In sum, the combination of PLEAF and chemometrics paved way for ultra-sensitive and minimally destructive multi-element analysis of complex samples. The analysis was all-optical and therefore could be done in air with no restriction on sample size. No sample preparation was needed. The analysis was fast, with a turn-around time of minutes. At the end, the sample was not visibly damaged even when examined under the microscope. If the ablation could be

congruent, 3-dimensional chemical profiling at tens to hundreds of μm lateral resolution and tens of nm depth resolution would be possible.