

Laser ablation of hard and soft materials – prospects and problems

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Abstract— Ablative laser technology (LA-ICP-MS) of solid samples is gaining popularity as a contemporary analytical technique. However, irradiation of soft samples presents a problem as they tend to splash and splatter, making analysis impractical. An original method has been developed in our research laboratory to ablate and analyze soft samples like pastes, gels and waxes. Samples were pre-treated with liquid nitrogen, petrified, and quickly analyzed before thawing set in. The technique has the potential to analyze soft samples, rapidly, without undergoing the tedious process of sample digestion. The technique functions by depth-profiling (petrified) soft samples to determine the elemental distribution within the matrix. An Nd:YAG deep UV (213-nm) laser ablation system was attached to a high-precision ICP-MS instrument. Irradiations were conducted with a flat-beam profile of 60% total energy and 50 μm beam diameter. The laser dwell time was 4 s; and repetition rate was 10 Hz. The laser ablated a total depth of 50 μm at 5 μm -intervals. Our hyphenated laser facility is capable of recording three-dimensional elemental profiles of soft samples (solidified), with minimal or no splashing effects. Elemental profiling is qualitative for heterogeneous solid targets due to the fact that matrix matched standards are generally not available for such variable matrices. However, quantitation is possible with homogeneous soft targets. The method is highly viable and makes a useful contribution to analytical science and to instrumental analysis, in general.

Index Terms— Laser ablation; depth-profiling; ICP-MS, gels/waxes/pastes; liquid nitrogen pre-treatment.

I. INTRODUCTION

Our research group has developed a creative method to examine the elemental profiles of soft samples like gels, pastes and waxes using the laser ablation technique. The laser technique is generally applied to the ablation of solid samples such as rocks, metals and core deposits. The ablated material is converted to the gaseous state followed by analysis using a tandem mass spectrometer. Several studies have successfully demonstrated the capability of laser ablation to profile solid samples [1-3]. Rapid analysis and minimal sample preparation are factors that make it a suitable option among a range of contemporary analytical techniques. Laser ablation studies of solids are generally qualitative or semi-quantitative due to the fact that matrix matched standards are difficult to find. However, quantitation can be potentially attained in ablation studies of soft samples. Advanced device control coupled with user friendly software tools facilitate regulation of laser parameters such as beam diameter, laser power, dwell time and repetition rate. The highly refined lasers available today make it easy to drill through the samples to

pre-determined depths by successive “hits”. The shape and size of the crater formed in the sample denotes the level of ablative uniformity as the beam delves deeper into the matrix. A well-defined crater (Figure 1a), often, indicates that the ablation is more or less uniform as the laser penetrates the sample. However, this is not always the case. Samples with a semi-solid or porous nature like certain oil well deposits, occasionally, result in craters filling up with debris falling back into the pit. Samples like polymers may experience splashing effects (Figure 1b) and this factor could result in poor ablation, especially if the beam parameters are not well controlled. But with well-defined and fine-tuned laser beams, it is possible to successfully profile the metal content in a wide variety of samples[4].

In addition to depth-profiling studies, the laser is also capable of spatial evaluation across a pre-defined grid on the sample surface (Figure 1c). Thus a rapid three-dimensional analysis is possible for advanced elemental profiling. Very few contemporary instrumental methods possess the depth-profiling capability of LA-ICP-MS [5, 6]. This factor is emblematic of the technique – to

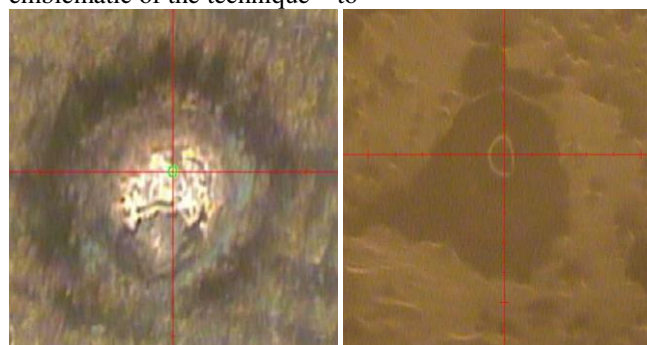


Fig. 1a. Screen shot of a well-defined crater

Fig. 1b. Screen shot of “splashing” effects in a gelatinous sample

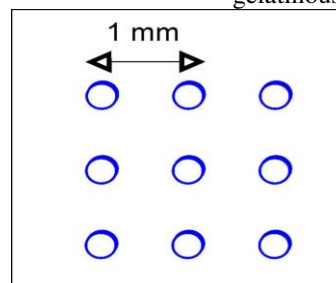


Fig. 1c. 9-point grid where the laser hits the sample delve to discreet depths below the exterior of a sample and to conduct uniformity studies in bulk materials [7-9]. ICP-MS is superior to its ICP-OES counterpart on account of its lower detection limits, higher sensitivity and enhanced interference suppressing capabilities[10, 11]. The multi-element capability and rapid scanning speed of the technique across the entire mass spectrum makes it a valuable analytical tool [12-14].

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II. MATERIALS AND METHODS

A. Liquid-nitrogen sample treatment / Instrumentation

Sample material (waxes, soft pastes) were procured from local retail outlets. As mentioned earlier, to complement the capability of the laser facility we have devised a novel sample introduction method for soft samples. Sample preparation was rapid and straightforward. Suitable soft samples were petrified instantaneously (Figure 1a), by briefly immersing in liquid nitrogen (99.99%, Air Products, Dubai, UAE) in a polystyrene container for about a minute, removed quickly with plastic tweezers and subjected to irradiation. The sample had to be quickly transferred to the laser ablation sample chamber (5cm x 5cm). The petrified samples remained intact in the solid form long enough to conduct the irradiation.

Laser irradiation with a micro-beam is independent of the shapes of the petrified samples (Figure 2a), which is an advantage. Different samples (waxes and pastes) tend to “thaw” at different rates. However, on average, samples remained petrified for about three minutes, which was adequate to conduct depth-profiling measurements to specified depths. Figure 2b represents a gel sample at the point of thawing in the sample chamber.

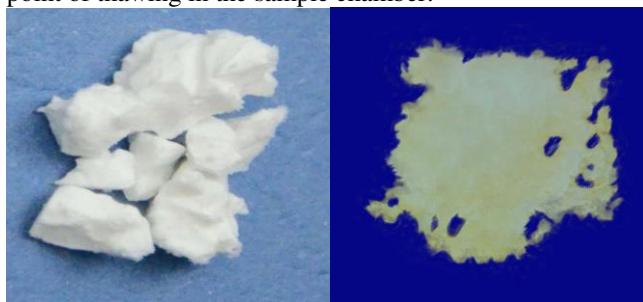


Fig. 2a. Petrified sample sample chamber

Fig. 2b. Point of thawing in of soft paste

Samples were investigated with a Perkin Elmer SCIEX DRC-e ICP-MS (Ontario, Canada) fitted with a New Wave UP-213 laser ablation system (Figure 3). Two high-vacuum diaphragm pumps and a turbo molecular pump in tandem provided the required ultra-high vacuum ($\sim 2.2 \times 10^{-6}$ Torr) within the mass spectrometer region. The unique quadrupole mass filter, typical of most ICP-MS instruments, ensured high selectivity and sensitivity[15]. The instrument also had a collision/reaction cell to curb matrix-related interferences. All petrified samples were placed in the special sample holder, flushed continuously with a stream of argon. Samples were subjected to 213-nm laser irradiation; the level of the beam energy was 60%, with a beam diameter of 55 μm . The laser was programmed to ablate successive depths of 5 μm at each point and is capable of penetrating the sample to a depth of about 50 μm . Additional beam characteristics were as follows: fluence at the sample surface: $\sim 4.5 \text{ J/cm}^2$; dwell time: 4 s; repetition rate: 10 Hz. The technique displays the elemental intensities in proportion to their concentrations, and produces an elemental profile. The study was qualitative in the absence of standardization and depth-profiling spectra were recorded for each measurement. Iterative scanning of the sample using a 9-point grid pattern (Figure 1c) distributed both horizontally and vertically across the sample surface was applied to determine spatial and depth dispersions. Gelatinous standards of matching matrix were not available for direct comparator analysis. However, a point to note is that although the current study was not quantitative, and undertaken mainly

to establish the viability of the approach with “soft” samples, quantitation with homogeneous soft samples is feasible [4]. The instrument was validated for precision, and repeatability data of less than 5% relative standard deviation were attained.

III. RESULTS AND DISCUSSION

A. “Soft” samples / “splashing” effects

Depth-profiling is an ultra-sensitive technique similar to ‘drilling’ through a sample to acquire information on metal dispersion with depth. The beam profile is usually flat-circular and can be broadened from 5 μm to 100 μm in diameter for greater spatial effect. Narrow beams act like hypodermic needles, pinpointing microscopic areas of interest. Clearly, the impingement of a high-powered laser on waxy or jelly-like samples is prone to “splashing” (or splattering) akin to forcefully throwing a stone into water. This “splashing” effect is not limited to upward splatter, but tends to scatter sample material on all sides of the sample chamber, which could result in clogging of the lines leading into the core of the instrument. Both broad and narrow beams produce “splashing” which limits the amount of sample material vaporized and transported to the plasma source – thus producing diminished and erratic signals (in the absence of clogging). Figure 1b represents a screen-shot of “splashing” from a typical gelatinous sample. It is clear from the image that splatter is unmistakable and is spread randomly in all directions. The spectra resulting from “splashed” samples are depicted in Figure 4.

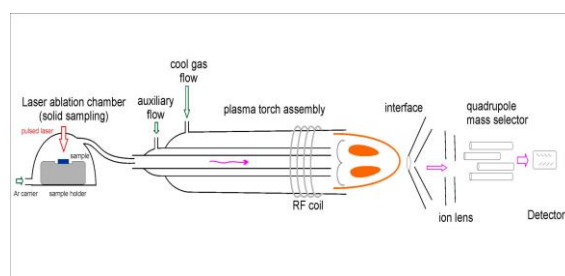


Fig. 3. Schematic diagram of the LA-ICP-MS system.

Observation of these spectra reveals that the format is highly intermittent, displaying mainly background, thus indicating that minimal sample material was transported to the plasma source. Figure 1a, on the other hand, represents a genuinely petrified sample ablated by a laser beam, resulting in a well-defined crater.

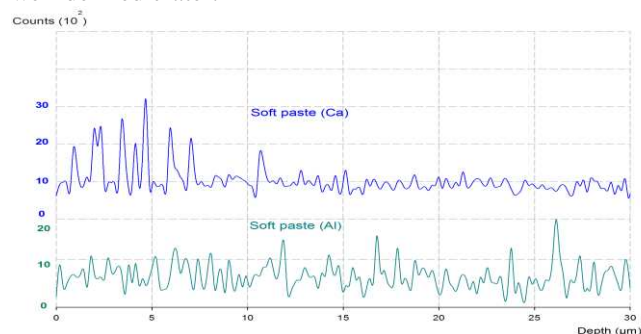


Fig. 4. Spectrum of a “splashed” paste sample showing erratic features

B. “Quick-frozen” samples / crater formation

As portrayed in Figure 2a, liquid nitrogen treatment of soft and gelatinous samples petrifies them (within seconds), thus leading to rapid phase-conversion of samples (to solids),

making them suitable for analysis by ablative laser technology. Compared to soft samples, solid samples tend to behave differently under ablation. “Splashing” effects are not observed. Instead craters are formed when the beam impinges the sample surface [9]. Gentle “sputtering” effects are observed, but the beam penetrates the sample with ease making depth analysis possible. As aforementioned, crater formation is not entirely without problems, and, re-filling of the crater with scattered material could produce a false sense of depth [1]. However, the prospects outweigh these minor difficulties; this particular problem is not significant and depth-related measurements are considered adequately accurate. Figure 1a is a screen-shot of distinctive crater formation. When compared to “splashing” in Figure 1b, it is evident that the features are easily distinguishable from splattering phenomena and dispersion of material is minimal. The laser could be also be programmed for surface analysis to irradiate spatially across a 9-point grid (Figure 1c). Time-dependent spectra (depth-profiles) recorded for paste and wax appear in Figures 5a-c. Minor peak broadening was attributed to inconsistent laminar flow of the vaporized material through the system *en route* to the mass spectrometer [16]. Compared to the spectrum depicting “splashing” in Figure 4, it is clear from the features of Figures 5a-c that the accumulation of data in petrified samples is identical to the process with solid samples [4]. This demonstrates that depth-profiling is viable with the liquid nitrogen pre-treatment approach, and can be applied on a routine basis. Thawing sets in after about 3 minutes and this is immediately observed as a sudden change from crater formation to “splashing” visible on the computer-screen of the instrument.

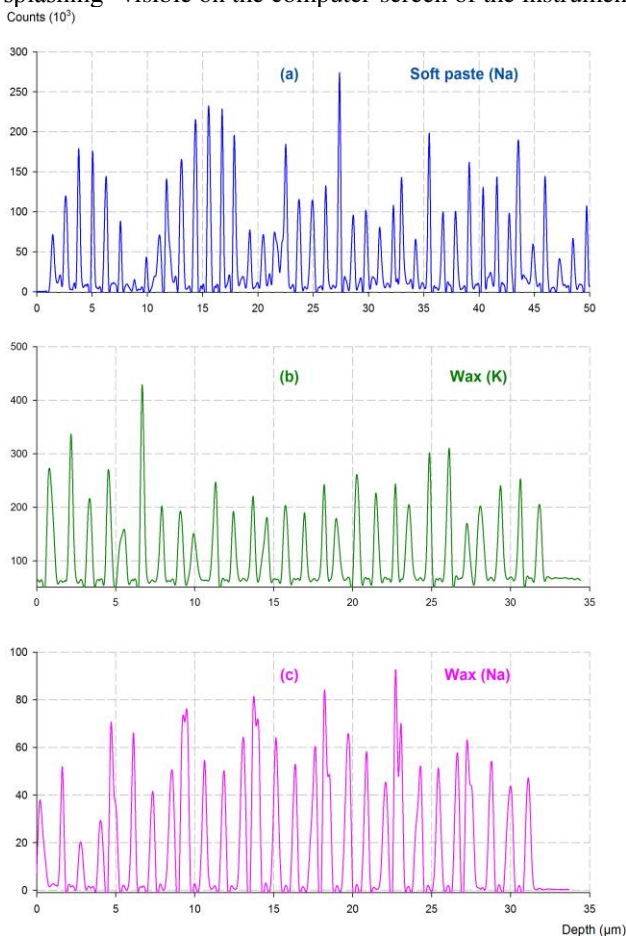


Fig. 5. Typical depth-profiling spectra from samples of paste and wax

C. Sample uniformity / “hotspots”

The primary contribution of the liquid nitrogen approach is to provide a means for direct multi-elemental analysis in such samples and also, to study sample uniformity, which reflects the level of mixing of additives. Many of these samples contain added chemicals as preservatives. Thus, it is necessary for these additives to be perfectly mixed into the material. Incomplete mixing could affect the distribution of the additive, which could result in undesirable consequences such as intermittent hardening or formation of lumps in parts of the sample. Figure 5c shows the distribution of Na in soft wax. The peak heights in the spectrum do not vary dramatically suggesting that, within experimental limits, this element is more or less evenly distributed with depth. The Na signal intensities (counts in Figure 5c) average out at about 50000-70000, and the level of homogeneity could represent the degree of uniformity of mixing in the material. Imperfect mixing could result in the sudden appearance of “hotspots” (intense peaks), Fig 6, with depth. Alternatively, these ‘hotspots’ could result from extraneous infiltration of impurities into the matrix either through sample processing or leaching from the container in which it is packed. Thus, our approach could also be used to quickly establish toxicity in “soft” samples.

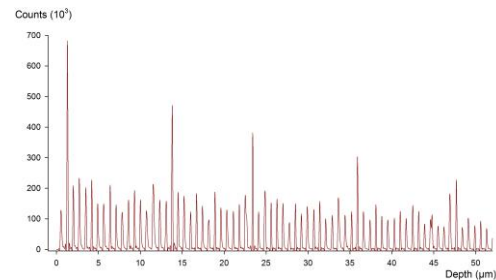


Fig. 6. Hot spots

D. Asphaltenes

Asphaltenes (Fig 6) is another area where this approach could be suitably applied especially to obtain V/Ni ratios that are needed in a range of such samples. This bypasses the time-consuming process of sample dissolution and preparation of aqueous solutions for analysis. The most prominent trace metals in asphaltenes are V and Ni. Figure 8 - depth- profiling spectra of Ni, V, superimposed, hard asphaltene sample, no liquid nitrogen treatment, single ablated spot - indicates that these elements tend to occur concurrently, although the Ni spectrum depicts three sharp lines at about 16, 21 and 23 μm, denoting the absence of vanadium. These isolated Ni lines could be emblematic of either nickel impurities or random nickel-porphyrins. The correspondence between the spectra at depths of 0-16 μm and 36-48 μm suggests the possibility of V/Ni cluster complexes. The V spectrum looks ‘erratic’ between 20 and 35 μm, which could be due to certain matrix phenomena or unknown interferences in the proximity of V - not present in the vicinity of Ni. A comparison with our technique on soft asphaltenes using liquid nitrogen treatment, corroborated these phenomena [17].

E. Impact of the study

The liquid-nitrogen approach makes laser ablation studies of waxy and soft samples feasible. The work could be extended to pharmaceuticals and crude oil and other soft samples. Pharmaceutical gels and soft body tissue and organs can be

now be directly profiled by laser ablation following solidification with liquid nitrogen. Our research, therefore, established the need for production of suitable “soft” high-quality certified standards for a variety of applications. The scope of this work could extend to clinical gels/pastes/creams and medical specimens where rapid depth and spatial analysis could be accomplished to establish material homogeneity and toxicity. With a higher frequency of beam pulses it may be possible to attain greater depths ahead of thawing.



Figure 7: Asphaltene sample

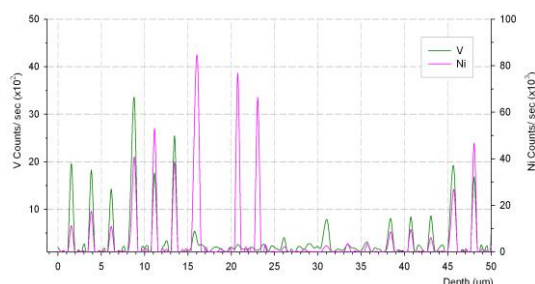


Figure 8: V/Ni in asphaltene

IV. CONCLUSIONS

The study demonstrates the successful application of liquid nitrogen to rapidly solidify gelatinous samples prior to laser ablation. This approach is convenient, facile, and adapts itself to direct multi-elemental analysis, thus obviating the tedium of converting such samples to aqueous solutions. The technique can be extended to establish homogeneity/toxicity in a wide variety of samples, including pharmaceutical creams/waxes and biomedical specimens. It could also be applied in food analysis and to soft polymers, such as visco-elastic gels.

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