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Deep-UV Ablative Laser Technology: A Technical Review

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Review Article

ABSTRACT

Ablative laser technology has been used successfully as a tool in scientific applications particularly to evaluate the homogeneity of materials and to depth-profile samples with the object of attaining elemental distribution at subsurface levels. Pulsed micro-beams strike a target with pinpoint accuracy and produce trace elemental information both spatially and in the substrate. Exploring different strata of a sample can produce data on impurities buried deep within the sample matrix. This is particularly important in cases where hidden impurities can make a difference to the performance of certain samples, such as semi-conductors or biomedical specimens. Stochastic effects such as imperfect crater formation, erratic energy pulses and unpredictable drift in beam energy could significantly affect the results of research applications. These technical features are controlled by sophisticated software, which plays a salient role in stabilizing the instrument. Samples are usually heterogeneous in nature, such as rocks, reservoir cores and concrete structures, and sample heterogeneity, therefore, is a factor that precludes adoption of conventional protocol for standardization of the technique. Soft samples such as gels and waxes could undergo standardization under special conditions. However, the technique is largely semi-quantitative for solids and is particularly attractive for exploring the homogeneity of solid targets, which reflects the level of elemental distribution within the sample matrix. The laser unit is coupled to a Perkin Elmer ICP-MS instrument and maintenance of consistent operation parameters is crucial for accurate and reproducible results. The laser beam wavelength is in the deep UV region and the system is operated with a beam of 213 nm of variable diameter between 5-100 μm, gas flow of 0.8 L/min, energy pulse rate of 60 MHz, and beam energy between 30-60%. Compared to other current instrumental techniques, ablative laser technology is superior for depth-profiling and surface analysis.

Keywords: Laser ablation, Heterogeneity, Soft samples, ICP-MS

INTRODUCTION

Research in the area of laser ablation technology (LA-ICP-MS) is particularly useful for specific applications, including particle-size measurements [1], geochronology applications [2-4], nuclear studies and bio-imaging of metals [5-10]. The technique is attractive because of the following features: (i) limited sample preparation; (ii) depth-profiling potential; (iii) surface analysis; (iv) homogeneity/distribution studies; (v) solid and soft target capability; and (vi) rapid acquisition of elemental data. The instrument employed in our research program consists of a 213-nm deep-UV laser unit attached to an ICP-MS system (inductively coupled plasma mass spectrometer) that operates at 40 MHz with an argon gas flow of 0.8 L/min. The laser radiation is in the form of a micro-beam that can expand in diameter from a "pencil" beam of 5 μm to a wider shaft of 100 μm. The pencil beam is highly practical for pinpointing inclusions within a target. The wider beam can be used to scan surfaces for spatial information. The beam itself can be pulsed or continuous. A pulsed beam is more applicable for depth profiling studies as each burst tends to "drill" deeper into the sample with greater impetus. The energy of each pulse can be controlled by software. Pulsed beams tend to vary in energy from 30% to 60%, depending on the hardness of the sample. Thus the laser can be envisaged as a "drilling" tool for accumulation of sub-surface data. As will be discussed later in this article calibration or standardization of analytical applications tends to be difficult due to wide heterogeneity of sample composition. As a result the procedure adopted is to calibrate the ICP-MS with certified

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standards for satisfactory performance [11-13]. This is an acceptable procedure as the final analysis is accomplished within the plasma and optical region of the ICP-MS and detection is achieved via quadrupole selector system and electron multiplier detector (**Figure 1**). The actual operation of the laser is as follows: the beam vaporizes a point on the target and this vapor is transported to the hot plasma (6000 K) where it is atomized, ionized, and the ensuing ions are swept through the instrument and selectively directed to the detector under an operational electromagnetic field provided by the electrostatic lenses (ion optics) and quadrupoles. The laser chamber itself is a specially constructed sample holder that is swept with gas flow of 0.8 L/min. Sample dimensions can reach up to 5 cm x 5 cm. Minimum sample handling of solid targets makes the technique particularly attractive. Solid and soft targets have been analyzed with considerable accuracy both spatially and within the sample matrix. Compared to similar current instrumental techniques the laser technique dominates in terms of sample handling and analysis time. XRF and charged particle beams [14,15] require sophisticated hardware and sample preparation. Overall, laser ablation is recommended for specific applications such as depth profiling and elemental distribution studies.

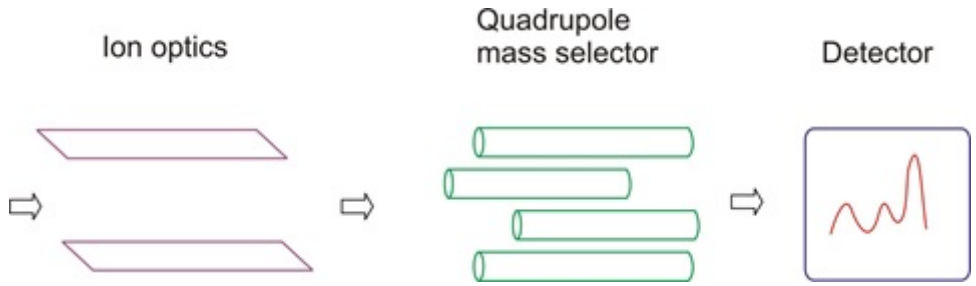

Figure 1. A Schematic of the optical and mass selector unit.

Pulsed Energy Beam, Depth Profiling and Time Spectra

Pulses of varying energy can be generated to penetrate successive strata in solid samples (depth profiling) [16-20]. The level of energy is pre-selected and as in the general case of attenuation of photon beams in matter the actual depth profiling is dependent on the density of the target. Metals with increasing densities such as aluminium, iron and lead would evidently require more energetic pulses to achieve specific depths. The point reached below the sample surface can be estimated by penetrating a thin copper or mastic film (for example) of known thickness (say 30 μm) and density resting on a metal substrate (for example iron). The time taken for a beam of pre-selected pulse to reach the substrate provides the necessary information relating depth as a function of energy. As a result time spectra can be converted to depth spectra. This is illustrated in **Figure 2** below where a thin film of mastic on an iron substrate was subject to laser irradiation. The substrate is reached at the point of peak formation on the spectrum and it is clear from the plot that the relationship between depth, pulse-energy and time can be estimated directly from parameters associated with the spectrum. Similarly, a polymer sample was probed for determination of metal inclusions at sub-surface levels. The depth profile was estimated as described above.

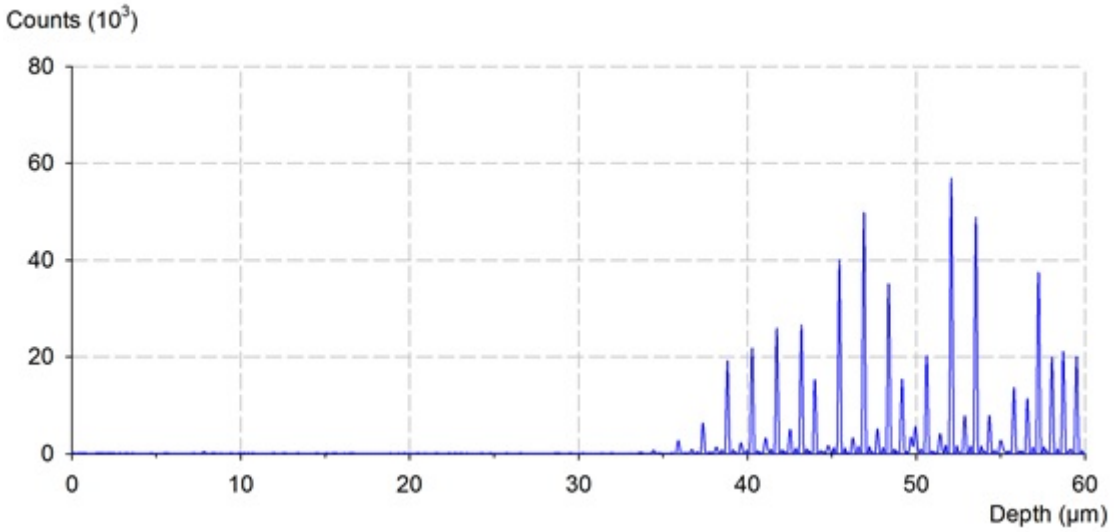

Figure 2. A Typical time spectrum.

It is useful to calibrate an ablative laser instrument by irradiating samples containing successive strata of pure metal films (of pre-determined thickness) with increasing energy pulses. This is a practical method to calibrate the system. For

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example a multiple thin film arrangement of aluminium resting on copper, iron and lead can provide useful data on energy versus density and thickness. This is part of our future work and could serve as a baseline reference for laser ablation studies.

Crater Formation

As depicted in **Figure 3**, the impact of each pulse results in the formation of a circular crater with a furrow-like border [6,21]. The beam itself vaporizes the point of impact leaving a pit which becomes deeper as more pulses strike it.

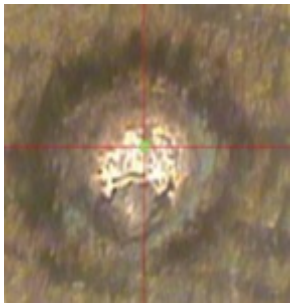

Figure 3. Crater formation during laser ablation.

Depth-profiling is jeopardized by debris from the "furrow" falling into the crater or pit. This could create a problem in delving to accurate depths. However, it was noted that this phenomenon could be marginal if the sweep gas or flow gas through the laser chamber is at the correct flow level to sweep away minute particles of debris leaving a "clean" crater. Typical flow gas levels are in the range 0.4-0.8 L/s. Evidently, penetrating depths at successive intervals, (10 μm for example), will lead to formation of more debris at each level. Selecting even lower penetration intervals, (5 μm for example) could lead to greater debris formation. No work has yet been conducted on the level of debris formation as a function of varying depth penetration interval. This is a delicate task and would require collection of the debris for mass or size estimation (if possible). Not much deliberation has been given to methods for clean crater formation and this could form part of a future study.

Spatial and Surface Studies

Laser ablation coupled to a highly sensitive ICP mass spectrometer had been widely used for spatial and surface analysis of various materials; the technique is rapid and does not require lengthy sample preparation [22-24]. **Figure 4** delineates a grid along which the laser traverses and serves as a useful irradiation plan for both surface and depth studies. For surface studies alone a controlled depth of 5 μm is attained by programming the instrument to provide energy bursts at a pre-selected level; and high precision to a distance of 1 mm between points is currently available for this research application [25,26].

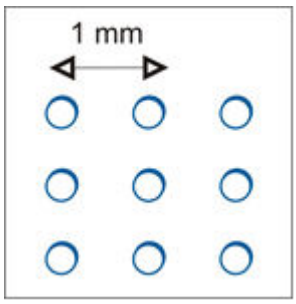

Figure 4. Typical laser grid for surface and depth studies.

In this particular case crater formation is not beset by continual debris formation and valuable trace elemental information could be gleaned by scanning the surface of a solid target (**Figure 5**). This particular technique is beneficial in thin film semi-conductor studies and biomedical investigations [4] (stents for example) where it is imperative that the surface of the sample is devoid of unwanted impurities. The advantage is that the method can acquire information rapidly, albeit qualitative data, and within minutes a spectrum provides results on trace impurities. For a typical hard target, peaks are identified by a directory built into the instrument. Other contemporary techniques such as XRF or even charged particle irradiations cannot accomplish accurate surface studies largely because depth control could be difficult to achieve. One interesting way of monitoring pollution control is to ablate the surface of leaves and the rind of fruit from areas suspected of rising pollution. The traces of metals and metalloids (such as arsenic, lead, cadmium, selenium, mercury) appearing on the surface of such specimens is an ideal indicator of rising pollution, especially if such

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environmental samples are monitored at regular intervals. The use of insecticides and pesticides containing undesirable trace metals are immediately detected [8].

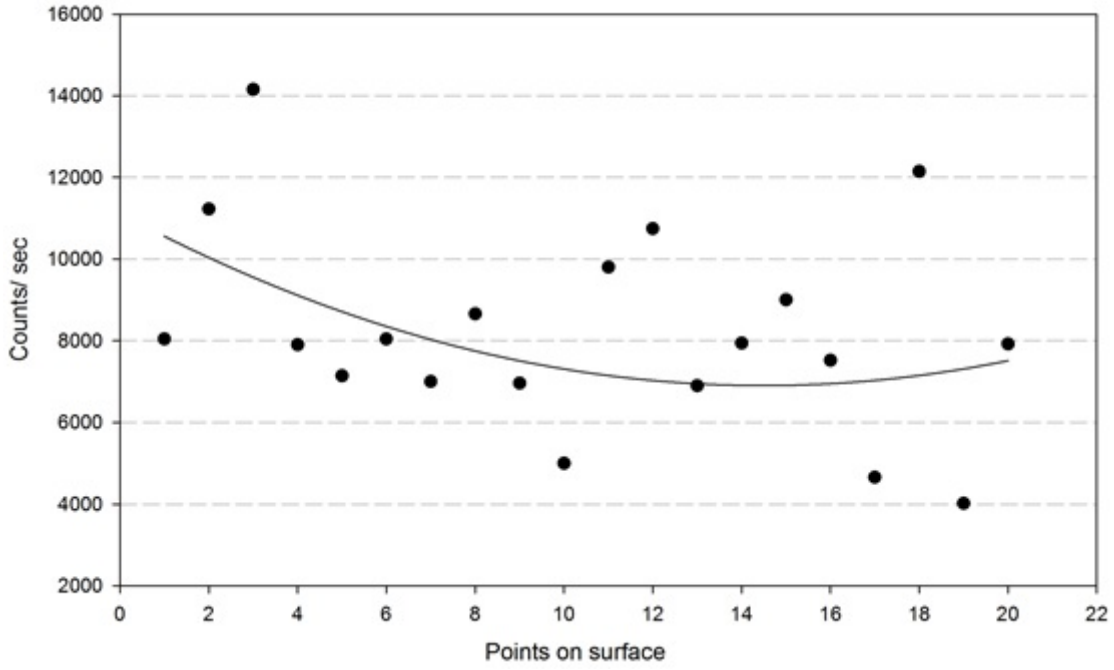

Figure 5. Surface study of a polymer sample doped with traces of Zinc.

Solids and Soft Targets

It is well known that ablative laser technology is deployed for solid targets [25,26]. Soft targets such as slurries and gels present a problem because the impinging laser energy pulse tends to spatter the sample, which results in diminished signal pulses and leads to impractical analysis. This problem has been remedied by hardening the soft sample by immersing in liquid nitrogen for a short spell and quickly transferring the solidified target to the laser chamber for irradiation [27-29]. The integrity of the solidified sample can be easily monitored by the absence of splashing and the appearance of a crater akin to those that appear in actual solid targets.

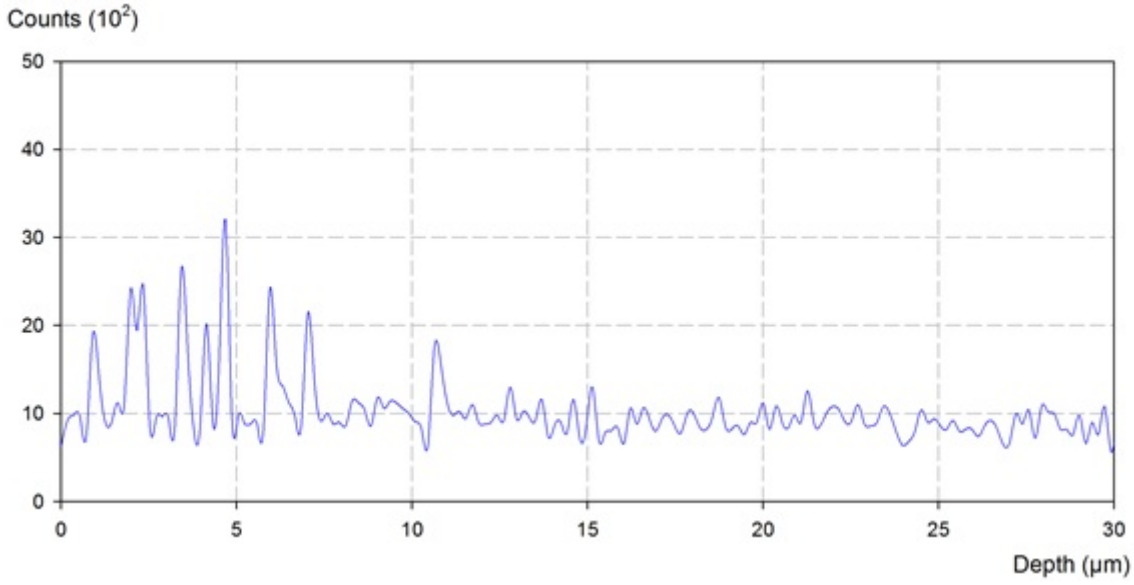

Figure 6. Erratic spectrum of soft target reflects “splashing” effects.

Figure 6 represents a spectrum from a gel. It is clear from this spectrum that it is of low quality with erratic peaks that correspond to “splashing” in the sample. After immersion in liquid nitrogen, the sample produced an unblemished crater indicating that the target is satisfactory for irradiation. One problem that arises in this method of solidification in liquid

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nitrogen is that after a brief period (about 3 minutes) the sample thaws. Transfer to the laser chamber and irradiation must be quick to obtain reproducible results. The degradation of the solid sample as it changes phase can be seen as melting. This is also obvious as the screen-shot of irradiation in **Figure 7** shows "splashing" in the form of a blotch rather than a solid crater. One major advantage of petrifying a soft sample such as homogeneous gels or waxes is that the solidified target is homogeneous and suitable for standardization. Slurries on the other hand could form incomplete aggregates on hardening and this particular aspect of slurry investigation lends itself to further study.

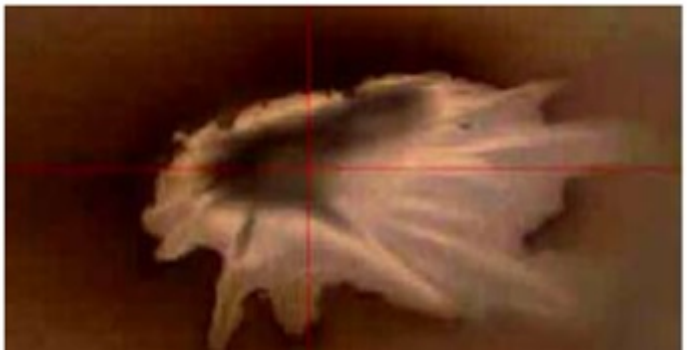

Figure 7. A screen shot of the "splashing" effect.

Homogeneity, Heterogeneity and Standardization

A primary advantage of ablative laser technology is that it is a useful contemporary tool for predicting homogeneity of solid samples both at varying depths and spatially. Distribution of trace metals at successive strata within a sample matrix provides valuable information on the presence and/or absence of inclusions in the target and could possibly provide vital clues as to the mechanism of such inclusions. A good example is the location and estimation of the dimensions of pore throats and aqueous inclusions in geological samples from oil reservoirs (**Figure 8**) [30]. Other known techniques tend to experience difficulty in achieving such measurements and the laser ablation technique demonstrates its superiority in evaluating such parameters. In the case of exploring homogeneity, an excellent example was our study of the distribution of metals purposefully loaded in homogeneous polypropylene samples (**Figure 5**) [31]. The results revealed that there was an uneven distribution of these additives with depth indicating clearly that the process of mixing these polymers was imperfect and could be improved. On the other hand a soft target such as wax was solidified by liquid nitrogen treatment and analyzed [32]. **Figure 9** represents the detected sodium in the wax sample, and the constancy in the heights of the peaks with depth reflects a broadly even distribution. Soft asphaltene samples, however, produced results that were decidedly divergent. **Figure 10** depicts the wide scatter of points with depth in a soft asphaltene sample that was irradiated under solidification. This spread of results denotes categorically that the technique is ideal for establishing inhomogeneity in samples, which is necessary for predicting formative and primeval processes in geoscience.

Figure 8. Reservoir core samples.

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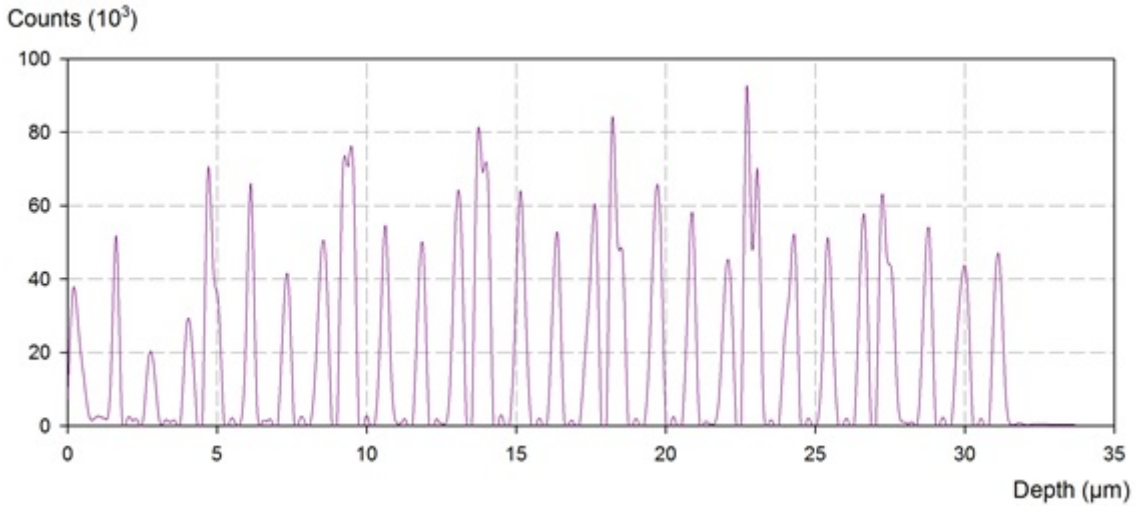

Figure 9. Laser spectrum of a wax sample showing regularity of sodium peaks.

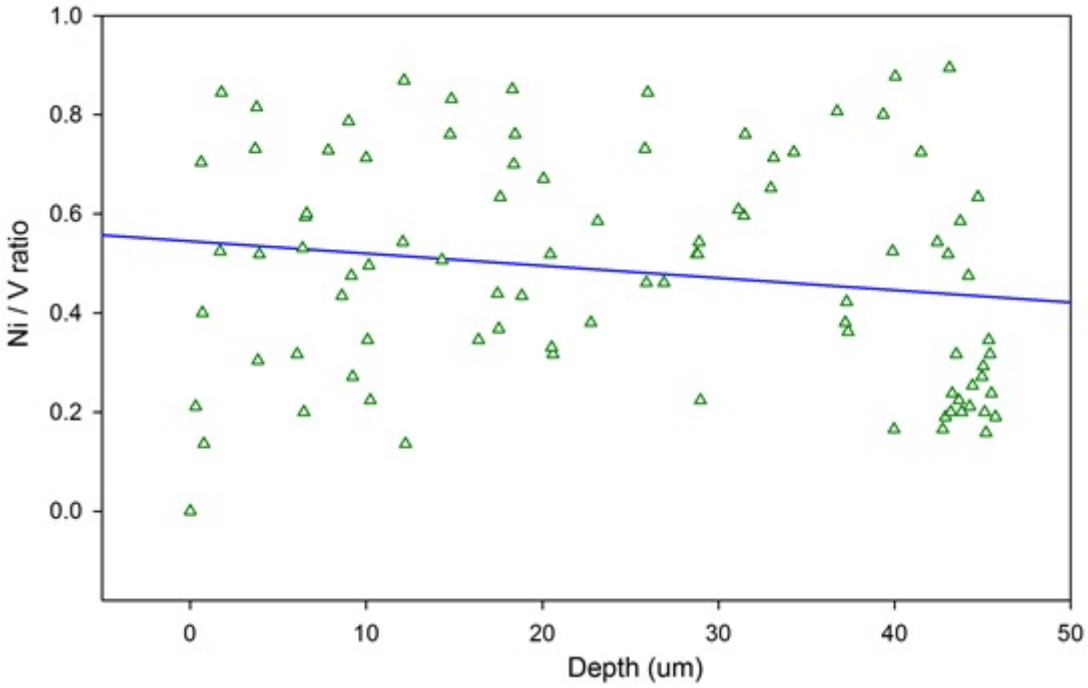

Figure 10. Wide scatter of data in a soft asphaltene sample.

Heterogeneity is a significant drawback for the simple reason that this particular feature makes standardization difficult and in some cases impossible. It is not easy to obtain reference standards of similar density and caliber for purposes of comparison. For example geological specimens such as reservoir cores and oil samples such as asphaltenes differ greatly in density and character and therefore, preparing or procuring specific standards for such highly heterogeneous targets is not possible. For this reason the analytical determination is largely semi-quantitative.

Depth profiling using LA-ICP-MS allows us to assess heterogeneity by tracking traces of certain transition elements (Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn) and toxic trace elements (As, Be, Cd, Hg, Os, Pb) in existing concrete structures erected offshore [11]. This assumes significance due to the fact that such toxic trace elements could be gradually released into the ocean, as parts of these structures are submerged in seawater. The released toxins could eventually pollute and harm marine life.

With fine tuning of the mass spectrometer, the concentration of chloride ions could also be tracked and relevant information could be provided using this tool to prevent costly corrosion damage [9]. These data could be useful for any construction in general and for offshore oil rigs in particular.

A level of standardization could be achieved for homogeneous gels and waxes, and part of our research program is to pursue the preparation of standards for this purpose. Alternatively, certified reference standards could be procured for some soft samples, such as toothpaste, but for others such as certain waxes and gels home grown preparation of standards taking into account the precise density of the material could be more appropriate.

CONCLUSION

The technical aspects of ablative laser technology (coupled to ICP-MS) were presented and some of the merits and drawbacks of the technique were discussed. A general comparison with other contemporary analytical techniques reveals that the laser is an ideal tool for depth-profiling studies and equally suitable for examination of surfaces. There are some difficulties that must be overcome especially with soft targets and it was shown that such soft samples can be solidified with liquid nitrogen and thus irradiated in the solid phase. Standardization is an obstacle that has yet to be overcome, largely because of the inhomogeneity of many solid environmental and rock samples. The ablative method is ideal for determining the level of homogeneity in samples that are considered to be of consistent composition. Some future work could involve surface studies of leaves and fruit; and obtaining hard information on depth-energy algorithms. Depth-profiling of low-level radioisotopes in meteorites could be another area for future exploration.

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