

RAPID LIQUID NITROGEN PRE-TREATMENT OF GELS, WAXES AND PASTES FOR DEEP-UV DEPTH-PROFILING STUDIES (ICP-MS)

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ABSTRACT

A rapid procedure involving liquid nitrogen pre-treatment of gelatinous samples prior to laser ablation was developed. Laser depth-profiling is usually limited to solid samples. Our technique with liquid nitrogen pre-treatment provides the unique capability to study elemental profiles in gels, waxes and “soft” samples. A range of samples including globules of hair gels, face creams, toothpaste and soap were petrified in aliquots of liquid nitrogen and immediately subjected to laser irradiation. The study was largely qualitative to demonstrate the potential of the pre-treatment approach. This format lends itself to direct multi-elemental analysis and obviates the tedium of digesting samples in mild acidic media. Depth-profiling was limited to specific depths, and rapid spatial and sub-surface distributions of metal components in the petrified samples were achieved well before “thawing” set in. 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 55 µm diameter. The laser dwell time was 5 s and the repetition rate was 10 Hz. Following iterative surface scanning on a 9-point sample grid, the laser ablated a total depth of 25 µm at 5 µm-intervals at each point. The experimental results showed promise and the distinct capability to record spectra in the absence of “splashing” effects. This pre-treatment approach is, therefore, highly viable, and a useful contribution to analytical science and instrumental analysis.

Keywords: ICP-MS, depth-profiling, gels/waxes/pastes, laser ablation, liquid nitrogen pre-treatment.

INTRODUCTION

Our group has developed a rapid procedure of ablating gelatinous samples (gels/pastes/waxes/creams) with a high-precision deep-UV laser (213nm) following swift solidification by immersion in liquid nitrogen. Liquid nitrogen pre-treatment of such samples produces a perfectly solid sample whose material characteristics are suitable for depth-profiling studies. The petrified samples were brittle and fractured into discrete fragments under stress. Normally, laser ablation is limited to hard solids (that can resist deformation) and studies of such “jelly-like” samples are usually not possible because of “splashing” effects. “Splashing” is a phenomenon that describes splattering of sample material at the point of impingement of the laser with the sample surface. The laser itself is linked to an ultra-sensitive ICP-MS instrument, which has overtaken the capability of the most sophisticated ICP-OES system (Williams and Pillay, 2011). The technique lends itself to direct solid analysis – in the absence of longwinded sample preparation procedures. It is also multi-elemental and capable of high-resolution detection over a wide range of elemental levels (Ammann, 2007; Williams *et al.*, 2012; Robinson *et al.*, 2005; Ghosh *et al.*, 2010; Pillay *et al.*, 2009; Fok *et al.*, 2011). Very few contemporary instrumental methods have the capability to study metal intensity with depth

(Pillay *et al.*, 2010). X-ray methods are useful, but lack the ability to control depth penetration. Nuclear particle irradiation, SEM, SIMS and XPS are equally useful, but such techniques tend to be limited to only a few microns below the surface. Depth-profiling is essential in certain material science studies to acquire fundamental information on sample homogeneity and elemental dispersion in substrates and strata with depth (Ghosh *et al.*, 2010; Pillay *et al.*, 2011). Uniformity of elemental distribution both spatially and depth-wise can be distinctly accomplished by iterative scanning with a high-precision laser beam. The competence, therefore, of the laser approach to delve to discrete depths below the surface of a sample is attractive for uniformity studies in bulk materials (Bassioni *et al.*, 2010; Elkadi *et al.*, 2010; Pillay *et al.*, 2010; Perkins *et al.*, 1993). The aim of this work, therefore, was to develop an approach to apply laser ablation to gelatinous samples following liquid nitrogen pre-treatment. The study was largely qualitative in nature to demonstrate the potential of the pre-treatment approach.

MATERIALS AND METHODS

Liquid-nitrogen sample treatment / Instrumentation

Sample material (hair gels/waxes, toothpaste, and body creams) were procured from local retail outlets. Sample

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preparation was rapid and straightforward. Blobs of each sample were submerged in liquid nitrogen (99.99% pure, Air Products, Dubai, UAE) in a polystyrene container for about a minute, petrified, removed quickly with plastic tweezers and subjected to irradiation. Laser irradiation with a micro-beam is independent of the shapes of the petrified samples (Fig. 1a), which is an advantage. Different samples (like gels and pastes) tend to “thaw” at different rates. However, on average, samples remained petrified for about 3 minutes, which was adequate to conduct depth-profiling measurements to specified depths. Figure 1b represents a gel sample at the point of thawing in the sample chamber.

Samples were investigated with a Perkin Elmer SCIEX DRC-e ICP-MS (Ontario, Canada) fitted with a New Wave UP-213 laser ablation system (Fig. 2). The petrified samples were placed in a special sample holder with

dimensions 5 cm × 5 cm. 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 ablated successive depths of 5 μm at each point and penetrated the sample to a depth of about 25 μm. Additional beam characteristics were as follows: fluence at the sample surface: ~4.5 J/cm²; dwell time: 5 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 distributed both horizontally and vertically across the sample surface was applied to determine elemental spatial and depth dispersions. Gelatinous standards of matching matrix were not available for direct comparator analysis. However, a point to underscore is that the current study



(a)



(b)

Fig. 1. Image of a) petrified sample of face cream, and b) point of thawing in sample chamber.

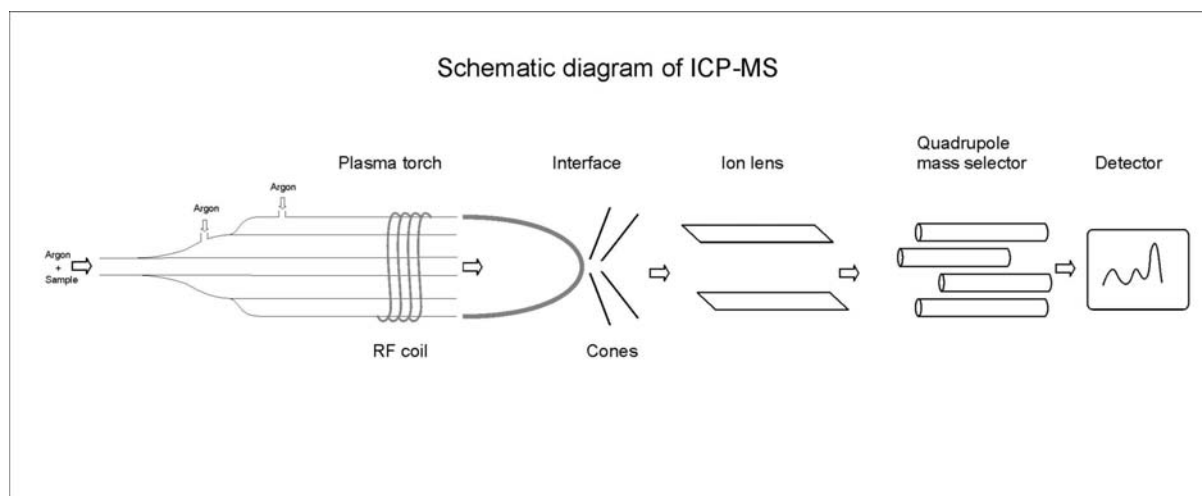


Fig. 2. Schematic diagram of the LA-ICP-MS system.

was not quantitative and undertaken mainly to establish the viability of the approach with “soft” samples. It was, nevertheless, essential to establish the analytical performance of the facility, which was accomplished as reported previously (Williams *et al.*, 2012). Accordingly, the instrument was validated for precision and, consequently, repeatability data of less than 5% relative standard deviation were attained.

RESULTS AND DISCUSSION

“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 10 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 3 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 spectrum resulting from a “splashed” sample is depicted in figure 4. Observation of this spectrum tells us that it is highly intermittent, showing mainly background, thus indicating that minimal sample material was transported to the plasma source.

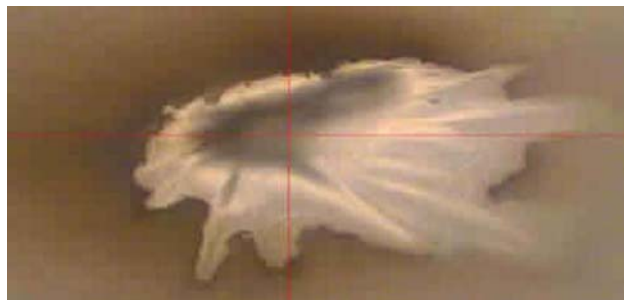


Fig. 3. Screen-shot of “splashing” effects in a gelatinous sample.

“Quick-frozen” samples / crater formation

As portrayed in figure 1a, liquid nitrogen treatment of ceraceous and gelatinous samples petrifies them (within seconds), thus leading to rapid phase-conversion of samples, making them suitable for analysis by ablative laser technology. Solid samples behave differently under ablation. “Splashing” effects are not observed. Instead craters are created at the point of impact of the beam with the sample surface (Momma *et al.*, 1996). Mild “sputtering” effects are observed, but essentially the beam delves through the sample making depth-analysis

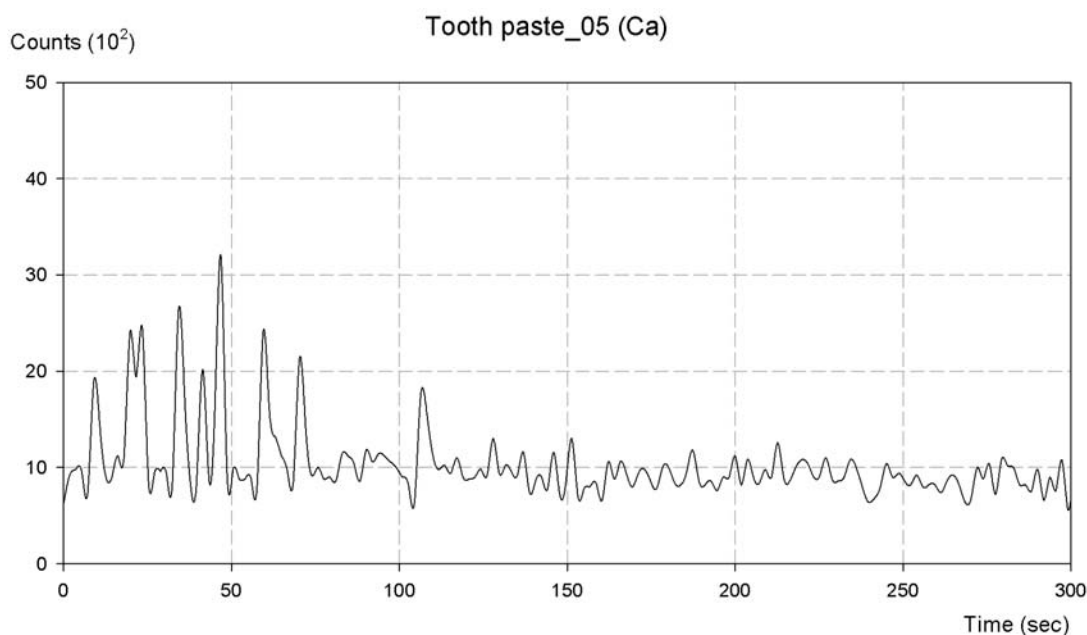


Fig. 4. Spectrum of a “splashed” gelatinous sample showing erratic features.

possible. Of course, crater formation comes with its own difficulties, and, as reported in a previous paper, partial re-filling of the crater with scattered material could give a false sense of depth (Pillay *et al.*, 2011). However, this particular phenomenon is not pronounced and depth-related measurements are considered adequately accurate. Figure 5 is a screen-shot of typical crater formation. When compared to “splashing” in figure 3, it is evident that the features are easily distinguishable from splattering phenomena and dispersion of material is minimal. Time-dependent spectra (depth-profiles) recorded for toothpaste, hair wax and hair gel appear in figure 6a-c. Minor peak broadening was attributed to inconsistent laminar flow of the vaporized material through the system en route to the mass spectrometer (Venable and James, 2001). Compared to the spectrum depicting “splashing” in figure 4, it is clear from the features of figure 6a-c that the accumulation of data in petrified samples is akin to the process with solid samples (Williams *et al.*, 2012). This demonstrates that depth-profiling is viable with the liquid nitrogen pre-treatment approach. 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.

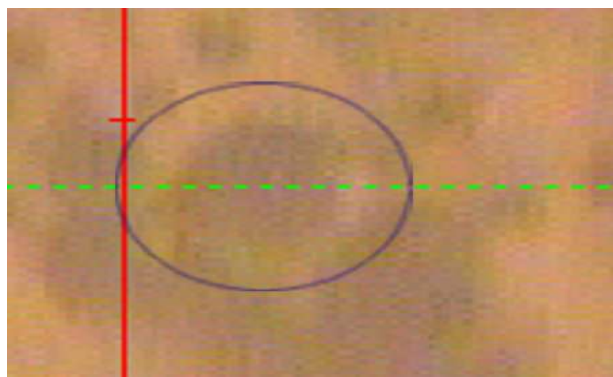


Fig. 5. Screen shot of crater-formation – pale area around the dark patch (in circle) represents the furrow of the crater.

Homogeneity / “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 homogeneity, which reflects the level of mixing of additives. Many of these cosmetics and toiletries contain added substances to satisfy certain nutritional or health purposes. Thus, it is necessary for these additives to be perfectly mixed into the material. Imperfect mixing could result in poor distribution of the additive, which in turn could produce other effects such as sporadic hardening or formation of lumps in parts of the sample. Figure 6c shows the distribution of Na in hair gel. 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 6c) average out at about 50 000-70 000, and the level of homogeneity could reflect the degree of uniformity of mixing in the material. Imperfect mixing could result in the sudden appearance of “hotspots” with depth. For example, figure 7a-c displays Al, Ti and Sr ‘hotspots’ in toothpaste. These elements may display a level of toxicity, and may not necessarily be additives, but could occur as residues via the chemical production process. Alternatively, these ‘hotspots’ could result from extraneous infiltration - introduced into the sample via leaching from the container in which it is packed. Thus, our approach could also be used to quickly establish toxicity in “soft” samples.

Impact of the study

The liquid-nitrogen approach makes laser ablation studies of ceraceous and gelatinous samples feasible. The work could be extended to pharmaceutical, biomedical and asphaltene/crude oil samples. Pharmaceutical gels and soft, flaccid body tissue and organs can be now subject to direct laser ablation analysis following petrification with liquid nitrogen. Our research, therefore, spawns the need for production of suitable “soft” high-quality certified standards to cater for diverse applications. This would be particularly useful for clinical gels/pastes/creams and medical specimens where quick depth and spatial analysis could be achieved to establish material homogeneity and toxicity. With a higher frequency of beam pulses, it may be possible to attain greater depths ahead of thawing. Asphaltenes 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 obviates the tedium of sample dissolution and preparation of aqueous solutions for analysis.

CONCLUSION

The study demonstrates the successful use of liquid nitrogen for rapidly solidifying gelatinous samples prior to laser ablation. This approach is convenient and highly adaptable, and lends itself to direct multi-elemental analysis, thus reducing the time needed to convert such samples to aqueous solutions. The technique can be extended to establish homogeneity/toxicity in pharmaceutical gels/pastes/waxes and biomedical specimens. It could also be applied to asphaltenes and soft polymers, such as visco-elastic gels. Another potential application of the liquid nitrogen pre-treatment approach could be for the analysis or simulation of the analysis of solid samples (that are normally in the liquid or gaseous state at 1 atm and 25°C) from inhospitable regions. As an illustration, the analysis of ice samples from the North and South Poles, and carbon dioxide and methane samples from other planets.

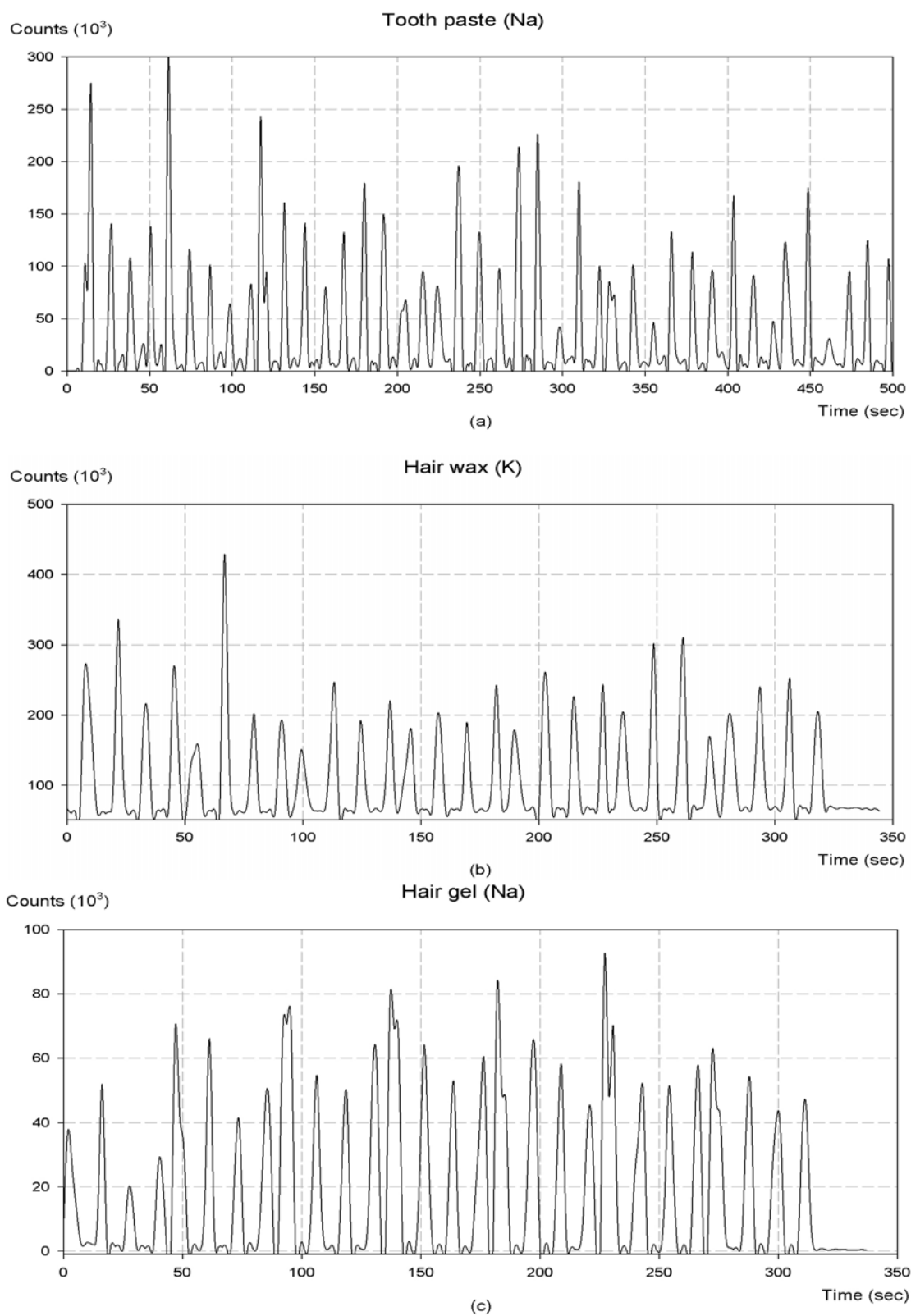


Fig. 6. Typical depth-profiling spectra from samples of a) toothpaste, b) hair wax and c) hair gel.

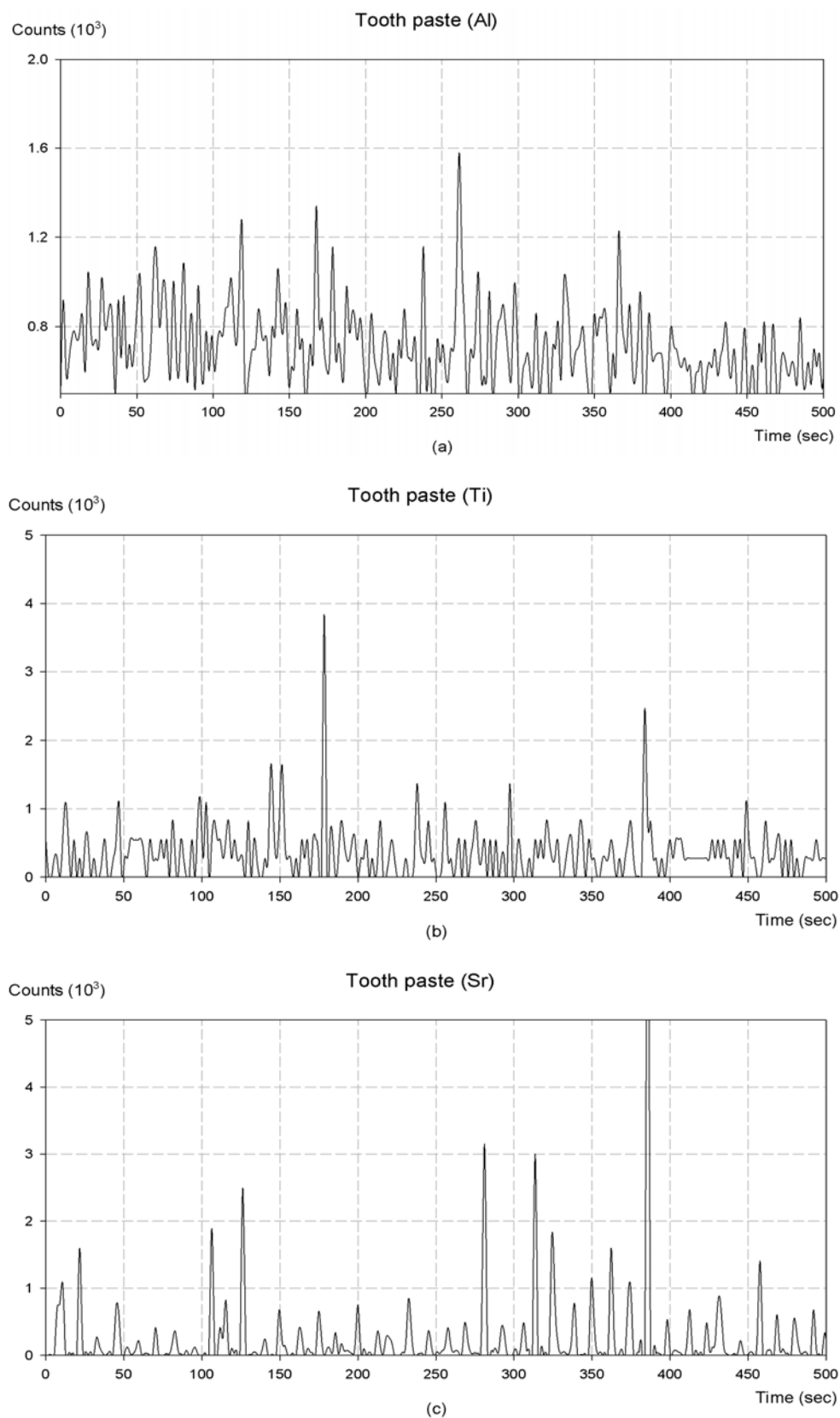


Fig. 7. 'Hotspots' of a) Al, b) Ti and c) Sr in toothpaste.

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