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A REVIEW OF TRADITIONAL ICP-MS AND RELATED HYPHENATED TECHNIQUES (LA-ICP-MS & HPLC-ICP-MS) - STRENGTHS, LIMITATIONS AND APPLICATIONS

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ABSTRACT

Traditional ICP-MS has evolved into more sophisticated instrumental methods of analysis particularly with the fusion of modern facilities to the host instrument such as laser ablation (LA-ICP-MS) and liquid chromatography (HPLC-ICP-MS).These advanced methods of analysis have led to the development of a collective trio of powerful analytical tools for deployment in diverse challenging applications. Many of these applications are associated with the detection of trace elements and chemical species in a variety of matrices such as: reservoir cores, metal coatings, asphaltenes, crude oil, pharmaceuticals, gels and waxes. Lower limits of detection at levels in the ng/L (parts per trillion) range are attainable; and miniscule sample volumes (~50 μL) can be used for aqueous analysis. These allied techniques have been widely applied in the petrochemical sector and in other areas such as forensic science, biomedicine, environmental science, corrosion studies, geology, food science and agriculture. The main advantages of these methods are: multi-elemental; high sample throughput; isotopic detection; sample speciation; depth-profiling; and surface analysis. This paper is a review of the breadth and depth of selected applications in these areas and some of the strengths and limitations encountered.

Keywords: ICP-MS, LA-ICP-MS, HPLC/ICP-MS, Cr^{3+}/Cr^{6+}, As^{3+}/As^{5+}, crude oil, creams, polymers.

TRADITIONAL ICP-MS

The advent of ICP-MS (Inductively Coupled Plasma Mass Spectrometry) in the early 1980s revolutionized trace elemental analysis (Houk, 1986; Greenfield, 1994). ICP-MS is perhaps one of the most competitive contemporary analytical techniques available for trace elemental analysis (Elhameed *et al*., 2016). It has the potential to reach lower limits of detection in the realm of μg/L and ng/L (ppb and ppt) for most elements in the periodic table (Pillay *et al*., 2014). The technique operates by aspirating a liquid sample into a nebulizer and transferring the nebulized droplets to a hot plasma (~6000K) where they are vaporized, ionized and transported to a mass detector via a magnetic selector system (Fig. 1) (Stephen *et al*., 2014). A finely tuned quadrupole system makes it possible for detection of isotopes.

Our laboratory houses a Perkin Elmer SCIEX DRC-e ICP-MS fitted with a dynamic reaction cell (DRC). It possesses the capacity to detect toxic and heavy metals (in aqueous samples) such as: V, Cr, Ni, Se, Cd, Sb, Bi, Th, and U in the 1-10 ppt range. It tends not to be as suitable for determination of H, C, N, O, the halogens and the inert gases. Few other techniques have this capability. For example neutron activation is still used by many researchers but this particular analytical tool is limited by several drawbacks (Pillay, 2002) such as: half-life of the product nuclide (if this is too short it escapes detection); moderate detection limits with liquid samples; and above all the need for suitable nuclear facilities. Electrothermal atomic absorption (ETAA) or graphite furnace analysis is another technique (Govender *et al*., 2001) that can compete with ICP-MS, but here again certain disadvantages accompany the method including low sample throughput and lack of multi-elemental data. Other nuclear and atomic methods of analysis such as PIGE (particle induced gamma-ray emission) (Peisach and Pillay, 1993; Pillay and Peisach, 1992), PIXE (particle induced X-ray emission) (Renan *et al*., 1995), XRF (X-ray fluorescence) (Punyadeera *et al*., 1997) and ICP-OES (Pillay *et al*., 2005) tend to be deficient in providing detection limits as low as ICP-MS. One notable feature of ICP-MS is its ability to provide information on isotopes. This is an asset, which gives it an added dimension that X-ray and atomic techniques lack.

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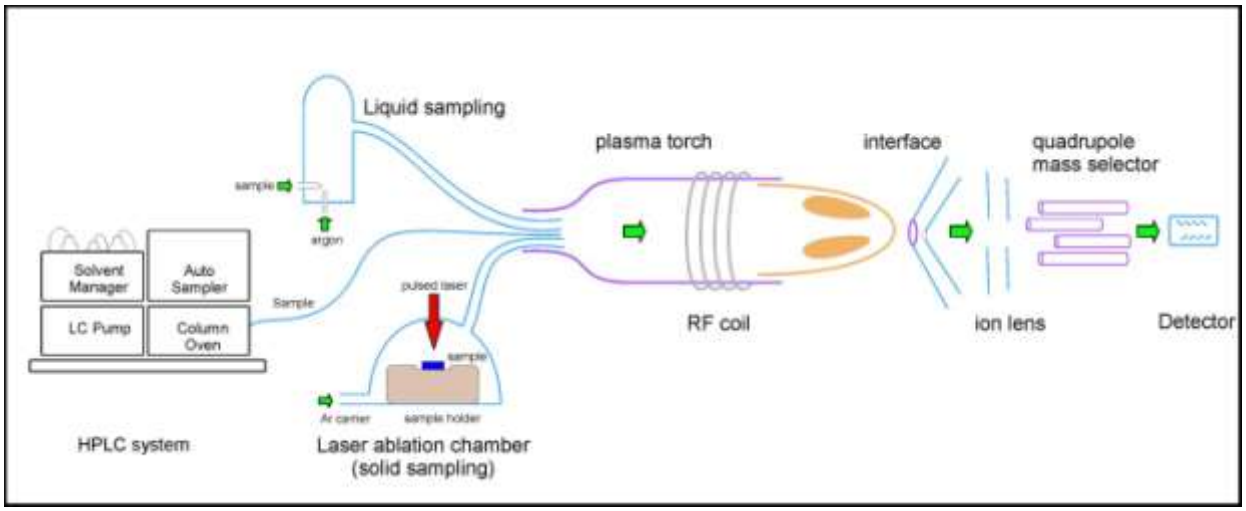

Fig. 1. Schematic of the ICP-MS showing the LA-ICP-MS and HPLC-ICP-MS units.

It is common knowledge that traditional ICP-MS has been applied to a wide range of samples prepared in aqueous media, including biofuels, beverages, asphaltenes, crude oil, toothpaste, pharmaceuticals, gels and waxes (Elkadi *et al*., 2014; Williams *et al*., 2010). The technique is also useful in areas such as nuclear science and nanotechnology (Lee *et al*., 2014; Grain, 1996; Kim *et al*., 1991). Future work could include toxic speciation in honey, rice and other foodstuffs such as oats and cereals. Dissolution of samples in aqueous acid media is facilitated by microwave digestion. The turnover times from the point of sample digestion to acquisition of the results could be less than an hour in some cases. Current high-performance software that controls the system plays a crucial role in producing rapid, accurate results. Instrumental drift, linear calibration, background correction and matrix interferences are resolved by application of suitable software programs. Excellent reproducibility can be attained if these parameters are finely tuned and carefully controlled. In addition, the software controls the lens voltage, anode voltage, gas flow rate, and laser energy (in laser ablation studies). Mass flow controllers regulate several gas flows – plasma gas flow, nebulizer gas flow, cooling gas flow, and collision/ reaction cell gas flow. In many countries, and in a wide number of food, forensic, biomedical and environmental laboratories, ICP-MS has become a routine technique and has proved to be a valuable asset (Stephen *et al*., 2015). More enhanced and more modern ICP-MS facilities are being developed; and application of the technique in a vast number of research projects is also growing (Elkadi *et al*., 2014).

LASER ABLATION (LA-ICP-MS)

Depth-profiling/ homogeneity/ reservoir cores: Depth-profiling is a practical analytical technique for obtaining useful information across the surface of a sample and at different depths within a matrix (Elkadi *et al*., 2010). The technique is especially capable of producing information of geological significance (Ghosh *et al*., 2010). However, several other authors have applied the technique to a wide range of samples including environmental and biomedical samples (Durrant, 1992; Durrant and Ward, 2005; Hu *et al*., 2007). This particular application employs a micro-beam laser (213 nm) to irradiate samples, ablating material by delving to specified depths in the sample under controlled conditions. Suitable software makes it possible to monitor and modulate the irradiation parameters. Standardization of the ablation technique tends to be problematic largely because of the difficulty in obtaining suitable homogeneous standards. However, the procedure is favored for acquiring information on the levels of homogeneity for a variety of materials by observing the consistency or fluctuation of elemental signals from the sample matrix (Fok *et al*., 2011). A typical homogeneity study is represented in Figure 2, where a polypropylene sample doped with zinc was irradiated to determine the distribution of the zinc in the matrix. The spectrum displays 'hot-spots' or accumulation of zinc at different depths in the sample. The spectrum also tapers off at certain depths suggesting that there is an uneven distribution of zinc at some points in the sample. For a more uniform distribution of the analyte factors such as mobility of the dopant in the molten phase or fusion effects within the sample during cooling could be considered (Pillay *et al*., 2010).

The technique of depth-profiling has also been successful in extracting diagenetic data from sedimentary rock and reservoir cores (Ghosh *et al*., 2010). Physical and chemical changes in geochemical rock species over vast periods of time reflect depositional and post-depositional transformations (diagenesis). Depth-profiling as an

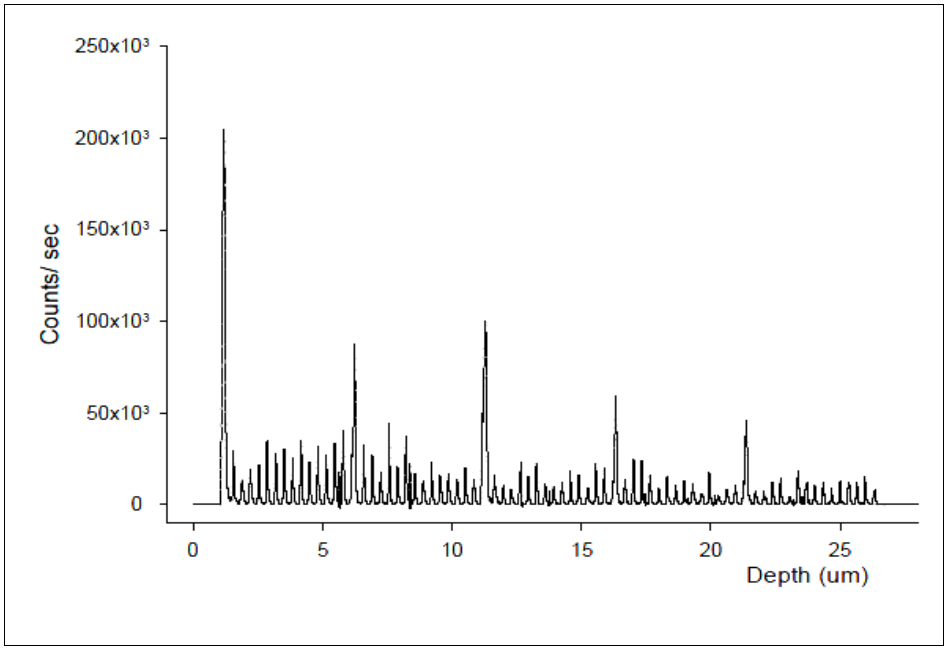

Fig. 2. Depth profiling of zinc in polymer matrix showing hot-spots (Pillay *et al*., 2010).

analytical tool has the ability to estimate the magnitude of pores and pore-throats in core fragments (Ghosh *et al*., 2010). Measurement of such parameters has a distinct impact on the field of geosciences.

Soft samples/ asphaltenes / toothpaste: Of considerable novelty was the development of a unique sample introduction technique relating to the ablation of soft samples (Williams *et al*., 2012). Laser ablation is generally confined to irradiation of hard samples. Soft samples such as gels, creams and waxes tend to cause "splashing" during irradiation (Fig. 3). As a result it was not possible to submit soft targets to laser irradiation. However, treatment of soft samples by submerging in liquid nitrogen to harden them facilitated such analysis. Figure 4 represents a typical laser spectrum of Na from a "hardened" toothpaste sample (Pillay *et al*., 2013). The distribution is not entirely even suggesting that even in creams and pastes agglomeration of embedded chemicals is not uncommon, and the mixing process could be enhanced for uniform distribution. Soft asphaltene samples underwent similar treatment and Figure 5 displays the ratio of nickel/vanadium data recorded from a set of asphaltene samples at different depths beneath the sample surface (Pillay *et al*., 2016). It is clear from this distribution that the Ni /V ratio varies considerably and there is a need for a correction parameter to adjust this ratio to account for factors that could affect it, such as the influence of sulphur on the vanadium concentration (Pillay *et al*., 2016).

Metal coatings/ thin films: Of emerging interest is the application of the laser technique using time-spectra to evaluate corrosion or degradation of thin-film coatings on metal surfaces (Fok *et al*., 2011). The laser is deployed to scan the coated metal surface and penetrate selected spots on the sample surface. The time taken to reach the metal substrate is recorded as soon as peaks characteristic of the substrate (Fe) are observed. However, if the coating is broken or degraded the substrate is reached almost immediately after irradiation demonstrating that the coating has corroded or weakened at these spots (Fok *et al*., 2011). Detection of weakening or gradual degeneration in thin-films in this way is quite original and has wide reaching applications in material science.

Liquid chromatography (HPLC-ICP-MS)

Produced water/biofuels: The coupling of an ICP-MS facility with an HPLC unit is designed largely to de-convolute interferences that occur in standard HPLC procedures (Dolan, 2003). Our work was confined to resolving toxic species, Cr^{3+}/Cr^{6+} and As^{3+}/As^{5+}, in a variety of samples. However, studies in agriculture, food science and environmental science demonstrate the versatility of the technique (Zheng *et al*., 2001; Stadlobera *et al*., 2001; Vonderheide *et al*., 2002; Chang and Jiang, 2001). Ordinary HPLC techniques fail to resolve these species, which are essential to certain environmental studies. Figure 6 displays typical interferences between $Cr^{3+}$and As^{5+}peaks under regular HPLC determination (Pillay *et al*., 2014). By coupling the HPLC unit to the ICP-MS system each component is transported and detected individually thus producing a discrete method of analysis. The combined system employs a dynamic reaction cell (DRC) that facilitates the measurement of the species of interest. Passage of oxygen through the DRC

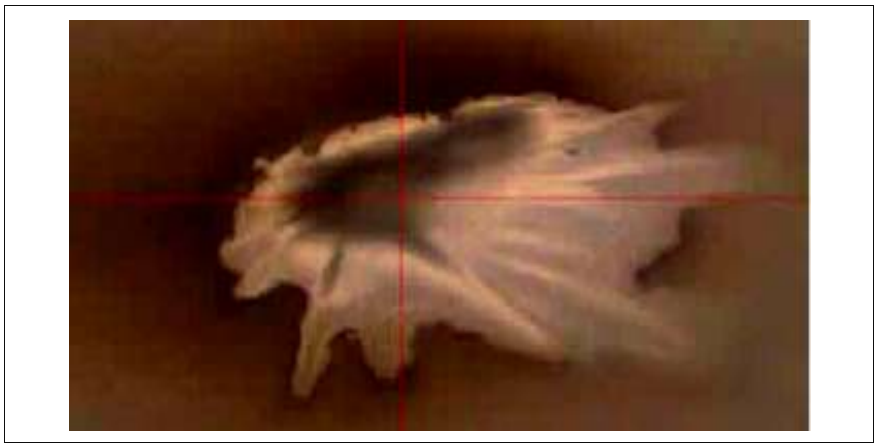

Fig. 3. Screen shot displaying "splashing" effects in soft sample (Pillay *et al*., 2013).

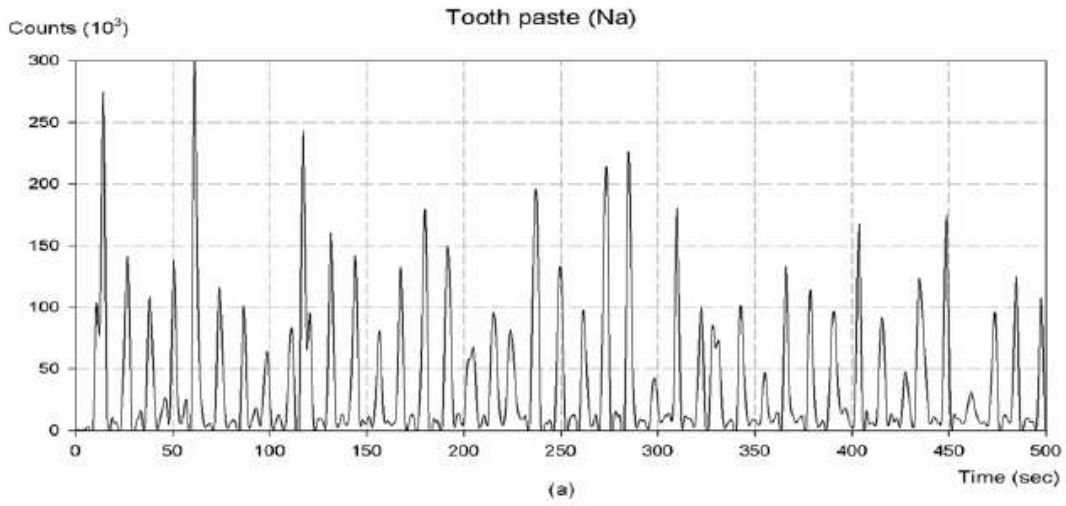

Fig. 4. Laser spectrum of toothpaste sample after liquid nitrogen treatment (Pillay *et al*., 2013).

enables detection of arsenic as AsO^+, m/z 91, to bypass specific unwanted interferences. Produced water from oil yielded up to 2000 ppm Cr^{3+}; 10 ppm Cr^{6+}; 20 ppm As^{3+}; and 5 ppm As^{5+}. The Cr^{3+} results were particularly elevated, and a cause for concern, prompting the need for remedial measures (Pillay *et al*., 2014).

Characterizing neem biodiesel in terms of trace toxic species Cr^{3+}/Cr^{6+} and As^{3+}/As^{5+} is relatively unexplored territory and is considered seminal research in the field of biofuels. Clearly the use of impure biodiesel in machinery and vehicles could severely impact the environment and the release of toxic chemical species into the atmosphere would be detrimental to sustainable living. Preparation of biodiesel using crown ethers revealed selective reduction of Cr^{6+} and As^{3+} in the biodiesel phase when the process is combined with standard catalysts NaOH and KOH (Li *et al*., 2015). The application of HPLC-ICP-MS thus demonstrated clearly that toxic species can be selectively removed from the biodiesel fraction by deploying specific agents, such as crown ethers, in the transesterification process.

Crude oil/asphaltenes: The occurrence of these toxic species in crude oil and its asphaltene derivative is equally significant in terms of the environment and sustainability. Asphaltenes are known to be used in building roads and in roofing material and therefore, information on its toxicity is necessary for sustainable development. In addition, crude oil sludge is deployed as conditioning agent on land farms, and excess sludge is returned to the environment as waste product (Taha *et al*., 2001). Knowledge of the toxicity of crude oil is thus equally important for environmental purposes. Digested samples of crudes and asphaltenes were subjected to analysis by HPLC-ICP-MS and essential data on Cr^{3+}/Cr^{6+} and As^{3+}/As^{5+} were recorded. We found that Cr^{3+} occurred in the range 1-20 mg/L, and $Cr^{6+}/As^{3+}/As^{5+}$fell in the 1-5 µg/L range. These results were deployed successfully in fingerprinting studies,

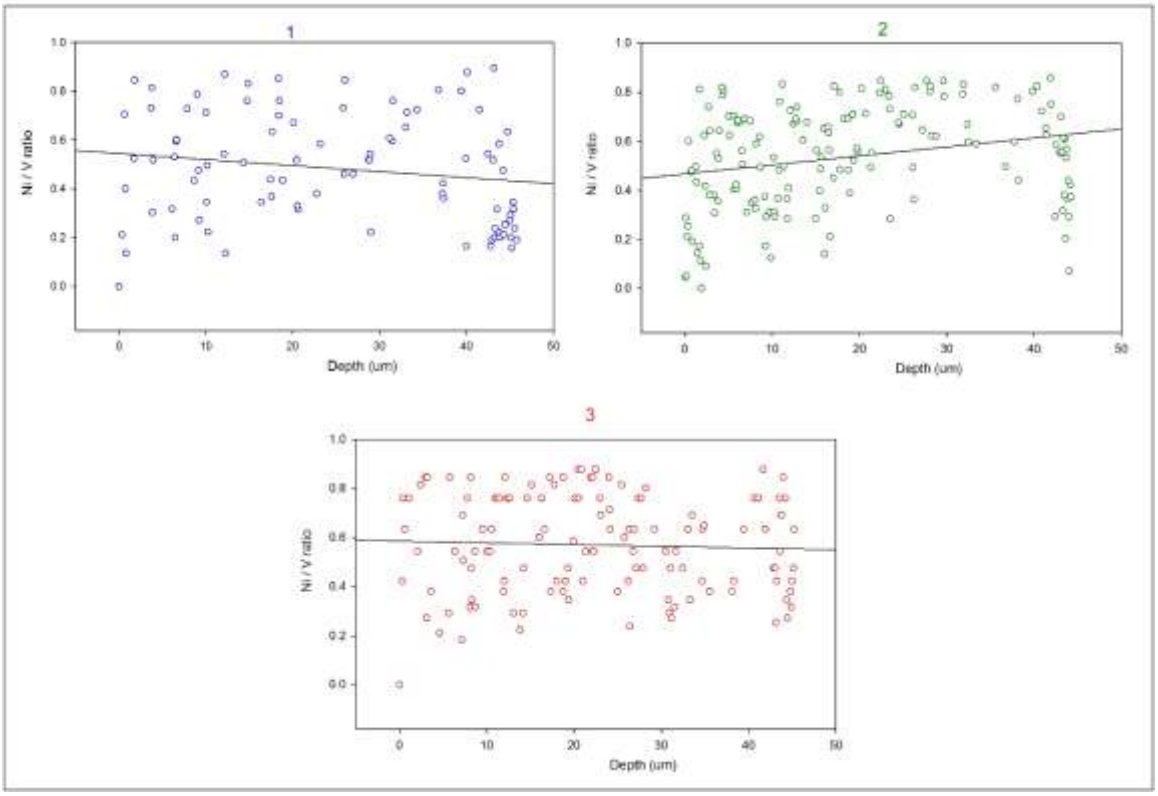

Fig. 5. Ni/V ratios from laser ablation of asphaltene samples (Pillay *et al*., 2016).).

which heralds a new area for future research in toxic speciation (Pillay *et al*., 2016).

Adsorption/ desorption phenomena: Groundbreaking research was achieved by using the HPLC-ICP-MS facility to evaluate adsorption/desorption effects in polypropylene immersed in a biofuel medium by using Cr^{3+}/Cr^{6+} and As^{3+}/As^{5+} as natural "markers" to track this phenomenon (Stephen *et al*., 2015). The results indicated that these effects tend to be governed by polarity of the medium and the strength of the ionic charge on the chromium/arsenic species that were utilized as "markers." It was found that higher water content in the biofuel increased the rate of adhesion. The kinetics of these adsorption and desorption effects is reflected in Figure 7. The study is significant from the perspective of the corrosive impact that biofuels can have in polymeric materials such as hoses and pipes in automobiles and machinery.

OVERALL STRENGTHS AND LIMITATIONS

None of the foregoing techniques is suitable for macro-analysis i.e. analysis at levels exceeding 1 ppm of analyte. Clearly highly concentrated liquid samples can be diluted down, prior to analysis, provided that the excessive dilution does not affect the composition of the material to be analyzed. As mentioned above, standardization in laser ablation tends to be a problem largely because the samples subjected to irradiation are highly heterogeneous, making the preparation of standards difficult (Pillay *et al*., 2013). In such cases the best that can be achieved is semi-quantitative analysis where elemental peak heights at different depths in a sample matrix are compared to gauge relative concentration levels. Nevertheless, despite lack of standards, laser depth profiling is successful and rapid in supplying and verifying qualitative information on trace elements spatially and with depth in a sample.

Speciation studies with HPLC-ICP-MS rely on the integrity and condition of the chromatographic column (Stephen *et al*., 2015). Fluctuations in the conditions of the column could lead to minor aberrations in the recorded results, which could affect reproducibility. However, most columns are adequately robust and durable to withstand continued use. Other factors that could affect standard HPLC columns such as temperature, solvent composition, composition of the stationary phase, and elution rate also play a role here, and could lead to slight perturbations in performance. However, the overall advantages of this particular application far surpass any minor operational drawbacks that could be encountered.

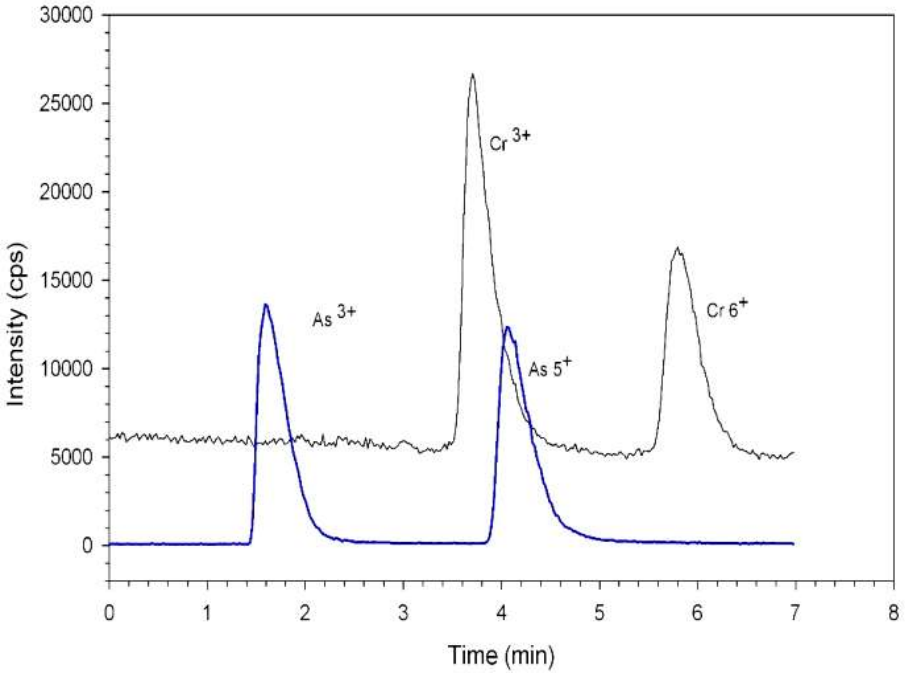

Fig. 6. Standard HPLC chromatogram showing overlapping peaks of toxic species (Pillay *et al*., 2014).

Table 1. Summary of strengths and limitations of ICP-MS, LA-ICP-MS, HPLC-ICP-MS.

Technique	Strengths	Limitations	General Comments
ICP-MS	Ultra-sensitive, ppb, ppt range; High accuracy, reproducibility; Produces isotopic information; Diverse applications.	Cannot determine C,N,O; Digestion of certain solid samples can be tedious; Mainly aqueous samples.	Multi-elemental; Highly quantitative; Facile standardization; Toxic metal analysis.
LA-ICP-MS	Depth profiling, surface analysis; Miscellaneous applications; Analysis of gels and soft samples; Crystal, rock analysis; No sample preparation.	Standardization is difficult due to heterogeneity and density of samples; Penetration depth limited by laser energy.	Hard and soft samples; Rapid qualitative information; Multi-elemental; Thin film studies.
HPLC-ICP-MS	Speciation studies; Ultra-sensitive, ppb, ppt range; High accuracy, reproducibility; Complements standard HPLC; Diverse applications.	Conditioning columns can be tedious; Special mobile phases for different species; Collision cell needed to reduce interferences.	Useful for monitoring variety of toxic species; Can be used in leaching studies; Applied to wide range of aqueous samples.

Not many laboratories in the world possess LA-ICP-MS and HPLC-ICP-MS facilities. This is largely due to the high cost of these systems, which could be considered a major limitation, especially for research groups in developing countries where research funding is deficient. However, the combined value and benefit that all three hyphenated techniques can provide surpasses any of the limitations mentioned here and the main attraction is the versatility and scope that these techniques can offer. Table 1 summarizes the main points.

CONCLUSION

The three techniques discussed in this paper have proved to be greatly beneficial as instrumental tools in a wide variety of applications. There is no doubt that each

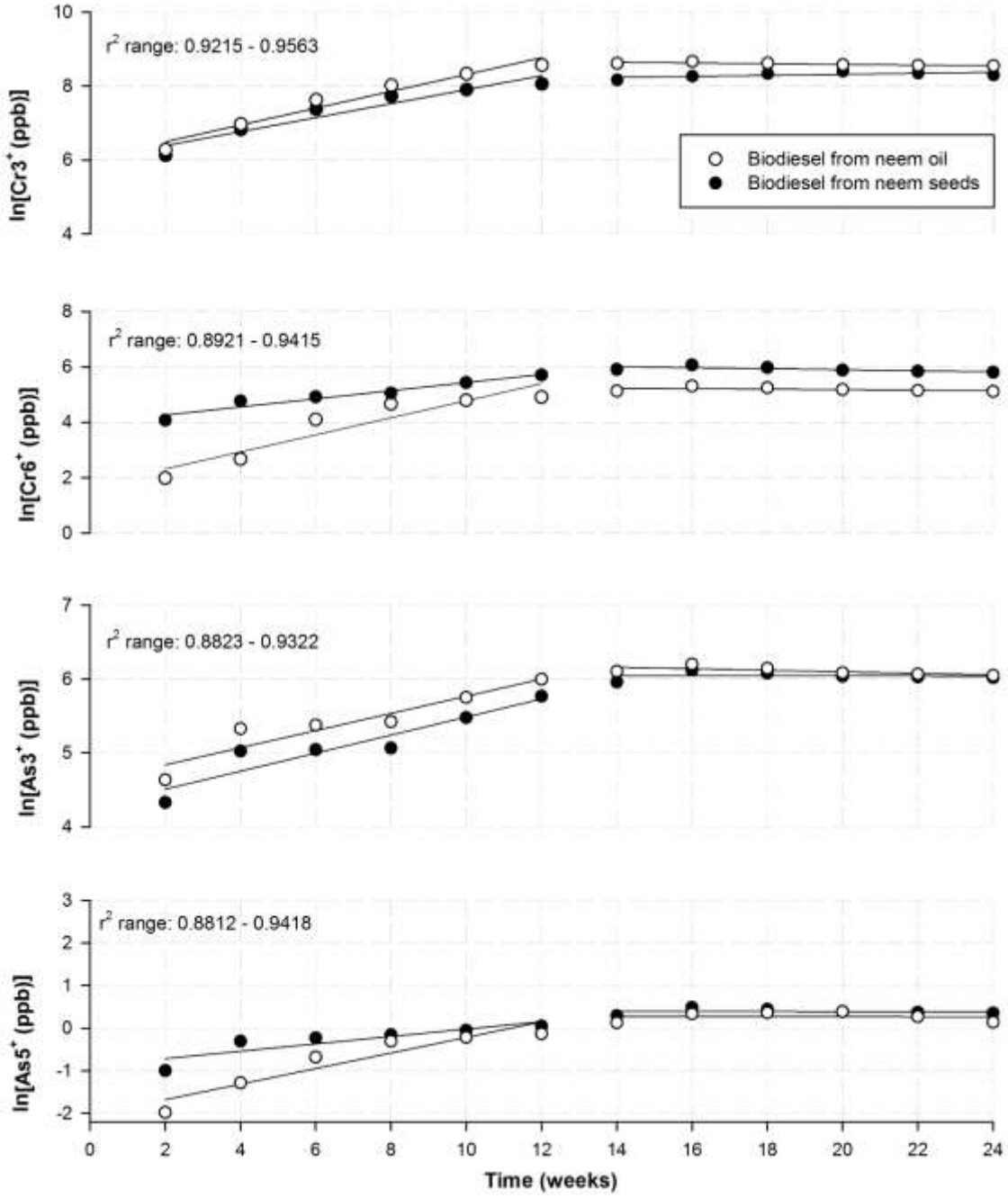

Fig. 7. Kinetics of adsorption/desorption effects using HPLC-ICP-MS (Stephen *et al*., 2015).

technique comes with its own specific drawbacks and advantages, however, their strengths outweigh any accompanying limitations. Many disciplines, including biomedicine, petro-chemistry, forensic science, environmental studies and food science, have enhanced their own analytical capabilities by deploying these instrumental techniques both in research and in routine applications. With the advent of advanced hardware and more elaborate software each one of these methods has the potential to extend its individual capacity to reach lower limits of detection.

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