



focus on **Mass Spectrometry**

Overcoming the challenges of direct organic elemental analysis with ICP-MS

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Analysing organic matrices for trace elements is a challenging proposition and frequently involves complex sample preparation steps. This is time consuming and potentially risks introducing contaminants or losing elements of interest. Sample digestion or wet ashing methods result in an aqueous matrix which can then be analysed by conventional ICP-OES or, where superior detection limits are required, by ICP-MS. However, the direct analysis of organic matrices by ICP techniques has historically presented a number of challenges.

ICP-MS technology has the sensitivity and multi-element capabilities required, but the nature of organic matrices makes their analysis very difficult. The volatility of organic liquids means the vapours can overload the plasma, which may reduce sensitivity or destabilise, if not extinguish, the plasma. The high carbon content of such solvents causes soot or carbon particles to be deposited on the sampler cone, reducing the aperture and causing signal drift. Excessive carbon can also result in high levels of polyatomic interferences from $^{12}\text{C}^{14}\text{NH}^+$ and $^{13}\text{C}^{14}\text{N}^+$, which overlap with $^{27}\text{Al}^+$ and similarly $^{40}\text{Ar}^{12}\text{C}^+$, which interferes with $^{52}\text{Cr}^+$. It is essential that these interference issues are addressed for ICP-MS to be successfully applied to the analysis of organic matrices.

Preventative measures

Minimising reduced ICP-MS sensitivity and retaining instrument stability when analysing organic solvents is particularly important. Wet ashing organic samples is one procedure that can alleviate the issues caused by high carbon content and sample volatility. This decomposes the organic matrix and ultimately solubilises the elements in an aqueous matrix. However, this method is both time intensive and involves significant sample manipulation, which increases the risk of contamination and element loss. Direct sample analysis is a much more accurate and efficient technique – if matrix issues can be addressed. Chilling the spray chamber lowers the solvent vapour pressure and reduces the vapour loading on the plasma. Carbon build up on the sampler cone, which would result in drift and reduced sensitivity, is removed by the addition of oxygen into the nebuliser stream and the interfering polyatomics can be addressed with the use of reaction gases in a Dynamic Reaction Cell (DRC).

Enabling direct organic analysis

Naphthas are a class of organic liquids produced as a by-product of the crude-oil refining process within the petrochemical industry. The term covers the volatile, middle-distillate hydrocarbon mixtures, falling between light gases and the heavier kerosene. Differentiated by the hydrocarbon fractions, there are many types of naphtha; the lighter ones usually contain higher levels of paraffin, with naphthenes and aromatics forming a higher percentage of the heavier naphthas.

As naphthas are used as fuel in combustion engines, any contaminating elements can potentially cause serious problems. Calcium, magnesium, sodium and potassium can form hard deposits and create excessive wear on engine components. There are also potential environmental concerns. Emissions from combustion engines and the refining process can release heavy metals, such as arsenic, mercury and lead into the atmosphere; it is for this reason that monitoring of these elements is extremely important.

The effectiveness of ICP-MS to analyse highly volatile organic mixtures was studied using three different naphthas; petroleum ether and ligroin, representing the light naphthas with boiling-point ranges of 35–60°C and 60–80°C respectively, and Stoddard solvent, a heavier naphtha with a boiling-point range of 154–202°C. Herein lies a significant challenge. When it comes to such a wide array of hydrocarbon composition and boiling-point ranges, how can the naphthas be successfully and accurately analysed in one run? Adequate sample-introduction conditions need to be developed to effectively handle the wide range of mixtures to be tested and suitable calibration methods need to be employed.

Two approaches can be combined to enable direct analysis of the naphthas – cooling the spray chamber and introducing oxygen into the nebuliser stream.

Chilling the spray chamber lowers the naphtha vapour pressure, which reduces the solvent vapour loading on the plasma allowing plasma conditions to stabilise. The sample is aspirated through a glass Meinhard® nebuliser into a PC³-LT Peltier-cooled glass spray at a temperature of -20°C. Even at this temperature, significant differences are noted in the plasma conditions, internal standard recoveries and degree of signal suppression.

To address this issue of inconsistency, the naphthas were diluted. In this case the solvent employed was semiconductor-grade xylene (mixed isomers), also used as the rinse. As xylene and naphtha are in the same carbon chain group (C₈) it is ideally suited as a diluent: the two liquids are readily miscible and have similar boiling-point ranges. Conostan® organometallic standards were used as commercial calibration standards are not yet available in a naphtha or xylene matrix. Supplied in concentrations from 100 to 1000 µg/g in 75 centistoke base mineral oil, mixed and single-element oil analysis standards from Conostan were prepared by dilution with xylene. The use of semiconductor-grade solvent ensures that the naphtha samples are not contaminated with elements of interest. Calibration curves were constructed using standards at 0.2, 1 and 10 µg/L. Naphtha samples were diluted 1:10 with xylene, which minimised any sample/standards matrix variations, whilst still enabling sub-ppb detection limits.

During analysis, ammonia was used as the reaction gas to remove the argon and carbon-based interferences including $^{12}\text{C}^{12}\text{C}^+$, $^{12}\text{C}^{14}\text{NH}^+$, $^{40}\text{Ar}^{12}\text{C}^+$ and $^{40}\text{Ar}^{16}\text{O}^+$ overlapping $^{24}\text{Mg}^+$, $^{27}\text{Al}^+$, $^{52}\text{Cr}^+$, and $^{56}\text{Fe}^+$ respectively. The standard sample-introduction system was adapted to cater for the high organic content and volatility of the samples.

ICP-MS success

No commercial standard reference materials are available for naphtha, as such, each of the three diluted naphthas were spiked with low concentrations of target elements (0.2 – 1.0 µg/L) to demonstrate the efficacy of the method. Each spiked sample was measured seven times and the standard deviation then multiplied by 3.14 to determine the method detection limits of the naphthas. *Table 1* shows the detection limits that were achieved for the three samples.

Table 1: Detection limits for the three naphtha solvents.

Detection Limits in Naphtha Solvents (ng/g).				
Element	Mass	Stoddard Solvent	Ligroin	Petroleum Ether
V	51	0.200	0.015	0.012
Mn	55	0.038	0.031	0.017
Ni	58	0.062	0.017	0.015
Cu	63	0.080	0.015	0.017
Se	82	0.150	0.051	0.043
Cd	114	0.036	0.031	0.017
Sn	120	0.084	0.025	0.012
Ba	138	0.067	0.022	0.018
Hg	202	0.170	0.022	0.015
Pb	208	0.044	0.017	0.017
Al*	27	0.017	0.048	0.025
Cr*	52	0.030	0.040	0.012
Fe*	56	0.025	0.024	0.017

* = DRC mode

Table 2: 5 µg/L spike recovery data for Stoddard solvent.

Spike Recoveries in Stoddard Solvent.				
Element	Mass	Solvent (µg/L)	Spike (µg/L)	%Recovery
V	51	0.01	5.06	101
Mn	55	0.06	4.97	98.2
Ni	58	0.02	4.83	96.2
Cu	63	0.03	4.64	92.2
Se	82	0.06	4.66	92.0
Cd	114	0.01	5.07	101
Sn	120	0.06	4.91	97.0
Ba	138	0.01	4.82	96.2
Hg	202	0.02	4.87	97.0
Pb	208	0.01	4.85	96.8
Al*	27	0.07	4.82	95.0
Cr*	52	0.00	4.86	97.2
Fe*	56	0.01	4.87	97.2

* = DRC mode

Table 2 shows the high degree of accuracy that can be achieved through ICP-MS, even for the heavier naphtha, across all elements analysed. To demonstrate the stability of the method, a series of elements was monitored over a 2.5 hour period, Figure 1 shows the high degree of stability that was achieved.

This study demonstrates that with a high quality, robust ICP-MS instrument – such as PerkinElmer's NexION 300 ICP-MS – it is possible to analyse trace-level metals in

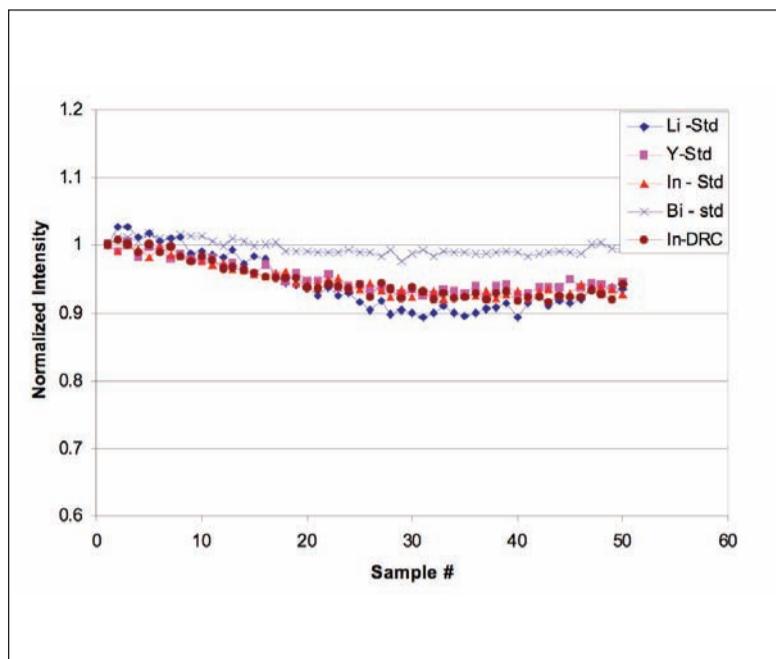


Figure 1: Results of normalised intensities show 2.5-hour stability of petroleum ether.

complex and highly variable naphtha solvents, under a single set of instrumental conditions. The high-power plasma conditions and chilled spray chamber enable the highly volatile solvent matrix to be handled easily. Introducing oxygen prevents the build-up of carbon on the sampler cone, thereby maintaining sensitivity and the use of ammonia in the DRC enables the removal of polyatomic interfering species. These factors combine to provide excellent stability, proving the efficacy of ICP-MS for the determination of elements at sub ppb concentrations in challenging organic matrices.

Routine Quantitative LC-MS Software

Thermo Fisher Scientific, Inc introduced Thermo Scientific TraceFinder 1.1, its latest software for clinical research, forensic toxicology, food safety and environmental testing laboratories performing routine, high-throughput quantitation by LC-MS. The software retains all of the capabilities of its predecessor and has been expanded to include complete integration with the Thermo Scientific Transcend system. It is also compatible with all Thermo Scientific quantitative mass spectrometry platforms, including the Thermo Scientific Exactive and LTQ family of systems.

"Our customers asked for easy-to-use software for routine LC-MS quantitation that integrates seamlessly with their front-end system of choice - the Transcend System - and all of the Thermo Scientific quantitative LC-MS systems, including the LTQ series and the Exactive," said Ian Jardine, Vice President of global R&D, Thermo Fisher Scientific. "We enhanced TraceFinder 1.1 specifically to meet these needs, and now customers have one software solution for method development, data acquisition, data processing and report generation that they can use with our Thermo Scientific TSQ Series triple stage quadrupole system, the Exactive, Orbitrap or one of our ion trap systems. This will enable them to significantly improve laboratory productivity."

The TraceFinder™ software is designed to make routine LC-MS quantitation and targeted analysis simple, fast and productive. The software offers a four-step, workflow-driven method setup and fully automated data acquisition, data processing and reporting. It includes an extensive choice of preconfigured methods and more than 50 report templates, as well as compound data stores for selected reaction monitoring (SRM) experiments in environmental testing, food safety residue analysis, clinical research and forensic toxicology applications. Data review is easy with the ability to specify and report multiple flags. To protect the integrity of analytical data, the software includes a rights-based secure user login system.

The Transcend™ system combines the power of automated online sample preparation and multiplexing to increase throughput without compromising data quality or sensitivity. The unique multiplexing technology of the Transcend system brings the productivity of up to four separate, parallel LC systems to a single mass spectrometer, enabling clinical research, forensic toxicology, food testing and environmental laboratories to achieve a four-fold increase in sample throughput. Thermo Scientific TurboFlow Technology automates sample preparation and can reduce the time spent on this task by up to 95%.

Circle no. 512

New Technique to Revolutionise Proteomics Mass Spectrometry

Scientists at **ETH Zurich** and **AB Sciex** are working together to deliver the first mass spectrometry-based technique that will allow quantitation of every peptide in a single proteomics sample analysis. SWATHTM Acquisition is a breakthrough for proteomics mass spectrometry users to conduct simultaneous quantitative and qualitative detection of all proteins and peptides in a single analysis.

AB Sciex is developing enhanced MS/MSALL functionality to enable SWATHTM Acquisition on the AB Sciex TripleTOF™ 5600 System as part of the MRMAtlas collaboration with Dr Ruedi Aebersold and his team at ETH Zurich. Existing high resolution and orbital trapping mass spectrometry systems can only qualitatively detect a subset of proteins in complex samples due to their relatively slow speed of MS/MS acquisition, and samples are often re-analysed on additional instruments for better quantitation. The technique is expected to generate exciting proteomics discoveries and overcome the diminishing scientific returns of iterations on current mass spectrometry platforms.

SWATHTM Acquisition provides a complete quantitative and qualitative archive of the sample, which can be retrospectively interrogated in silico as new hypotheses are developed. This new technique is a perfect complement to the MRMAtlas, which is a database that provides mass spectrometry-based assays to a large proportion of the human proteome.

The active collaboration with Dr Aebersold and his team will continue to develop the software processing approach to interpret the data based on the MRMAtlas. SWATHTM Acquisition, which is an extension of AB Sciex's MS/MSALL technology, can only be done on the TripleTOF™ 5600 due to its unique combination of ultra-high acquisition speed with quantitative capabilities, accurate mass and high resolution. MS/MSALL has previously been used successfully in infusion methods for the quantitation and characterization of lipid species. Now, expanding on this capability, MS/MSALL using SWATHTM Acquisition gives a vast increase in duty cycle to enhance coupling with LC/MS – a significant advancement in mass spectrometry technology.

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