Coupling Quadrupole ICP-MS with a Dual Syringe Pump Sample Introduction System for Fast and Accurate Determination of Trace Metals in Organic Solvents

Tomoko Oki, Shona McSheehy and Meike Hamester, Thermo Fisher Scientific, Bremen, Germany

The presence of trace metals in volatile organic solvents, even at trace level concentrations, has been associated with poisoning of industrial catalysts and subsequent contamination of final products. As a consequence, it is necessary that volatile organic solvents are analysed for trace metals in an accurate and reliable manner. Inductively coupled plasma mass spectrometry (ICP-MS) has been traditionally used to perform such analyses, however, the efficiency of the method is limited. This article provides an overview of volatile organic solvents and the challenges that their analysis poses when using ICP-MS. An innovative technique, combining quadrupole ICP-MS with an advanced dual syringe pump sample introduction system, is discussed as a viable alternative. An experiment is used to demonstrate how this new method enables direct, efficient, accurate and contamination-free analysis of trace metals in volatile organic solvents.

Organic solvents are carbon-based solvents that share a common structure, low molecular weight, lipophilicity and high volatility. Many different classes of chemicals can be used as organic solvents, including aliphatic hydrocarbons, aromatic hydrocarbons, amines, esters, ethers, ketones and nitrated or chlorinated hydrocarbons. Organic solvents are useful because they can dissolve oils, fats, resins, rubber and plastics. They exist in liquid form at room temperature and are routinely used in the production of an extended range of products, such as paints, varnishes, lacquers, adhesives, glues, polymers, plastics, textiles, printing inks, degreasing/cleaning agents, agricultural products and pharmaceuticals.

Many organic solvents are designated by the National Institute for Occupational Safety and Health (NIOSH) as carcinogens, reproductive hazards and neurotoxins. As well as being life-threatening environmental pollutants, organic solvents can also poison industrial catalysts and contaminate the final products through the trace metals they may contain. In the petrochemical industry, for example, trace metals such as mercury (Hg) in naphtha can poison the precious metal-based catalysts during the cracking of hydrocarbons, jeopardising subsequent processing and contaminating the end products. Arsenic (As) can also poison catalysts at trace concentrations as low as 50μg/kg and cause problems with high temperature naphtha cracking tubes due to the formation of coke build-up. This build-up can result in the eventual failure of the tubes and subsequently reduce production capability. As a consequence, the determination of trace metals in volatile organic solvents is of significant importance. ICP-MS has been traditionally used for this type of analysis. However, organics analysis with ICP-MS has been associated with a number of challenges.

The Limitations of Traditional ICP-MS

Routine autosampler-based trace element analysis of organic solvents using conventional ICP-MS technology has historically been considered difficult due to a number of potential problems. Sample introduction of organic solvents using a peristaltic pump is complicated by possible chemical incompatibility while chemically resistant tubing can be a major source of contamination. As a result, sample introduction based around self-aspiration is often the only choice available to analysts. When using self-aspiration, however, differing viscosities and specific gravities may lead to unreliable uptake times when analysing different solvents in an analytical run. Nevertheless, as a general rule, a constant flow of solvent, regardless of sample viscosity or specific gravity, is necessary for accurate and reliable trace element analysis of organic solvents.

Analyses are further complicated due to the high volatility of many organic solvents, which results in increased sample transport efficiency and subsequent undesirable effects such as plasma instability. To overcome this problem, dilution or other sample pre-treatment is often employed in order to reduce the volatility of the respective organic solvent prior to introducing it into the plasma. The sample can be diluted with another solvent such as kerosene, or it can be cooled using a cooled spray chamber. Of these two methods, the second one is preferable as the first can decrease the sensitivity of the analysis. Additionally, dilution as with any other sample pre-treatment method, introduces a timely step in the analytical protocol while also increasing the potential for sample contamination. Hg, for example, is a particularly sticky element and requires extensive washing regimes when using traditional introduction systems to minimise contamination of subsequent samples.

In order to overcome these analytical challenges, the use of a quadrupole ICP-MS analyser in conjunction with an advanced dual syringe pump sample introduction system has been investigated.

An Innovative New Method

Coupling a quadrupole ICP-MS analyser with an advanced dual syringe pump sample introduction system enables efficient, precise and contamination-free analysis of various volatile organic solvents. The dual syringe pump sample introduction system is based around a vacuum loaded injection valve and sample delivery by syringe pumps, dramatically improving the analysis of organic solvents. This complete automated sample introduction system increases productive instrument time and sample throughput by reducing sample uptake, stabilisation and rinse steps.

Many important benefits of the dual syringe pump sample introduction system are associated with the syringe pumps, which are able to reliably deliver constant flow rates of organic solvents with different physical properties. Additionally, the syringe pumps have been specifically designed to eliminate the need for peristaltic pump sample delivery. A further significant benefit is that the syringe pumps smoothly deliver highly volatile organic solvents at low flow rates from < 5µL/min to 50µL/min, thereby avoiding any overloading of the quadrupole ICP-MS analyser.

Additional advantages include the complete elimination of peristaltic pump memory effects, improved data quality, lower reagent costs as well as lower cost of consumables and routine maintenance. All surfaces of the sample introduction system that the sample comes into contact with are also made from PFA, which allows for an inert, non-contaminating sample introduction.

An experiment was performed to demonstrate the unique capabilities of ICP-MS for efficient, accurate and contamination-free analysis of volatile organic solvents when coupled with a dual syringe pump sample introduction system.

Experimental

A quadrupole ICP-MS (XSERIES 2, Thermo Fisher Scientific, Bremen, Germany) was coupled with a microFAST 2 advanced dual syringe pump sample introduction system (SC-FAST DX with Continuum, Elemental Scientific Inc, Omaha, NE, USA) to demonstrate the competence of the new method. The dual syringe pump sample introduction system uses syringe pumps to load samples onto and inject samples from a six-port vacuum loaded switching valve.

Direct Trace Metal Analysis of Organic Solvents

Naphtha

The multi element and single element Hg standards used in this experiment were sourced from CONOSTAN®, USA. Naphtha from Fisher Scientific (Reference N/0050/PB17) was used in all analyses. The powerful collision cell technology (CCT) of the quadrupole ICP-MS system with a single H_2/He cell gas mixture was used for the analysis of Ca, Cr and Fe in order to remove spectral interferences resulting from the high carbon content in the sample. All other elements were analysed in standard non-CCT mode.

For quantification of trace elements in naphtha, fully quantitative external calibrations were performed. 95Mo was used as an internal standard. *Figure 1* shows the calibration line for Hg in naphtha.

The background equivalent concentration (BEC) determined for 202Hg in the naphtha sample was 53 ppt and a detection limit (calculated from 3 sigma of 10 blank measurements) of 10 ppt was determined.
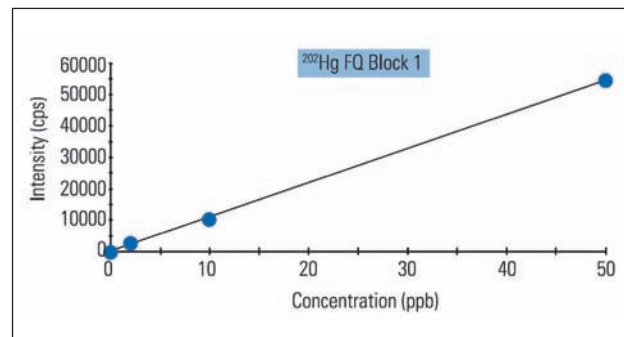

Figure 1. Fully quantitative calibration for Hg in naphtha.

Mercury Memory Test

In order to determine the washout characteristics of the introduction system used, replicate analyses of pure naphtha were made directly after the analysis of a 50 ppb Hg spiked standard. *Table 1* shows that seven minutes after the analysis of the 50 ppb Hg naphtha standard, the Hg background recorded in a pure naphtha sample had dropped down to a background subtracted equivalent concentration of < 50 ppt (less than 0.1% washout). In order to test the stability of the analysis, a sample of naphtha spiked with 10 ppb of a range of elements was repeatedly analysed over a four-hour period. Normalised results illustrating the recovery of the 10 ppb spike are shown in *Figure 2*.

Table 1. Mercury memory test results.

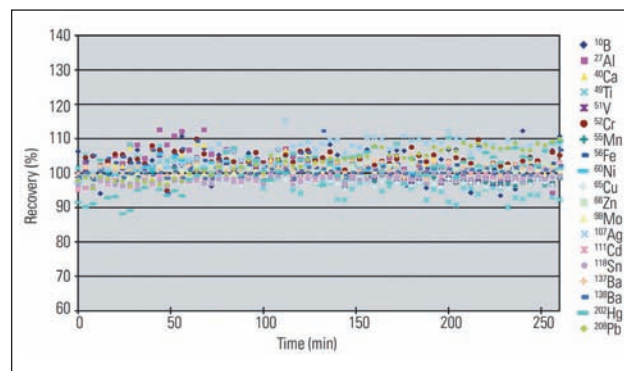| Sample List	Run Times	202Hg Count Rate
Naphtha	13:40	58
Naphtha Hg 2 ppb	14:43	1869
Naphtha Hg 10 ppb	13:47	11152
Naphtha Hg 50 ppb	13:50	54221
Naphtha	13:52	311
Naphtha	13:55	134
Naphtha	13:57	96

Figure 2. Recoveries for 10 ppb spiked naphtha sample over 250 minutes (200 runs).

Hexane

With the dual syringe pump sample introduction system, direct analysis of the challenging hexane solvent was possible. Fully quantitative calibration curves were generated for a number of trace elements in hexane (PN H303-1 or H/0355/15, Fisher Scientific) using the same ICP-MS acquisition parameters as naphtha. *Figure 3* shows calibration lines of 24Mg, 40Ca, 52Cr and 56Fe. BECs and limits of detection (LODs) were calculated for each analyte (*Table 2*).
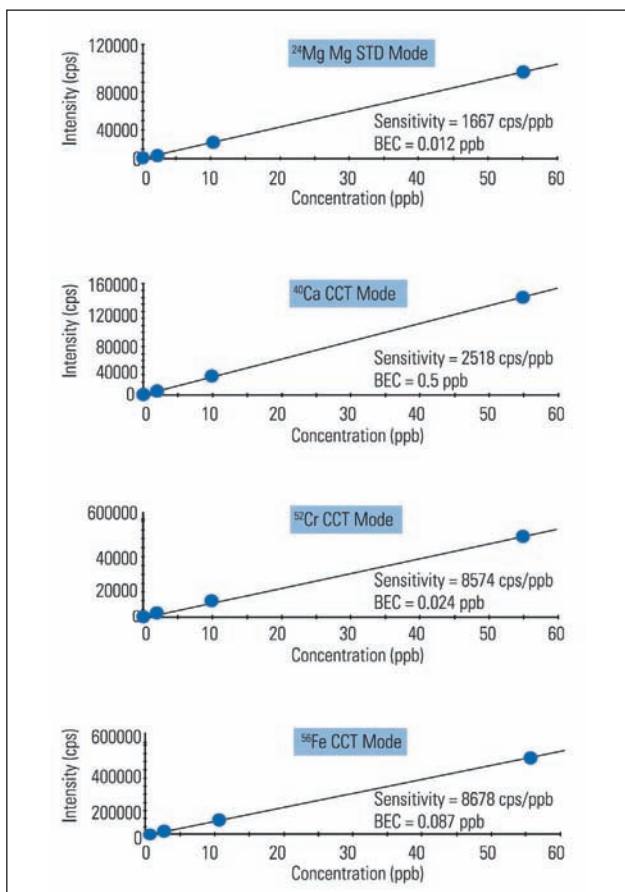
Figure 3. Calibration lines in hexane.

Table 2. LOD and BEC data for trace elements in hexane. All values are shown in units of ppb.

	LOD (3 σ)	BEC
^{10}B	0.491	4.69
^{24}Mg	0.002	0.012
^{39}K	0.127	4.66
^{40}Ca	0.032	0.50
^{51}V	0.097	0.220
^{52}Cr	0.002	0.024
^{55}Mn	0.064	0.073
^{56}Fe	0.012	0.087
^{60}Ni	0.068	0.095
^{65}Cu	0.030	0.070
^{66}Zn	0.059	0.139
^{98}Mo	0.002	0.002
^{107}Ag	0.003	0.003
^{111}Cd	0.003	0.001
^{118}Sn	0.001	0.004
^{138}Ba	0.001	0.0004
^{208}Pb	0.001	0.0004

Conclusion

The direct and automated trace metal analysis of volatile organic solvents using ICP-MS has traditionally been a problematic and challenging application. By coupling quadrupole ICP-MS technology with an advanced dual syringe pump sample introduction system, the analytical challenges are efficiently overcome and accurate analyses are achieved. Sample handling is fully automated, meaning that batch analysis of volatile organic solvents can become completely routine, whereas the dual syringe pumps of the sample introduction system provide a constant flow rate for different organic solvents in a contamination-free environment. In addition, quadrupole ICP-MS, operated in third generation CCT mode, offers maximum sensitivity while also eliminating polyatomic interferences. The combination of advanced sample handling with robust and high-performance ICP-MS technology offers a fast and accurate approach for determining trace elements in organic solvents.