Techniques for the Analysis of Organic Chemicals by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Petrochemical

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Abstract

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is used for the routine monitoring of trace and ultra-trace metal contaminants in aqueous-based chemicals. Recent advances in ICP-MS technology and methodology have extended the analytical capability of the technique to the determination of similarly low levels of metal contamination in organic solvents and other complex matrices. The new instrument hardware overcomes previous limitations in ICP-MS sample introduction systems, while advances in applications development enable complete removal of carbon-based spectral interferences from organic sample matrices using the Agilent cool plasma technique.

Using the new ICP-MS methodology, virtually any organic material can be analyzed, either directly or after simple dilution with a suitable solvent, without the need for matrix removal or digestion. New developments include the use of organic solvent resistant materials in the sample introduction path and precise control of sample delivery and solvent volatility to avoid system overloading. Optimization of plasma parameters allows the carbon matrix to be decomposed completely and gives complete removal of carbon-based as well as argon-based interferences allowing the routine analysis of key elements like Mg, K, Ca, Cr and Fe at levels previously only possible with Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).

Introduction

ICP-MS is widely used for the determination of metals in aqueous sample matrices because of its multielement capability, excellent sensitivity, flexibility and reliability as a routine analytical tool. However, the analysis of organic samples is more challenging, because of difficulties in sample introduction and the spectral interferences that arise from the physical properties and high carbon content of the organic sample matrix. Hardware and operating methodology unique to Agilent ICP-MS instruments have overcome these problems and are providing the capability to routinely analyze for metal contamination at the trace and ultra-trace levels in a range of organic sample matrices.

Handling Organic Solvents

Water-miscible organic solvents can simply be diluted with water or dilute acid and treated in a similar fashion to other aqueous based samples for analysis by ICP-MS. The many organic solvents which are immiscible with water must be handled in a different way. In many such cases, digestion or evaporation is not a suitable sample preparation alternative due to the potential for uncontrolled reactions, the possibility of contamination and the loss of volatile analytes. Where possible, direct analysis of the organic solvent is the preferred method of analysis, either untreated or simply diluted in a suitable solvent. Direct organic solvent analysis demands some specific features and capabilities of the ICP-MS instrument, particularly in the sample introduction and plasma systems. Details are given in the following sections:

Solvent resistant hardware

Many ICP-MS instrument fittings, such as sample uptake and drain tubing, connectors, and spray chamber o-rings, are fabricated from polymers which may dissolve or degrade (swell or harden) after extended contact with organic solvents. These fittings must be replaced with solvent resistant alternatives and, in the case of the sample uptake tubing, care must also be taken to avoid contamination of the sample through contact with the tubing material. For routine analysis of organic solvents, the normal peristaltic pump tubing is replaced with PTFE tubing connected directly to a nebulizer that draws the sample solution into the spray chamber by self-aspiration. The spray chamber and plasma torch are made of high-purity quartz and any seals in the sample introduction and drain systems are replaced with solvent resistant materials.

Control of vapor pressure

Compared with aqueous samples, organic solvents may be considerably more volatile. The high vapor pressure of some solvents, even at room temperature, can disrupt or even extinguish the plasma. For routine analysis of such solvents, it is essential that the vapor pressure is controlled by cooling the spray chamber, where the sample aerosol is generated. This can be best affected by means of a Peltier device, which controls the spray chamber to a selected temperature, usually between 0 and –5^{o}C. A Peltier device is used because it has superior heat transfer efficiency compared to a water jacket, enabling rapid cooling and stable operation at temperatures as low as -5 ^{0}C. At these low temperatures, the vapor pressure of even the most volatile solvent (such as acetone) is sufficiently reduced to allow stable plasma operation.

Removal of carbon

The presence of high levels of organic solvent in the sample aerosol can lead to deposition of carbon (soot) on the sampling cone, eventually leading to clogging of the cone orifice and a reduction in sensitivity. To prevent carbon deposition, the carbon in the sample is decomposed by reaction with oxygen, to form CO_2. Water miscible organics, when diluted with water, usually contain sufficient oxygen (from the water) to achieve complete sample combustion. These sample types can be analyzed under essentially standard sample flow and plasma conditions for Agilent ICP-MS instruments (100-400 uL/min sample uptake rate). Typical examples of water-soluble organic samples include tetramethyl ammonium hydroxide (TMAH), ethyl lactate and water-based photoresist strippers, such as hydroxylamine/ choline-based post-etch cleaners.

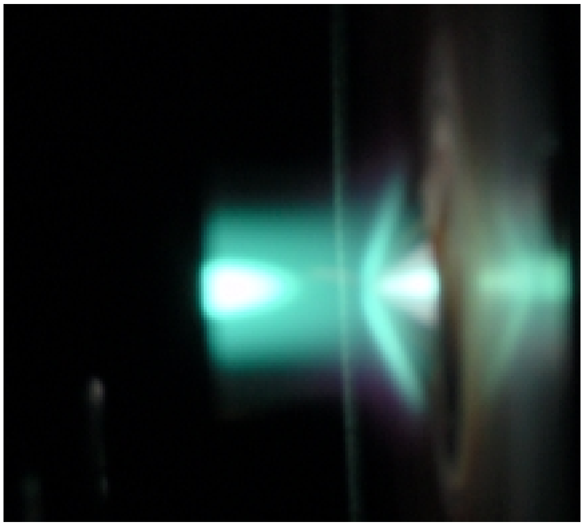


Figure 1. Visual optimization of the oxygen level in the plasma

In the case of non water-soluble organic solvents, oxygen cannot be derived from the water solvent and so another source of oxygen is required. For this second group of organic solvents, the oxygen for carbon decomposition is provided by addition of a small percentage of oxygen directly into the argon carrier gas, which transports the sample aerosol droplets into the plasma. Typically, a 20% oxygen in argon is used, rather than pure oxygen, avoiding the use of highly flammable or explosive gases in the laboratory. The oxygen is added either in the spray chamber or using a T-connector before the torch. When oxygen is added to the plasma, the plasma environment becomes considerably more reactive, and so the use of platinum-tipped interface cones instead of the standard nickel cones is recommended.

Optimization of the appropriate level of oxygen for a particular organic solvent is a simple procedure, provided that the operator has a clear view of the plasma. A default flow of oxygen is added to the carrier gas flow (e.g. Oxygen at 5% of the total argon carrier flow) and the organic solvent is aspirated at an appropriate flow rate. The oxygen flow rate is reduced slowly, until a build up of carbon on the sampling cone is observed. The oxygen flow is then increased until the carbon deposits are decomposed and the green C_2 emission "tongue", visible in the central channel of the plasma, is seen to stop well before sample cone orifice. This indicates that the organic matrix has been decomposed, see Figure 1. Once the optimum oxygen level for each solvent is determined, it can be automatically implemented and does not require routine adjustment. Table 1 shows typical oxygen concentrations and sample introduction configurations used for a range of solvents for which routine methods have been established.

Performance

The ICP-MS sample introduction setup for the analysis of volatile organic solvents such as isopropyl alcohol (IPA) involves the use of a lower sample flow rate, a chilled spray chamber (-2°C), oxygen addition at approximately 5% (Table 1) and an ICP torch designed to maintain a stable plasma with organics. Many other organic solvents, including xylene, kerosene, pentane and toluene are also analyzed under these operating conditions – the only change being the amount of oxygen addition, which is optimized for each different sample type. With this setup, the analysis of organics is stable and reproducible. Figure 2 shows a 4-hour stability plot for a series of trace elements (at the 2ug/L level) in xylene, obtained without the use of an internal standard. Figure 3 shows a calibration for ^{208}Pb in pentane.

Even highly volatile solvents such as acetone can be successfully analyzed with the correct set up. In this case, a very low sample uptake is used, a spray chamber temperature of -5°C, and a narrow ID torch to maintain plasma stability.

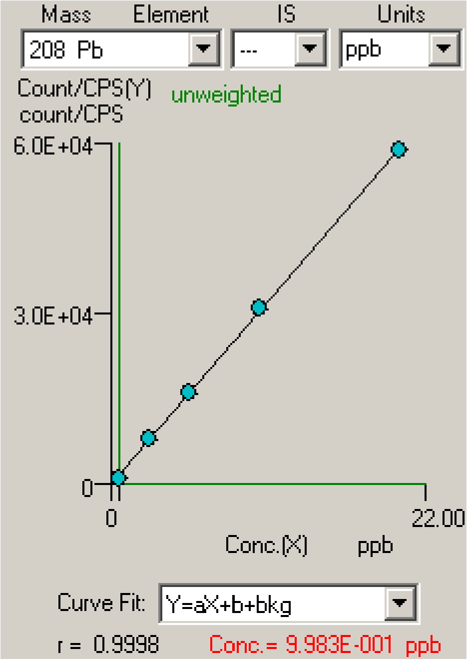

Mass: 208 Pb
Element
IS: ---
Units: ppb
Count/CPS(Y) unweighted
Curve Fit: Y=aX+b+bkg
r = 0.9998 Conc.= 9.983E-001 ppb

Figure 3. Standard addition calibration for Pb (0, 2, 5, 10 and 20 ppb) in Pentane

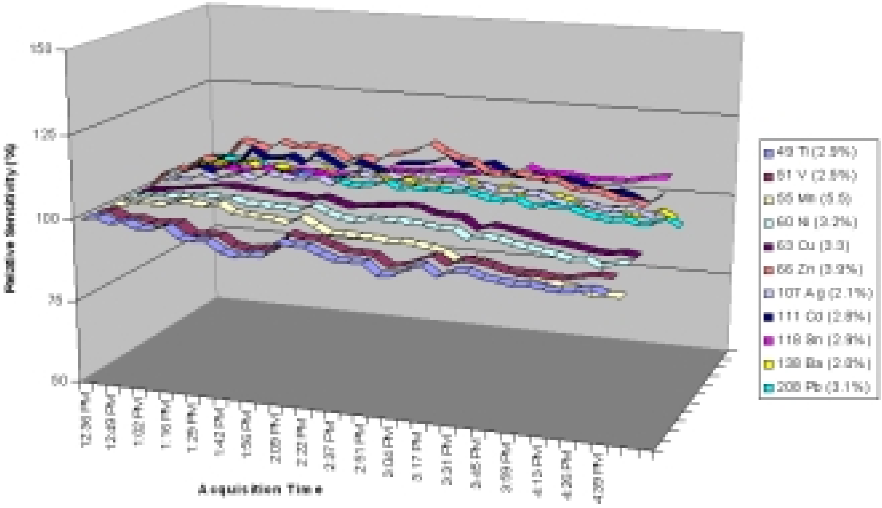


Figure 2. Trace Elements in Xylene - 4-Hour Stability at 2ug/L Level. No internal standard.

Table 1. Recommended Conditions for analysis of various organic solvents

Organic solvent	*Sample tubing id (mm)	Torch injector id. (mm)	**Oxygen Flow (% of carrier gas)	**Oxygen Flow (mL/min)
ethyl alcohol (Ethanol)	0.3	1.5	3	35
propylene glycol mono-methyl ether acetate (PGMEA)	0.3	1.5	3	35
ethyl lactate	0.3	1.5	3	35
kerosene	0.3	1.5	5	60
methyl iso-butyl ketone (MIBK)	0.3	1.5	8	100
xylene	0.3	1.5	10	120
toluene	0.3	1.5	12	150
acetone	0.16	1	5	60

* Assumes a length of 50 to 70cm.

** 5x this amount of a 20% oxygen in argon blend is added, for safety reasons

Removal of Spectral Interferences

Under standard operating conditions, the argon plasma generates several interfering polyatomic species that overlap analyte ions of interest. When the components of the sample matrix are also taken into account, additional interferences may be formed, as illustrated in Table 2. For quadrupole ICP-MS (ICP-QMS) the established and most effective method of reducing polyatomic interferences in high purity matrices is the use of the ShieldTorch System and cool plasma conditions.

In cool plasma operation, the plasma forward power is reduced, and the carrier gas flow rate and sampling depth are adjusted, so that the ions are sampled from a region of the plasma where the ionization is carefully controlled.

Thus, ionization of the elements of interest can be maintained, but the potential interfering polyatomic ions can be attenuated, due to the fact that they are ionized in a different region of the plasma.

This method is most effective if the plasma potential is minimized, which can only be achieved effectively by grounding the plasma using a metal shield plate (Agilent ShieldTorch System).

Table 2. Potential interferences on preferred analyte isotopes

Argon-based Interference:

Element	Overlapping Species
^{39}K	$^{38}Ar^{1}H$
^{40}Ca	^{40}Ar
^{56}Fe	$^{40}Ar^{16}O$

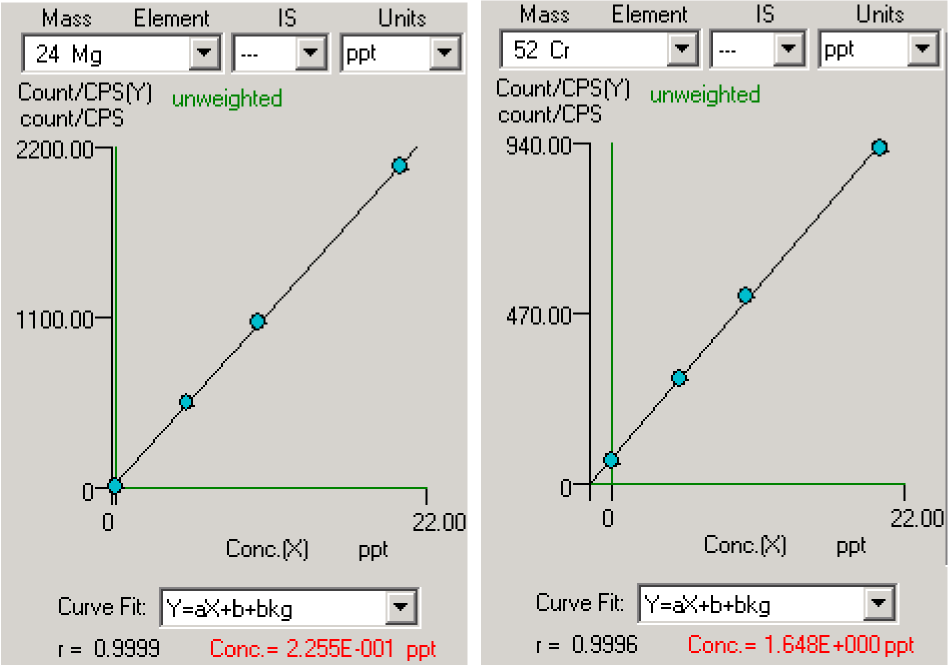
Organic matrix-(carbon)-based Interference:

Element	Overlapping Species
^{24}Mg	$^{12}C_2$
^{52}Cr	$^{40}Ar^{12}C$

Without such a plate, only partial grounding of the plasma can be achieved, but this does not allow effective reduction of the plasma and matrix interferences at high forward power levels, so such systems must operate at very low power (around 600W). At such low forward power, there is insufficient plasma energy to decompose the sample matrix of samples such as organic solvents, so sample digestion or desolvation may be required. When the ShieldTorch System is used, by contrast, the cool plasma technique is extremely efficient at removing carbon and plasma-based polyatomic interferences, matching the performance of even high resolution ICP-MS. With the ShieldTorch, cool plasmas can be applied to the analysis of virtually all organic sample types, including oils, liquid crystal and heavy photoresist solutions.

Recently, collision/reaction cell (CRC) technology has gained popularity as a means to remove polyatomic interferences. The Agilent 7500c, featuring the Octopole Reaction System (ORS) works well for the removal of carbon-based interferences. The ORS employs simple reaction gases (H_2 and He), and therefore does not suffer from the formation of new “cluster” species observed with the use of more reactive gases such as ammonia. The performance of CRC based ICP-MS instruments cannot, however, match the detection capability of the ShieldTorch System in high purity matrices. This application note deals only with the use of cool plasmas for the analysis of organics, and this technique is available to any Agilent ICP-MS system fitted with the ShieldTorch System and a mass flow controller capable of adding oxygen to the plasma. In routine operation, automatic switching between one set of cool plasma conditions and one set of normal plasma conditions is employed, to cover all the required elements in a single acquisition.

Figure 4 shows single figure ppt calibrations for ^{24}Mg and ^{52}Cr in undiluted IPA. The calibration plots in the various organic matrices highlight the interference removal and reproducibility of the system.



Mass Element: 24 Mg
IS: ---
Units: ppt
Curve Fit: Y=aX+b+bkg
r = 0.9999 Conc.= 2.255E-001 ppt

Mass Element: 52 Cr
IS: ---
Units: ppt
Curve Fit: Y=aX+b+bkg
r = 0.9996 Conc.= 1.648E+000 ppt

Figure 4. Cool plasma analysis calibrations in IPA. Standard addition at 0, 5, 10 and 20 ppt, showing effective removal of $^{12}C_2$ and $^{40}Ar^{12}C$ (potential interferences on ^{24}Mg and ^{52}Cr respectively).

Conclusions

With a well-designed plasma RF generator and sample introduction system, combined with interference removal technology and appropriate operating conditions, the direct analysis of virtually any organic solvent becomes a routine task. The use of sample introduction hardware that is resistant to organic solvents eliminates system contamination and degradation. Together with excellent control of solvent vapor pressure, plus an optimized, oxygen enriched plasma, this achieves complete decomposition of the sample organic content, allowing trace elements to be determined free from spectral overlaps. The ability to use both normal and cool plasma conditions, with automatic switching between conditions for appropriate analytes, overcomes both plasma and carbon-based interferences on all target trace metals. With the correct combination of hardware and methodology, ICP-MS can be used for the routine, high throughout analysis of organics at levels previously only possible with Graphite Furnace Atomic Absorption Spectroscopy.

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