Interference-Free, Environmental Monitoring at High Sensitivity: Spectral Features of In-Torch Vapourization-Inductively Coupled Plasma- Mass Spectrometry (ITV-ICP-MS)

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Abstract—A set of background spectra is presented for an in-torch-vapourization-inductively coupled plasma-mass spectrometry (ITV-ICP-MS) system. Compared to the background spectra measured when aqueous solutions are nebulized into the plasma (wet plasma), ITV background spectra are considerably simpler. Primarily due to the elimination of water in ITV systems, there is a significant reduction and even elimination of several background species, particularly those containing oxygen and hydrogen. As well, it is shown that ITV-ICP-MS could be used as an alternative solution to the problems of spectral interference effects that are encountered in quadrupole ICP-MS with pneumatic nebulization systems. A differential thermal vapourization, afforded by ITV, can be used to eliminate some interferences by separating the analyte from the matrix or interferent in time.

Introduction

Despite their relative simplicity, inductively coupled plasma mass (ICP-MS) spectra are not interference-free. In addition to the inherent inter-element (isobaric) spectral overlaps, there are several sources of molecular species (poly-atomic interferences) including basic back-ground species from argon, water, and air; molecular species derived from the analytes and matrix in the sample.[1] This is particularly true in complex samples of environmental origin. Some typical examples of these interferences are summarized in Table 1.

Regardless of their origin, such interferences become significant considering the unit resolution of the typical quadrupole-based ICP-MS systems utilizing nebulizer-based sample introduction of aqueous samples. Reduction or elimination of the adverse effects of spectral interferences is currently being addressed by using Dynamic Reaction Cells (DRCs) or their equivalents.[2]

In-torch vapourization (ITV)[3] as a newly developed micro-sample introduction system is an alternative solution to the problem of spectral interferences. Fig.1 shows a schematic diagram of an ITV-ICP-MS system. Liquid, slurry, or solid micro-samples are deposited into or onto a sample probe, a rhenium (Re) filament or cup. The sample probe is secured on a retractable metallic or ceramic rod inserted in a glass, vapourization chamber. An external power supply applies electrical power to the probe for *in-situ* drying, charring, and subsequent vapourization of the sample. A short plug of sample passes through the central channel of the plasma by means of a carrier gas. A time-domain signal from the analyte is the result.

In contrast to pneumatic nebulization, where solvent (e.g., water) is continuously aspirated into the plasma, ITV involves introduction of a dried/charred micro-sample into a "dry" plasma. Hence, a majority of spectral overlaps due to oxide species are minimized in a dry plasma, since water is considered as the major source for oxygen in wet plasmas. Matrix-induced inter-ferences are also reduced or completely eliminated, as the sample matrix is removed during a charring step prior to the vapourization of the analyte. In essence, rather than allowing interferents to form and later destroying them

via reactive collisions, in ITV approach, some molecular ions are not allowed to form at all.

Dry plasmas are also used in electrothermal vapourization (ETV)[4] and direct sample insertion (DSI)[5,6]. However, in both methods carbide formation is a key limitation.

This paper attempts to show an update of studies performed so far on ITV-ICP-MS. It also provides some preliminary data on background spectra of a wet (nebulization based) versus dry (ITV) plasma. Examples of some possibilities of spectral interference elimination using ITV-ICP-MS are also shown in this report.

Table 1 Some typical examples of spectral interference effects in ICP-MS.

Type	Mass	Species	Elements Affected
Isobaric overlaps			
Analyte	48	$^{48}Ca^+$	$^{48}Ti(73.81)$
Matrix (i.e., Fe-rich samples)	58	$^{58}Fe^+$	$^{58}Ni(68.01)$
Basic plasma species			
Mono-atomic	40	$^{40}Ar^+$	$^{40}Ca(96.94)$
Poly-atomic	80	$^{80}Ar_2^+$	$^{80}Se(49.61)*$
Solvent/matrix-induced species			
Mono-atomic	35	$35Cl^+$	$^{35}Cl((75.77)$
Poly-atomic	51	$^{35}Cl^{16}O^+$	$^{51}V(99.76)$
	75	$^{40}Ar^{35}Cl^+$	$^{75}As(100)$
Oxides	56	$^{40}Ar^{16}O^+$	$^{56}Fe(91.72)$
	152	$^{136}Ba^{16}O^+$	$^{152}Sm(26.72)$
	133	$^{101}Ru^{16}O^{16}O^+$	$^{133}Cs(100)$
Hydroxides	55	$^{38}Ar^{16}OH^+$	$^{55}Mn(100)$
	103	$^{87}Sr^{16}OH^+$	$^{103}Rh(100)$
	153	$^{136}Ba^{16}OH^+$	$^{153}Eu(52.2)$
Doubly-charged species	75	$^{150}Nd^{2+}$, $^{150}Sm^{2+}$	$^{75}As(100)$
	69	$^{138}Ba^{2+}$	$^{69}Ga(60.11)$
Argides	63	$^{40}Ar^{23}Na^+$	$^{63}Cu(69.17)$

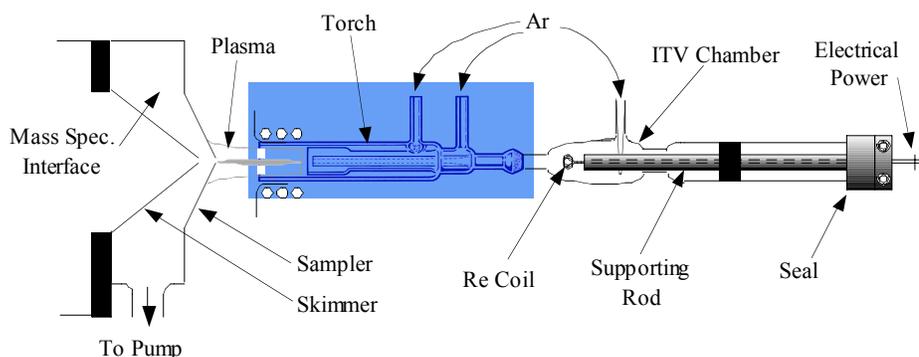* Ar-dimer isotopic combinations potentially interfere with all Se isotopes.

Fig. 1 Schematic diagram of a typical ITV-ICP-MS system (diagram not to scale).

Experimental

An ITV device was coupled to an ICP-MS (Sciex, Elan 250, Concord, ON, Canada). The configuration is schematically shown in Fig.1. Industrial-grade argon was purchased from Praxair, Paris, ON, Canada. High purity argon with a built-in purifier (BIP™) was purchased from Air Products (Brampton, ON, Canada). Rhenium wire (99.97% pure, 0.25 mm thick) was purchased from Alpha Aesar, Ward Hill, MA, USA. Electrical power was applied to the ITV Re coiled filament via an external power supply (model XHR 20-30, Xantrex Technology, Burnaby, BC, Canada). De-ionized water (18.2 MΩ) was supplied by a Millipore Milli-Q purification system. A mass flow controller (model 0151E, Brooks Instruments, Hatfield, PA, USA) was used for controlling the argon carrier gas. Other operating conditions used for this work are listed in Table 2.

Further Modifications

A question now arises as to other sources of oxygen. Three other possible sources can be identified: impurities in the argon supplies used (e.g., O_2 <5 ppm, H_2O <3 ppm, CO_2 <1 ppm, THC <1 ppm, N_2 <10 ppm, H_2 <1 ppm used for this work as industrial-grade argon), permeation through the pneumatics (argon tubing), and air entrainment.[5] In fact, these three sources are also major origins of nitrogen and carbon, two other species that also cause spectral interferences on several masses by forming molecular species (e.g., $^{40}Ar^{12}C^+$, $^{40}Ar^{14}N^+$, $^{14}N^{16}O^+$, $^{12}C^{16}O^{16}O^+$).

In order to eliminate these remaining sources, further modifications were performed in the system.

Instead of regularly purchased argon cylinders, a high-purity argon (99.999%) cylinder with a built-in purifier (BIP™) was utilized as argon supply. The certificate of gas analysis showed the following levels of impurity: O_2 <10 ppb, H_2O <20 ppb, THC <100 ppb, N_2 <5 ppm.

The pneumatics within the instrument (argon transfer tubing) was replaced with Teflon-lined stainless steel tubing to eliminate permeation of air components into the gas lines.

In an attempt to reduce air-entrained species, a torch extension (i.e., a sleeve) that fit over the ICP torch was utilized. The argon exiting the torch would escape from a small gap (1-2 mm) between the sampler and the sleeve. This would minimize air entrainment.

Table 2 ICP-MS operating conditions.

|	
Common ICP conditions	
RF forward power	1.25 kW
RF reflected power	<5 W
Torch	Fassel Type
Outer-tube gas	16 L/min
Intermediate-tube gas	1 L/min
Wet plasma	
Nebulizer gas	0.95 L/min
Sampling depth	15 mm (TOLC)*
Sample uptake	1.4 mL/min
Dry plasma (ITV)	
Carrier gas	1.1 L/min
Sampling depth	11 mm (TOLC)*
Vapourization power	20 W

Comparison of Background Spectra

Background spectra of a wet plasma were acquired and compared to those of a dry (ITV) plasma. Operating conditions were those mentioned in Table 2.

Since no significant spectral features have been reported above mass 85, the mass range covered was from mass 1 to 85.[1] For brevity and to facilitate comparisons, the spectra of wet and dry plasma are converted to bar graphs with logarithmic intensity and shown in Fig. 2.

A quick comparison reveals that the dry background spectrum is considerably simpler. The intensity of some species (e.g., C^+, N^+, O^+, OH_2^+) has been reduced by up to ~100 times. In some cases, background ions have been completely disappeared (i.e., where no white bar is present at specific masses in Fig. 2)

The significance of using a dry plasma is better appreciated at mass 56 where $^{40}Ar^{16}O^+$ interfering species prevent the determination of ^{56}Fe at high sensitivity with wet plasmas. A dry (ITV) plasma can simply eliminate the formation of $^{40}Ar^{16}O^+$ and improve the detection

-1

Counts.s
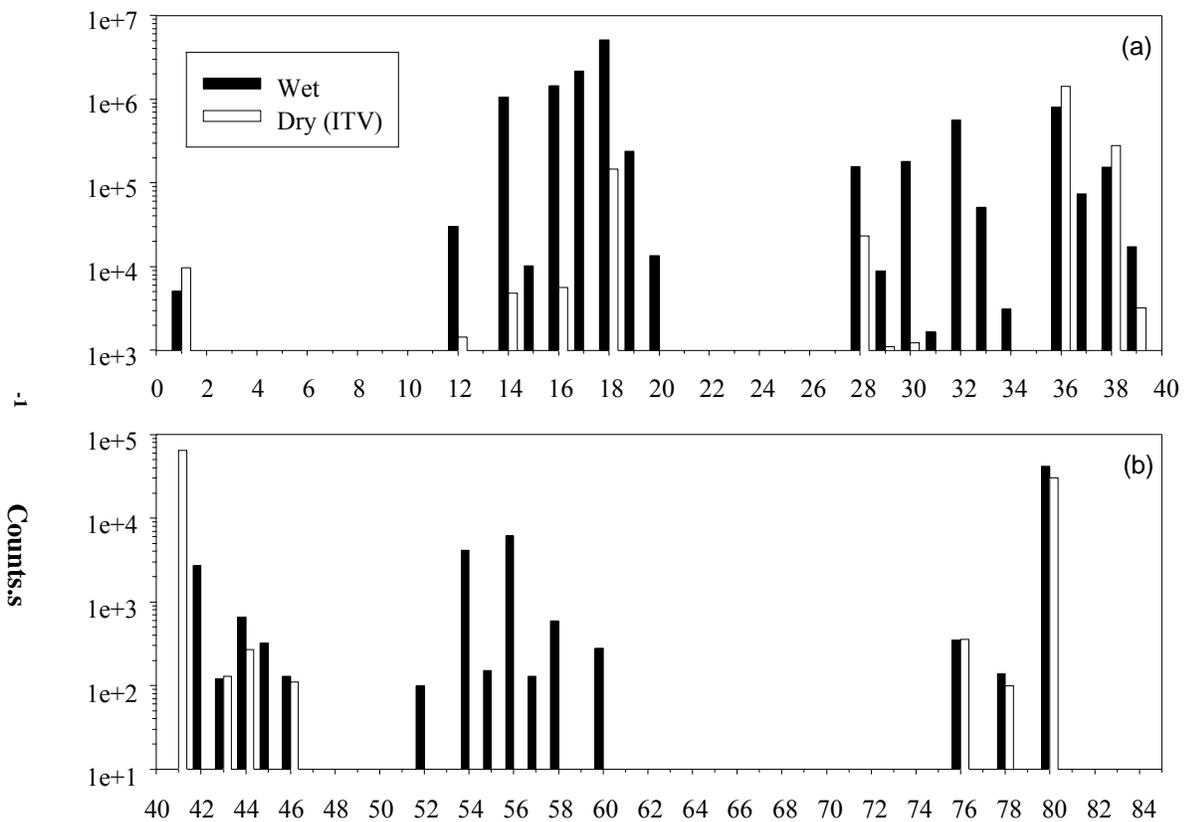
limits of iron by ICP-MS.

Experiments showed that the levels of species in plasma background spectra (wet or dry) are very much dependent on operating conditions (e.g., gas flow rates, RF forward power, sampling depth). Hence, the operating conditions used for this set of experiments were determined based upon typical values used for the pneumatic nebulizer and ITV experiments in our lab.

Despite its promising results, dry (ITV) plasma was not problem-free. The problem was a contamination originating from the ITV device during ITV "ON" mode (i.e., electrical power applied to the Re coiled filament). The rhenium wire that made the ITV sample probe was only 99.97% pure. The supporting rod (ceramic or metallic) also became hot during spectral scans. The ICP-MS system used was sensitive enough to detect the impurities (e.g., Fe, Cr, Mg, Na) originating from these two sources, especially with high vapourization powers (>20 W). This problem requires more investigation and is currently being addressed in our lab by using a higher purity rhenium and increasing the distance between the Re filament and the supporting rod.

Example of Elimination of an Interferent

Analyte and sample matrix based oxides (MO_n^+) represent one of the most common sources of spectral interferences in ICP-MS. These species can cause significant spectral interference, especially if they arise from an element which is present at high concentration in a sample and if they overlap with a low concentration sought-for analyte. An example of the elimination of this type interference by ITV-ICP-MS is presented here.

Ruthenium (Ru) is a readily oxide forming element. Ruthenium oxide species can potentially interfere with 28 isotopes (almost 10% of the isotopes in the periodical table). The elimination of the spectral interference of

$^{101}Ru^{16}O^{16}O^+$ was investigated for mono-isotopic ^{133}Cs using ITV-ICP-MS. With the mass spectrometer parked at mass 133, a 5-_L standard solution containing 50 pg Cs was run with the ITV system. Fig. 3(a) shows a transient signal from Cs. A 5-_L solution containing 5 ng Ru (100 times higher in concentration) was run next (at mass 133). No signal was observed as shown in Fig. 3(b). From this experiment, it can be concluded that $^{101}Ru^{16}O^{16}O^+$ is not formed at this concentration level, since oxygen sources are considerably reduced in a dry (ITV) plasma. This enables interference-free determinations at mass 133.

Differential Thermal Vapourization

Another important characteristic of the ITV technique is differential time behaviour. Analytes and matrix species are not necessarily vapourized from the sample probe at the same time. It can be shown that this differential time behaviour could be useful in eliminating some spectral interference problems. Fig. 4 helps to better illustrate this capability of ITV. After drying and charring the sample, a multi-stage temperature programming can be used to vapourize the analyte and the matrix in different times (vapourize 1, and 2 in Fig. 4).

A slurry sample of coal fly ash (NIST SRM 1633b, 2 mg/10mL) was used to demonstrate this concept. The determination of ^{64}Zn may be hindered by the formation of $^{48}Ti^{16}O^+$. Despite

Cs (50 pg)   Ru (5 ng)

Counts.s^{-1}

Time/s
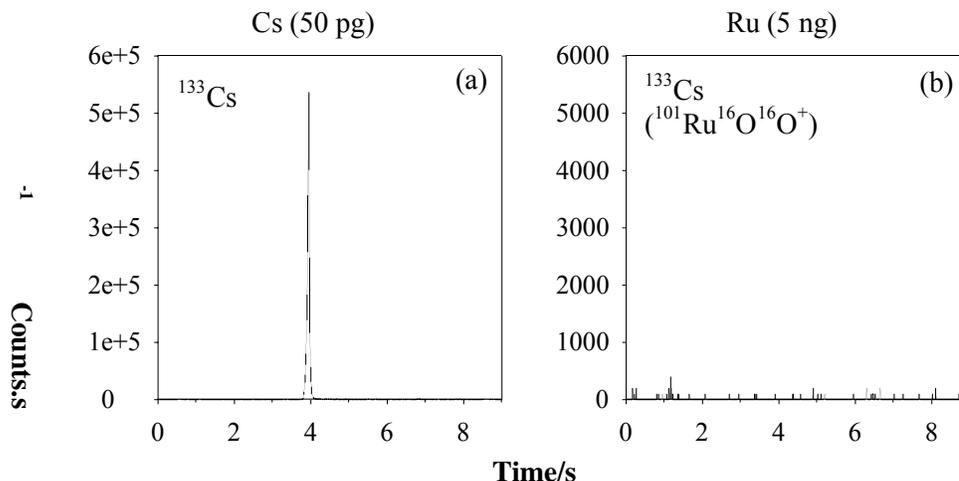
much lower oxygen levels in the ITV dry plasma, formation of $^{48}Ti^{16}O^+$ is inevitable due to the large amounts of titanium present in the sample (0.791%). However, zinc species are more volatile than titanium species. Thus, a differential thermal vapourization could be applied to introduce first the analyte (Zn) and then the interferent (Ti) into the plasma. Fig. 5 shows a signal obtained by vapourizing 5 _L of the coal fly ash slurry, using differential thermal vapourization. The signal assigned to Zn is well resolved from the interfering TiO.
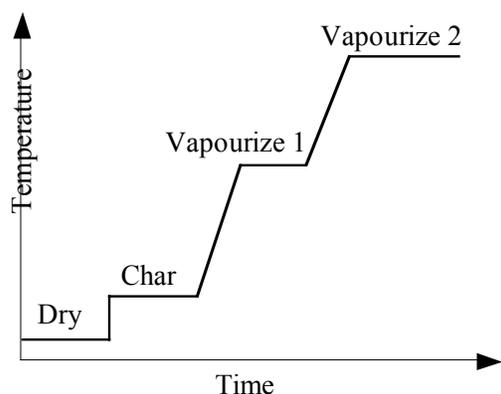

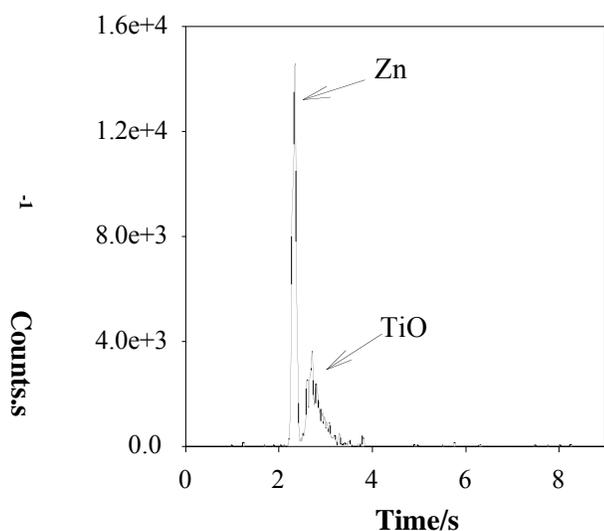**Fig. 4** Conceptual diagram of a multi-stage temperature programming used in ITV- ICP-MS.

Fig. 5 Differential thermal vapourization of a coal fly ash sample for Zn analysis using

ITV-ICP-MS.

Conclusion

Dry (ITV) plasma offers an attractive alternative to other technologies (e.g., collision cells) for solving some spectral interference effects encountered in quadrupole ICP-MS. This is mostly due to the removal of water as the major source of oxygen in plasmas.

Other sources of oxygen (and also nitrogen and carbon) such as argon supplies, permeation through the pneumatics, and air entrainment can also be reduced by using a higher purity argon, switching to a non-permeable tubing, and adding an extension (i.e., sleeve) to a typical torch.

In this way, in-torch vapourization (ITV), can help eliminate or reduce a host of spectroscopic interferences by preventing the formation of oxygen-, nitrogen-, and carbon-containing molecular species.

Moreover, spectral overlaps caused by matrix components can also be reduced, or in some cases completely eliminated, by utilizing the differential thermal vapourization offered by ITV. This way, spectral overlaps can be resolved in the time domain rather than in the spectral domain.

Undoubtedly, more work is required to solve the problems of contamination from the Re coil and the supporting rod (i.e., redesign the setup and use higher-purity rhenium). As well, the effect of plasma and ITV operating conditions on plasma background specrtra and ITV signals warrant more investigation.

References
1. A. Montaser, *Inductively coupled plasma mass spectrometry*, Wiley-VCH, 515, (1998).
2. V. I. Baranov and S. D. Tanner, *A dynamic reaction cell for inductively coupled mass spectrometry*, J. Anal. At. Spectrom., **14**, 1133, (1999).
3. H.R. Badiei and V. Karanassios, *Rhenium-cup in-torch vapourization inductively coupled plasma atomic emission spectrometry for liquid, slurry or solid micro-samples,* J. Anal. At. Spectrom., **15**, 1057, (2000).
4. D.C. Gregoire, *Discrete sample introduction techniques for inductively coupled plasma mass spectrometry, Chap.3: ETV for ICP-MS*, D. Barcelo (Ed.), Elsevier, 347, (2000).

5 . V. Karanassios and G. Horlick, *Background spectral characteristics in direct sample insertion-inductively coupled plasma mass spectrometry,* Spectrochim. Acta, **44B**, No. 12, 1361, (1989).

6. V. Karanassios and T. J. Wood, *Discrete sample introduction techniques for inductively coupled plasma mass spectrometry,Chap.5: Direct sample insertion,* D. Barcelo (Ed.), Elsevier, 503, (2000).