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An inductively coupled plasma/selected-ion flow tube mass spectrometric study of the chemical resolution of isobaric interferences†

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An inductively coupled plasma/selected-ion flow tube (ICP/SIFT) mass spectrometer has been constructed to permit the study of the kinetics and product distributions of reactions of ICP ions with neutral reagents. This has been achieved by modifying the SIFT mass spectrometer in the Ion-Chemistry Laboratory at York University to accept ions from a commercial ICP torch assembly and atmosphere/vacuum interface (Elan Series, Perkin-Elmer SCIEX). The operation of the combined ICP-SIFT instrument is illustrated for the determination of reaction rates and product distributions for the isobaric pairs ArO^+/Fe^+, Ar_2^+/Se^+ and ClO^+/V^+ reacting with a range of neutral modifiers. The results of these measurements permit the formulation of strategies for the use of ion–molecule reactions to move/remove isobaric interferences (termed chemical resolution) and so are useful in the selection of reagent gases used in ICP-MS reaction cells implemented to improve quantitative detection limits.

Introduction

During trace element determination using the ICP-MS technique, spectral interferences due to isobaric diatomic (and triatomic) species hinder the accurate quantification of many metals.[1] Similarly, isotopic overlap from neighboring elements can affect the accuracy of isotope ratio measurements.[2] Currently, there are several strategies for overcoming these spectral interferences. Cold plasma techniques[3–5] and modified plasma gas techniques[6,7] alter plasma chemistry to minimize the formation of some diatomic isobaric ions. These methods have found important application in some instances, but each has deficiencies that limit their general use. Cold and cool plasmas show reduced sensitivity to analytes having ionization potentials above *ca.* 8 eV, increase the oxides of refractory elements, and suffer from easily ionized element matrix effects in the plasma.[5] Mixed gas plasmas introduce different polyatomic interferences depending on the gas added to the plasma.

High-resolution mass spectrometry utilizes its inherent capability to mass-resolve these isobaric interferences but these instruments are more expensive than quadrupole systems, do not allow resolution of many isobars, and are less stable at high resolution. In addition, sensitivity and sample throughput can be reduced when operating in high-resolution mode.

High-energy collisional dissociation of these isobaric interferences has been demonstrated in rf-only multi-pole collision cells coupled to standard quadrupole ICP-MS instruments.[8] This process requires that the loss of diatomic species caused by collisional dissociation be significantly faster than the loss of atomic species caused by collisional scattering, and this is not always realized.[8] Furthermore, certain interferences cannot be collisionally dissociated, for example the Ar^+ interference with Ca^+, and other atomic isobars.

To protect the extensive investment in existing sample preparation methodologies developed in various laboratories specifically for implementation on atmospheric-pressure pure-argon-plasma quadrupole based ICP-MS, an extension to this favored instrument/methodology would be preferred. The dynamic reaction cell[9,10] offers one such opportunity. The use of gas phase ion–molecule chemistry for the selected removal of spectral interferences has been discussed in the literature for more than a decade.[8] Currently, there is a broad database of reaction rate constant information for ion–molecule reactions.[11] This database however lacks comprehensive surveys of transition metal ions and higher mass metals. The motive for the research presented here was to utilize an instrument recently constructed in our laboratory to provide the rate constant information absent in the current database of ion–molecule chemistry. This new information provides the basis for the development of new methodologies for the resolution of ICP-MS spectral interferences using ion–molecule reactions. Chemical resolution through the use of ion–molecule reactions can be effected in one of two ways: by removal of the isobaric interference or by moving the analyte mass of interest.

Here, we report results of absolute rate-constant measurements at 300 K with a novel inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer[12] that were directed towards a study of chemical resolution of isobaric ICP ions and are useful to the ICP-MS community and to ion chemists generally.

Experimental

The selected-ion flow tube (SIFT) mass spectrometer in the Ion-Chemistry Laboratory at York University, described in detail elsewhere,[13,14] has been modified to accept ions generated in an inductively coupled plasma (ICP) torch (Elan Series 5000, Perkin-Elmer SCIEX) through an atmosphere/vacuum interface (Elan Series 6100, Perkin-Elmer SCIEX). The ICP ion source and interface are shown schematically in Fig. 1. The interface was used as supplied with sampling and skimmer cones with orifice diameters of 1.14 and 0.88 mm, respectively. The shadow stop (5.0 mm diameter) prevents contamination of the ion optics by blocking unvaporized plasma particles and in this application also prevents UV photons from entering the reaction region of the

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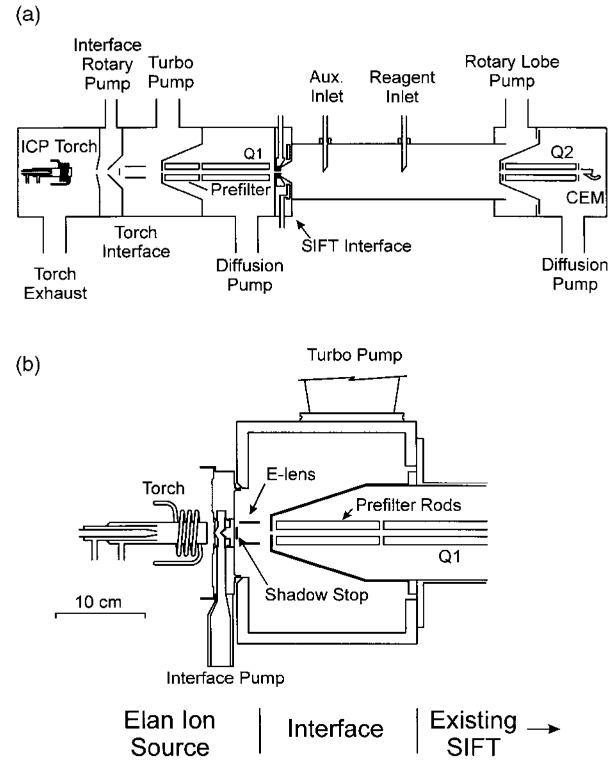

Fig. 1 (a) Schematic view of the working ICP/SIFT instrument. Ions created in the ICP torch pass through the torch interface and are focused into the pre-filter and mass-selected in Q1. Ions are entrained in the helium buffer gas as they pass through the SIFT interface where they experience *ca.* 4×10^5 collisions with the flowing buffer gas atoms prior to reaching the reagent inlet. Neutral molecules are introduced through the reagent inlet and ion–molecule reactions can occur between this inlet and the downstream nose cone. Reactant and product ions are determined by Q2 and counted with a Channeltron electron multiplier (CEM). (b) Scaled close-up of the ICP/SIFT interface.

flow tube. The region between the sampling cone and skimmer was pumped by a 1000 l min^{-1} rotary vane pump (Alcatel 2060) and that after the skimmer was pumped by a 200 l s^{-1} turbomolecular pump (Leybold Hy.Cone 200). The extraction lens potential was supplied by a Hewlett-Packard E3632A dc Power Supply. The potential applied to the extraction lens ranged between +5 and +10 V. To adapt the turbomolecular pump and atmosphere/vacuum interface to the existing instrument a vacuum housing was required. To couple the intense ion beam from the ICP ion source to the existing mass-resolving quadrupole, an extended rf only quadrupole pre-filter, 116 mm in length, was capacitively coupled to the first mass-resolving SIFT quadrupole (Q1) with a matched set of high-voltage 100 pf capacitors. The pre-filter was floated with a Hewlett-Packard Model 6102A dc power supply coupled through 20 MΩ resistors. The potential applied to the pre-filter was between −20 and −36 V with respect to the instrument ground. The quadrupole pre-filter and the extraction lens possess ion focusing characteristics and both applied potentials, relative to instrument ground, were optimized for maximum ion transmission as a function of the ion mass selected in Q1.

Metal salt solutions were peristaltically pumped (Gilson Minipuls 3, two-channel) to a nebulizer at rates between 0.25 and 0.40 ml min^{-1}. The nebulizer was of cross-flow gem-tip design, spraying into a Scott-type double-pass chamber. The nebulized solution was carried to the plasma region through a ceramic (alumina) injector. The metal salt solutions were generally 5 mg l^{-1} in water generated by a Millipore Milli-Qplus water-purification system. Solutions were stabilized with 2–2.5% acid, either nitric or hydrochloric as the situation required.

The rf power supply was typically set to transmit 1000–1250 W of power (nominal free-running frequency, 40 MHz). The plasma torch was a standard demountable SCIEX design. The flows of argon into the three torch inputs were: 14–15 l min^{-1} (outer or plasma gas), 2 l min^{-1} (intermediate or auxiliary gas) and 1.0–1.2 l min^{-1} (inner or nebulizer gas). The nebulizer gas flow was adjusted to maximize the ion signal detected downstream of the SIFT.

The sampled plasma ions were analyzed with a quadrupole mass filter (Q1) and injected into the flow tube through a Venturi-type interface. Helium was used as the SIFT buffer gas at 46.7±1 Pa. The ion flow tube temperature was 296±2 K. The selected ions that entered the flow tube were allowed to thermalize by collisions with He (*ca.* 4×10^5 collisions) prior to entering the reaction region further downstream at the point of addition of the reagent gas. Reactant and product ions were monitored still further downstream by sampling the reacting mixture and analyzing the ions with a second quadrupole mass filter (Q2). Ions were counted with a Channeltron electron multiplier (CEM). The reagent gases had purities better than 99.5%.

In spite of the use of He buffer, the sampled ICP ions entering the reaction region downstream in the SIFT may not be completely thermalized. Kemper and Bowers have shown that some excited electronic states of some metal ions are not readily quenched to the ground state even after many collisions with noble-gas atoms.[15] However, different electronic states can be expected to react with different rates and even to form different products. A mixture of two electronic states reacting with different rates would lead to a non-linear semi-logarithmic decay that could be readily detected. In the experiments reported here and those we have reported previously using the ICP-SIFT there has been no indication of more than one electronic state involved in the ion–molecule chemistry.

Reaction-rate constants were determined from the measured semi-logarithmic decay of the reactant ion as a function of the flow of the added reagent gas.[13,14] The rate constants reported here have accuracy estimated to be better than ±30%. For slow reactions for which the statistical scatter in the data was significant compared with the slope of the reactant ion decay, an upper limit (based on the line of steepest slope through the data) is reported for the rate constant. Reaction efficiencies are reported as ratios of the observed reaction-rate constant to the collision-rate constant computed on the basis of the model of Su and Chesnavich.[16]

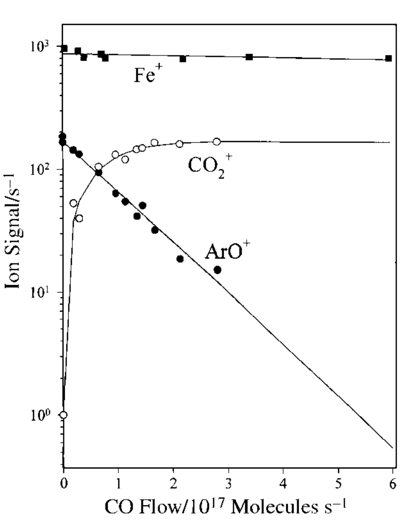

Fig. 2 Observed ion profiles obtained for the reaction of ArO^+ with CO (circles) and the reaction of Fe^+ with CO (squares) in two separate experiments. Reactant ions are shown as closed symbols and product ions are shown as open symbols.

Table 1 Summary of products and rate constants measured for reactions of nominal mass 56 u ions in He bath gas at 0.35±0.01 Torr and 296±2 K

Reaction	Primary product(s)	Rate constant/ cm^3 molecules^{-1} s^{-1}
$ArO^+ + NH_3$	NH_3^+	1.4×10^{-9}
$ArO^+ + CO$	CO_2^+	5.1×10^{-10}
$ArO^+ + H_2$	H_2O^+, $ArOH^+$	3.7×10^{-10}
$ArO^+ + N_2$	N_2O^+	1.6×10^{-10}
$Fe^+ + NH_3$	$Fe(NH_3)^+$	9.1×10^{-12}
$Fe^+ + CO$	None	$< 2 \times 10^{-13}$
$Fe^+ + H_2$	None	$< 1 \times 10^{-14}$
$Fe^+ + N_2$	None	$< 1 \times 10^{-14}$
$Fe^+ + N_2O$	FeO^+	3.4×10^{-11}
$Fe^+ + NO$	FeO^+	2.4×10^{-11}
$Fe^+ + C_2H_4$	$FeC_2H_4^+$	3.8×10^{-11}

Results and discussion

The operation of the ICP/SIFT instrument has been demonstrated for two modes of chemical resolution of isobaric interferences: moving the interfering ion to another mass and moving the analyte ion.

The ArO^+/Fe^+ interference

CO has been identified as a neutral reagent suitable for the chemical resolution of ArO^+ and Fe^+ (mass 56 ions). Observed ion profiles for ArO^+ and Fe^+ reacting with CO are presented in Fig. 2. ArO^+ is seen to react rapidly and Fe^+ immeasurably slowly. The reaction-rate constant for the formation of CO_2^+ from ArO^+ and CO was determined to be 5.1×10^{-10} cm^3 molecules^{-1} s^{-1}. This corresponds to a reaction efficiency of 0.65 (or a reaction at two out of every three collisions). The mechanism of the reaction appears to be oxygen cation abstraction. In performing the isobaric Fe^+ reaction, sufficient iron-salt solution was pumped into the plasma so that the $m/z = 56$ signal was predominantly due to Fe^+ rather than ArO^+. Under these conditions Fe^+ showed a complete lack of reactivity towards CO, $k \leqslant 2.0 \times 10^{-13}$ cm^3 molecules^{-1} s^{-1} or reaction in less than one out of every 4000 collisions. Thus, hypothetically, for an ion–molecule reaction cell pressurized with CO in which entering ArO^+ and Fe^+ ions experienced on average ten collisions during transit, the ArO^+ signal would be reduced in intensity by a factor of 36 000 while the intensity of the Fe^+ signal would decrease by at most 0.25%. This represents a significant improvement in the signal-to-noise ratio at nominal mass 56. Other ion–molecule reaction-rate constants, determined in this work, for ions at nominal mass 56 are shown in Table 1. From Table 1 it can be seen that the common gases NH_3, CO, H_2 and N_2 react rapidly with ArO^+ and slowly, if at all, with Fe^+; these would therefore be potential neutral reagents for the chemical resolution of ArO^+ from Fe^+. Other reagents (N_2O, NO and C_2H_4) react at moderate rates with Fe^+ and therefore would not be useful for chemical resolution of ArO^+ from Fe^+ since they could unduly deplete the Fe^+ signal regardless of their reactivity towards ArO^+. Provided that there were no isobaric interferences at the mass of the primary product ion of these Fe^+ reactions, one might consider determination of Fe as the primary product ion. However, these rate constants are sufficiently low that the extent of reactive conversion may be too low for trace analysis applications.

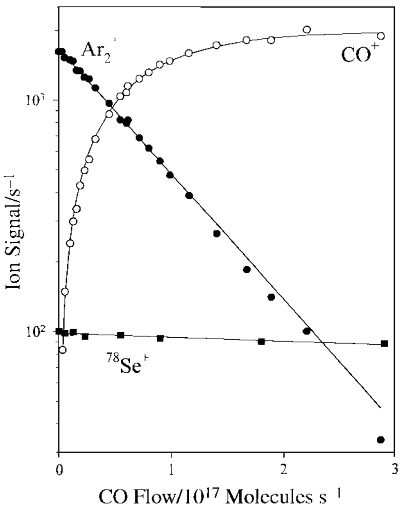

Fig. 3 Observed ion profiles obtained for the reaction of Ar_2^+ with CO (circles) and the reaction of Se^+ with CO (squares) in two separate experiments.

The Ar_2^+/Se^+ interference

Fig. 3 presents the observed ion profiles for Ar_2^+ and $^{78}Se^+$ reacting with CO. We were unable to generate amounts of $^{80}Se^+$ sufficient to dominate the $m/z = 80$ signal from the plasma source so, instead, measurements were taken with the ^{78}Se isotope. From the rate constant data it can be seen that the charge-transfer reaction between Ar_2^+ and CO is very efficient, occurring, within experimental error, at the computed[16] ion–molecule collision rate. In contrast, the upper limit of the rate constant for the depletion of $^{78}Se^+$ was determined to be 3.6×10^{-12} cm^3 molecules^{-1} s^{-1}, corresponding to at most one reaction in every 200 collisions. Other ion–molecule reaction rates, determined in this work for ions at nominal mass 80, are shown in Table 2.

The ClO^+/V^+ interference

Table 3 presents reaction-rate data for ClO^+ reacting with a variety of neutrals. With the exception of NO_2, for the selected neutrals ClO^+ seemed to be relatively unreactive. Fig. 4 presents the observed ion profiles for ClO^+ and V^+ reacting with NO_2. Clearly, both ClO^+ and V^+ react with NO_2 at similar rates and therefore no significant improvement in the signal-to-noise ratio would be expected for the chemical resolution of this isobaric pair by the selective removal of the isobaric diatomic species with NO_2. Thus, to resolve V^+ from ClO^+ chemically, we sought a chemical resolution scheme that added a known mass to the analyte (V^+). In Fig. 5 the

Table 2 Summary of products and rate constants measured for reactions of nominal mass 80 u ions (although $^{78}Se^+$ was used instead of $^{80}Se^+$) in He bath gas at 0.35±0.01 Torr and 296±2 K

Reaction	Primary product (s)	Rate constant/cm^3 molecules^{-1} s^{-1}
$Ar_2^+ + CO$	CO^+ (95%), $ArCO^+$(5%)	7.3×10^{-10}
$Ar_2^+ + H_2$	ArH^+(60%), ArH_2^+(40%)	6.3×10^{-10}
$Ar_2^+ + N_2O$	N_2O^+	6.2×10^{-10}
$Se^+ + CO$	None	$< 3.6 \times 10^{-12}$
$Se^+ + N_2O$	SeO^+	6.7×10^{-13}
$Se^+ + NO$	NO^+	2.6×10^{-10}

Table 3 Summary of products and rate constants measured for reactions of nominal mass 51 u ions in He bath gas at 0.35 ± 0.01 Torr and 296 ± 2 K

Reaction	Primary product(s)	Rate constant/ cm^3 $molecules^{-1}$ s^{-1}
$ClO^+ + NO_2$	NO^+, NO_2^+	8.7×10^{-10}
$ClO^+ + O_2$	—	$< 10^{-13}$
$ClO^+ + H_2$	—	$< 10^{-13}$
$ClO^+ + CO$	—	$< 10^{-13}$
$ClO^+ + N_2O$	—	$< 10^{-13}$
$ClO^+ + NH_3$	—	$< 10^{-13}$
$V^+ + NO_2$	VO^+	9.7×10^{-10}
$V^+ + O_2$	VO^+	2.8×10^{-10}
$V^+ + NO$	VO^+	4.0×10^{-11}
$V^+ + N_2O$	VO^+	2.4×10^{-10}
$V^+ + C_2H_4O^a$	VO^+	1.6×10^{-9}

^{a}Ethylene oxide.

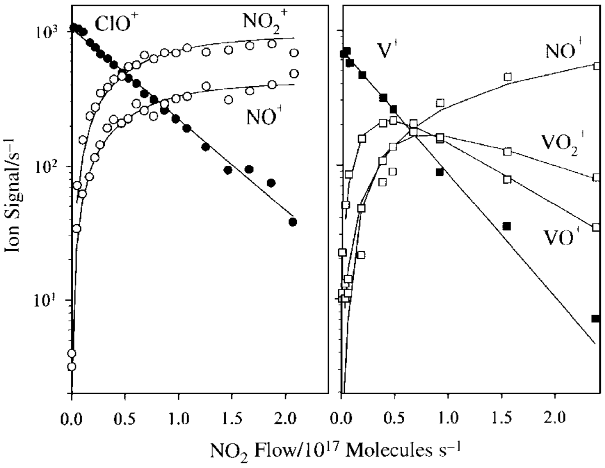

Fig. 4 Observed ion profiles obtained for the reaction of ClO^+ and V^+ with NO_2. ClO^+ was observed to react *via* electron transfer with NO_2 to form NO_2^+ and *via* dissociative electron transfer to form NO^+. Vanadium cations were observed to react at a similar rate with NO_2 to form VO^+, with subsequent oxidation to VO_2^+ and then dissociative electron transfer or oxygen anion transfer to form NO^+.

observed ion profile for V^+ reacting with O_2 is presented. The vanadium cation was found to react rapidly with O_2 to form the VO^+ ion. Subsequent reactions of VO^+ with O_2 are substantially slower. As a result after a maximum in VO^+ production is reached the VO^+ signal is fairly insensitive to the flow of O_2; this behavior is critical in quantitative analytical applications. From results presented in Table 3 it was generally found that V^+ reacted with oxygen-containing neutrals by oxygen atom abstraction. ClO^+ is unreactive with O_2, suggesting that the resolution of V^+ from ClO^+ by oxidation of the V^+ to VO^+ with O_2 is a feasible analytical approach.

Conclusions

Preliminary work has uncovered several strategies for the chemical resolution of mass spectral isobaric interferences using ion–molecule reactions. Work continues in our laboratory to determine reaction rate constants and product distributions for a variety of other background interference ions created in the ICP ion source as well as for atomic ions of elements routinely quantified using ICP-MS.

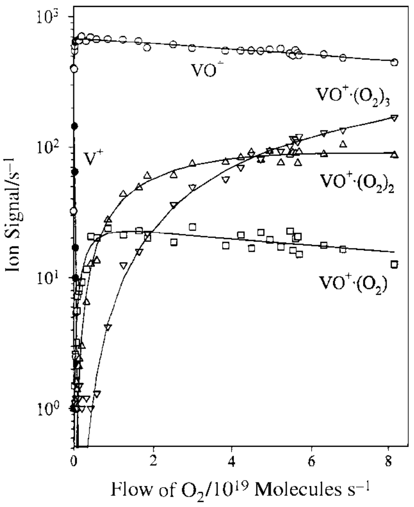

Fig. 5 Reaction profile obtained for the reaction of V^+ with O_2 highlighting the rapidity with which V^+ reacts to form VO^+ contrasted with the relatively slow rate at which VO^+ reacts further to produce higher oxide cations. ClO^+ was observed not to react with O_2.

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