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# Use of an ion guide collision cell to improve the analytical performance of an inductively coupled plasma time-of-flight mass spectrometer

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## Abstract

An axial-acceleration inductively coupled plasma time-of-flight mass spectrometer has been equipped with an octopole ion guide/collision cell. Ion-energy experiments prove that instrument duty cycle improves by up to 100% over values determined for conventional ion optics. Both sensitivity and noise were found to decrease with the ion guide in place. Consequently, limits of detection for most elements were found to be comparable to those calculated for conventional ion optics. The exceptions are low-mass ions that enjoy only a relatively small gain in duty cycle and thus exhibited significantly degraded detection capability. Collisional cooling caused the spectral resolving power to improve by up to 80% compared to the conventional optics. Ion chemistry within the collision cell permitted the determination under robust plasma conditions of potassium, calcium, and iron, elements that usually suffer from isobaric overlaps. Improved resolving power helped reduce the adverse effects of hydrocarbon background ions generated by reactions within the ion guide. (Int J Mass Spectrom 212 (2001) 49–63) © 2001 Elsevier Science B.V.

**Keywords:** Inductively coupled plasma; Time-of-flight mass spectrometry; Ion guide; Collision cell; Elemental analysis

## 1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is the premier technique for ultratrace elemental analysis. Strengths of ICP-MS include the ability to measure most of the elements in the periodic table with the exception of the halides and noble gases, excellent limits of detection (sub-pg ml<sup>-1</sup>); broad dynamic range (>6 orders of magnitude); few spectral interferences; and the capability to analyze gases, liquids, and solids [1].

Time-of-flight mass spectrometry (TOFMS) is a recent addition to the list of mass analyzers that have been combined with the ICP for elemental analysis. TOFMS simultaneously extracts all mass-to-charge ratios ( $m/z$ ) for analysis and generates complete mass spectra at rates greater than 20 000 per second. The combination of the ICP with TOFMS produces a technique capable of trace elemental analysis of fast transient signals such as those produced by chromatography [2,3], electrophoresis [4], electrothermal vaporization [5], and laser ablation [6–9].

Even though the strengths of ICP-TOFMS for transient analysis are obvious, widespread application has been restricted due to several performance limi-

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Dedicated to R. Graham Cooks on the occasion of his sixtieth birthday.

tations. The sensitivity of current TOFMS systems ranges from 500 to 10 000 counts per second (cps) per  $\text{ng ml}^{-1}$  per  $m/z$  (distribution produced by a bias against light-mass ions) [10]. Combined with noise that ranges from one to ten counts per second per  $m/z$  these sensitivities result in detection limits in the sub to single  $\text{pg ml}^{-1}$  level for most elements. These limits of detection are up to an order of magnitude worse than in conventional quadrupole-based instruments [1]. This lower sensitivity is initially surprising, considering the high transmission efficiency expected for TOFMS systems because of their open geometry. However, low sensitivity can be caused by several instrumental factors. Radial expansion of the primary ion beam within the vacuum interface results in a significant loss of transmission into the mass analyzer. Additionally, a low duty cycle ( $\sim 5\text{--}10\%$ ), defined as the percentage of the ions that are measured with respect to the total number presented to the mass spectrometer, results in the loss of greater than 90% of the possible ion signal. Lastly, commercial ICP-TOFMS instruments currently incorporate several gridded ion-optical elements, which reduce transmission throughout the ion path.

A resolving power ( $m/\Delta m$ ) of greater than 2500 full width half maximum (FWHM) is needed to eliminate many of the important isobaric interferences associated with ICP-MS [1]. Currently, axial acceleration (aa) ICP-TOFMS systems achieve resolving powers of approximately 500 to 1200 FWHM (mass dependent). To a large extent this resolution is limited by the significant energy distribution of ions of the same mass within the primary ion beam; this distribution results in a spread of arrival times at the MS detector.

Multipole ion guides have demonstrated several attractive properties for improvement of ion transmission characteristics. A radio-frequency (RF) field is applied to an even number of cylindrical rods arranged in a circular array. Placement of the multipole within a collision cell (a pressurized enclosure) allows the addition of inert or reactive gases to the ion guide. Douglas and French [11] demonstrated that elevated buffer gas pressures within an RF quadrupole resulted in enhanced ion transmission through subsequent conductance-limiting apertures. This experiment showed that collisions with the buffer gas reduced the

radial energy of analyte ions and resulted in a focused beam. A decrease in the geometrical cross section of the primary ion beam provided enhanced transmission and improved sensitivity. In the same experiment, Douglas and French [11] noted that elevated pressure within the quadrupole cell resulted in a significant reduction in the axial energy of transmitted ions. Since these early experiments performed with quadrupoles, other multipole arrangements have been investigated that offer collisional focusing and cooling [12,13].

The addition of a reactive collision gas to the multipole cell can alter mass spectra by chemical or charge-exchange reactions. Elimination (through charge-exchange) or redistribution (to another  $m/z$ ) of interferent ions can significantly simplify the measurement of analytes that are otherwise obscured by isobars. Rowan and Houk [14] showed that argon-related polyatomics such as  $\text{Ar}_2^+$ ,  $\text{ArO}^+$ , and  $\text{ArN}^+$  could be greatly attenuated through gas-phase collisions with xenon or methane. Eiden and coworkers [15] demonstrated that hydrogen gas added to a collision cell would greatly reduce transmitted argon ions through selective charge-exchange reactions. Baranov et al. [16–18] have shown that ion reactions within multipoles are strongly controlled by thermodynamics. Differences in reaction rates with collision gases permit the detection of  $^{40}\text{Ca}^+$  at the single  $\text{pg ml}^{-1}$  level in the presence of  $^{40}\text{Ar}^+$  that is up to nine orders of magnitude higher in concentration. Since the initial experiments, a large number of reactive gases have been employed to tailor the desired ion chemistry [16]. A second type of reaction involves alteration of the mass distribution of analytes or interferents. Eiden et al. [19] showed that oxygen could be used to shift the mass of more refractory isobars ( $^{90}\text{Y}^+$  and  $^{90}\text{Zr}^+$ ) to allow the detection of  $^{90}\text{Sr}^+$ .

The attractive analytical characteristics of ion guides have led to their recent incorporation into both quadrupole and sector-field ICP-MS instruments. These systems provide outstanding limits of detection [20,21], improved measurement precision [22], and suppressed isobaric interferences [20,23,24].

Ion guides and collision cells offer the potential for several additional performance benefits when combined with TOFMS. In TOFMS the average ion

energy and the distribution of ion energies dictate many of the instrument characteristics, including duty cycle and resolution. Cooling of the primary ion beam will result in lengthening of the time required to fill the TOF extraction region and thus will enhance instrument duty cycle [25]. Reduction of the ion-energy distribution will lessen demands placed on the reflectron ion mirror used in most systems, and will provide heightened resolution. Krutchinsky and co-workers [26] described a collisional dampening interface that coupled an electrospray ionization source to an orthogonal acceleration (oa) TOFMS that converted the isokinetic (same velocity) primary ion beam to one that was largely isoenergetic (same energy). This system lowered the radial and axial velocities of the ion beam and significantly reduced the mass dependent steering of the ions within the flight tube. Guzowski and Hieftje [27] have recently demonstrated similar mass independent steering in an ICP-*oa*-TOFMS equipped with a hexapole ion guide.

The current study demonstrates the performance of an axial-acceleration ICP-TOFMS fitted with an octopole ion guide. The average energy and distribution of ion energies were found to decrease with buffer gas added to the ion guide. However, contrary to results expected for collisional focusing and improved duty cycle, no significant improvement in sensitivity was noted. Argon-related continuum background was lowered by charge-exchange reactions with hydrogen gas. The reduced ion-energy distribution resulted in up to a two-fold improvement in spectral resolution. Although this elevated resolving power was found not to be adequate to overcome most common plasma-related isobaric interferences, it was sufficient for the separation of the majority of carbon-based ions produced by collisions within the ion guide.

## 2. Experimental

### 2.1. Instrumentation

Several performance characteristics were considered before the appropriate order (number of rod pairs) multipole was selected for use with the ICP-TOFMS.

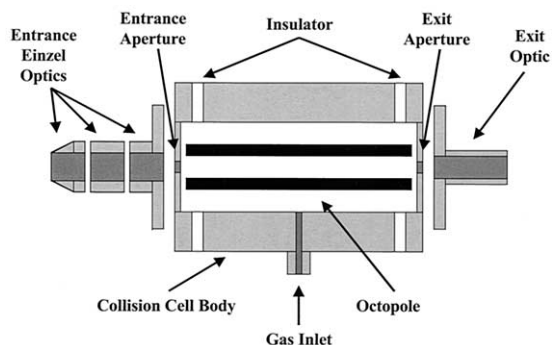


Fig. 1. Schematic diagram of the octopole collision cell and associated optics. Cell apertures are electrically isolated from the cell body and have orifice diameters of 1.91 mm.

The optimal system should provide radial focusing for enhanced transmission efficiency, energy dampening to improve duty cycle and mass resolving power, and allow the simultaneous passage of the entire elemental mass range ( $m/z$  1–238). In general, higher-order systems ( $n > 2$ ) generate spatially wider potential wells and transmit a broader mass range [17,28]. Additionally, the relatively flat field lines near the axis of higher-order multipoles should produce a narrower range of ion energies after collisional cooling. On the other hand, the steeper potential fields of lower-order systems provide better spatial focusing at the axis of the ion guide. Compression of the ion beam cross section will enhance transmission through subsequent conductance limiting apertures. An octopole ( $n=4$ ) was chosen for the present study because of its energy-dampening and broad mass-range characteristics. Although octopoles provide less collisional focusing than do lower-order ion guides, their transmission of the widest range of ion masses was judged to be best suited for coupling with the simultaneous extraction capabilities of TOFMS.

A diagram of the octopole collision cell is shown in Fig. 1. The octopole consisted of eight, 7.62-cm-long, 3.18-mm-diam rods inscribed on an 8.46-mm circle. The rods were held by two Macor mounts that provided electrical insulation from adjacent rods and from the collision-cell body. The octopole assembly was positioned within a stainless-steel collision cell. Electrical and gas connections to the collision cell were made through o-ring sealed side access ports.

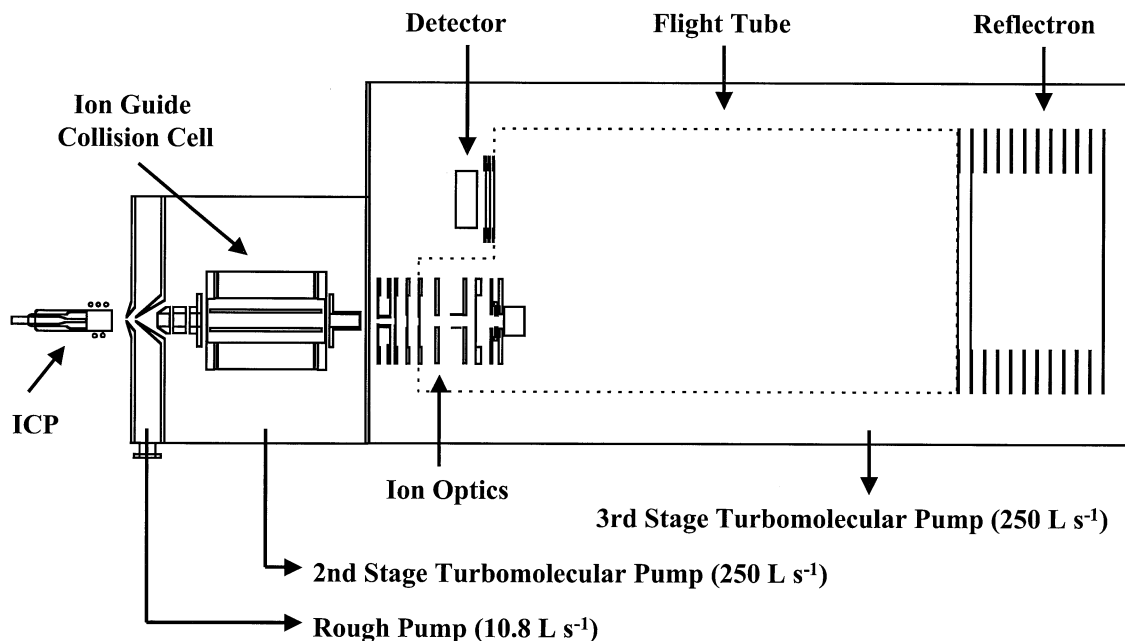


Fig. 2. Diagram of the modified axial-acceleration ICP-TOFMS. The second-stage vacuum chamber was extended to house the ion guide collision cell.

Aperture plates with 1.91-mm diameter orifices defined the entrance and exit of the collision cell. The aperture plates were insulated from the cell body to permit the application of independent potentials. In the experiments described in this study potentials of  $-100$  and  $-30$  V were applied to the entrance and exit apertures, respectively. A three-element ion lens was positioned at the entrance of the collision cell to focus the primary ion beam. A simple cylindrical optic was positioned between the collision cell and the third-stage vacuum aperture to provide additional ion manipulation.

An in-house built RF generator similar to one described by Jones et al. [29] was used to drive the octopole ion guide. This oscillator allowed the application of RF potentials of 20 to 600 V<sub>pp</sub> at frequencies between 1.3 and 6.3 MHz. Substitution of a second inductance coil in the oscillator enabled lower frequencies to be explored. Additionally, a DC potential could be superimposed on one or both poles of the ion guide (each pole contains 4 rods in an octopole). For all experiments describe in this paper, the same DC potential was applied to both sets of rods.

An ICP-aa-TOFMS (Renaissance, LECO, St. Joseph,

MI, USA) was used for elemental detection in all experiments. The ICP was operated at 40.86 MHz with a forward power of 1.3 kW. Argon gas flows of 16.0, 1.0, and 1.0 L min<sup>-1</sup> were used for the outer, intermediate, and central channels, respectively. A sample introduction rate of 1.0 mL min<sup>-1</sup> was pumped to a pneumatic nebulizer (TR-30-C1, J.E. Meinhard Associates, Inc., CA, USA) and Wu-Hieftje vertical rotary spray chamber. The ICP is coupled to the mass spectrometer with a three-stage differentially pumped vacuum interface. Nickel sampler and skimmer cones with apertures of 0.5 mm in diameter were used in all experiments. The third-stage aperture was 1.0 mm in diameter. Under conventional operating conditions, pressures of 1 Torr, 1 mTorr, and less than 1 μTorr are measured in the first, second, and third vacuum stages, respectively. A simple cylindrical electrostatic lens is positioned within the second vacuum stage to focus the primary ion beam. A potential of  $-564$  V on this lens was found to provide optimal sensitivity.

The ion guide collision cell was positioned within the second vacuum stage of the ICP-TOFMS in the location ordinarily occupied by the cylindrical electro-

static lens (Fig. 2). To accommodate the collision cell, a 10.16-cm-long extension was added to the vacuum chamber. The flow of collision gas (hydrogen, 99.999% pure, Air Products, Inc, Indianapolis, IN, USA) added to the ion guide was controlled by a needle valve. Pressure within the collision cell was monitored with a calibrated Pirani thermal conductivity gauge (325 Moducell, MKC Instruments, Inc., Boulder, CO, USA). Due to size constraints the pressure gauge was positioned outside the vacuum chamber and connected to the collision cell with a 6.36-mm-diam flexible metal tube. The conductance limit of the connection tube could result in slight errors in the calculated pressure within the cell.

The LECO Renaissance data acquisition system records spectral information in windows of 2 ns each. For enhanced spectral resolution an external data recording system was employed. The external trigger of the Renaissance was inverted with a gate and delay generator (model 416A, EG&G Ortec, Oak Ridge, TN, USA). The inverted trigger was used as the start input to a Picosecond Time Analyzer (PTA, model 9308, EG&G Ortec, Oak Ridge, TN, USA). The signal from the Renaissance gain-switching amplifier was fed to a constant-fraction discriminator (TC 454, Tennelec, Meriden, CT, USA) that was used as the stop input for the PTA. With this data acquisition system, spectra with 0.625 ns resolution were collected.

Operating conditions in this study were chosen to provide transmission of a wide mass range of ions. Enhanced performance (sensitivity and resolution) for specific elements could be achieved through sacrifice of the mass range that was covered.

## 2.2. Reagents

Multielemental solutions (CLMS-1,2, Spex Certi-prep., Metuchen, NJ, USA) were prepared by serial dilution in 1% nitric acid (EM Science, Gibbstown, NJ, USA) and doubly deionized water.

## 3. Results and discussion

### 3.1. Ion energy distribution

The kinetic energy of ions within the primary ion beam was measured by classical stopping-potential

Table 1

Elemental ion energy distributions for an ICP-TOFMS equipped with conventional ion optics<sup>a</sup>

Element	$m/z$	Most Probable Energy (V)	Average Energy (V)	Width (V, FWHM)	Width (V, 10%)
Li	7	2.8	2.9	1.5	2.5
Al	27	3.0	3.1	1.4	2.5
Y	89	5.2	5.4	1.6	2.6
Cs	133	6.4	6.6	1.8	3.2
Bi	209	8.6	8.8	2.5	5.0

<sup>a</sup> Second stage ion optic potential:  $-564$  V.

experiments [30]. The amplitude of a DC bias applied to the gridded repeller electrode controlled the transmission of ions into the TOF extraction region. As the positive repeller bias was elevated, ions with insufficient energy were retarded. The average and distribution of the ion energies can be calculated from the derivative of the stopping-potential curve.

Table 1 shows the ion energy statistics for a range of masses when the ICP-TOFMS was operated with its conventional ion optics. The most probable energy (highest point on a stopping-potential derivative plot) was found to be roughly equal to the average energy for every element, suggesting symmetrical peak profiles. The ion energies are dictated by a combination of the isokinetic energy gained from the vacuum extraction process (equal to the velocity of argon at the ICP temperature) and the largely isoenergetic ICP offset potential [31]. The ion energies listed in Table 1 are in good agreement with values calculated for a  $2350 \text{ m s}^{-1}$  argon velocity (5310 K) plus an offset potential of 2.6 V. Energy distributions measured at FWHM and at 10% peak height increased with mass.

Ion-energy statistics for the octopole-equipped ICP-TOFMS are listed in Table 2. The ion guide was operated at  $300 \text{ V}_{\text{pp}}$  (6.3 MHz) with a DC offset of +4.5 V and a hydrogen collision-gas pressure of 0.018 Torr. These operating conditions were found to be a good compromise for the transmission of the entire elemental mass range. Enhanced instrument performance (sensitivity and resolution) for limited mass windows could be achieved through alteration of RF voltage and frequency, DC voltage, and buffer-gas

Table 2

Elemental ion energy distributions for an ICP-TOFMS equipped with an octopole ion guide<sup>a</sup>

Element	<i>m/z</i>	Most Probable Energy (V)	Average Energy (V)	Width (V, FWHM)	Width (V, 10%)
Li	7	2.0	2.2	1.4	2.2
Al	27	1.8	1.9	0.9	1.8
Y	89	1.6	1.8	1.0	2.1
Cs	133	1.6	1.8	1.0	2.4
Bi	209	1.4	2.1	1.1	5.0

<sup>a</sup> Ion guide operating conditions: 300 V<sub>pp</sub> at 6.3 MHz, +4.5 V<sub>DC</sub>, 0.018 Torr, hydrogen collision gas.

pressure. However, these compromised operating conditions were chosen in an effort to maintain the simultaneous sampling capabilities of TOFMS.

Ion energies were found to be nearly independent of mass when the ICP-TOFMS was equipped with the pressurized collision cell. This result proves that collisional cooling of the ion beam within the octopole has overcome the isokinetic character of the vacuum-extraction process. The residual DC offset measured with the collision cell in place (approximately 2.0 V) is most likely caused by a potential difference between the exit of the ion guide and the entrance of the TOF extraction region. However, this DC offset could not be experimentally reduced. The difference between the most probable and average ion energy for bismuth is due to peak asymmetry and significant tailing. This skewed peak shape was experienced only with high-mass ions, which are expected to be less thermalized than light ions.

The energy distribution of bismuth collected with the conventional ion optics is shown in Fig. 3(a). The average energy was 8.8 V with a distribution of 2.5 V FWHM (5.0 V at 10% height). Figs. 3(b)–3(d) shows the effect of collision-cell pressure on energy distributions. At a pressure of 0.001 Torr, bismuth displayed a broad energy profile (6.7 V FWHM, 9.4 V at 10% peak height) with an average energy of 3.8 V. A cell pressure of 0.027 Torr resulted in a reduced average energy of 1.4 V with a distribution 1.2 V FWHM (3.8 V at 10% height) wide. At the highest pressure explored, 0.052 Torr, the average ion energy was 1.3 V with a width of 1.1 V FWHM (2.5 V at 10% height). The change in average energy and distribution both suggest significant collisional cooling of the ion beam as a function of pressure.

### 3.2. Duty cycle and Limits of detection

Use of the ion guide collision cell should result in improved ion transmission and duty cycle, with both factors enhancing the sensitivity of ICP-TOFMS. Duty cycle is related to the efficiency of the instrument in terms of the percentage of incoming ions that are presented to the mass analyzer. For TOFMS, the duty cycle is computed by the following equation [25];

$$\text{Duty cycle} = \frac{f \cdot x}{\nu_s + \nu_o} \quad (1)$$

where *f* is the extraction frequency (Hz), *x* is the length (m) of the extraction region,  $\nu_s$  is the ion

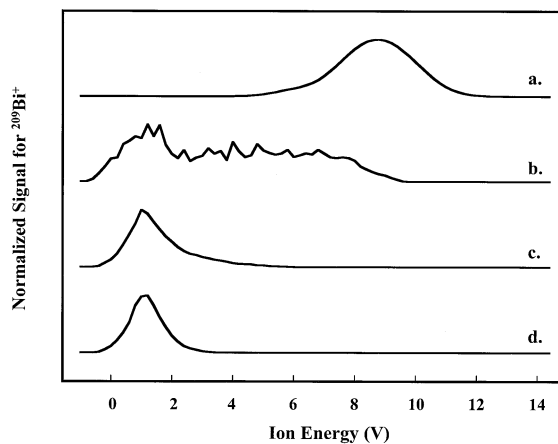


Fig. 3. Bismuth ion-energy distribution for the ICP-TOFMS equipped with either (a) the conventional ion optics or the ion guide collision cell at pressures of (b) 0.001, (c) 0.027, or (d) 0.052 Torr. Collision cell operating conditions: 300 V<sub>pp</sub> RF potential at 6.3 MHz, +4.5 V<sub>DC</sub>, with hydrogen gas. Energy distributions were determined by stopping-potential experiments. Each trace is normalized to its own maximum value.

velocity ( $\text{m s}^{-1}$ ) produced during the isokinetic vacuum extraction process, and  $v_o$  is the ion velocity induced by the plasma offset potential.

Although several methods might serve to raise the duty factor, each imposes possible instrument-performance limitations. Use of a higher spectral generation rate ( $f$ ) will improve duty cycle, but will require an increased acceleration potential or a shorter flight tube to produce a complete mass spectrum before the start of a subsequent extraction event. In turn, a higher acceleration potential and reduced drift length result in a shorter total flight time to the detector and degraded resolving power, defined as  $T/2\Delta t$ , where  $T$  is the total flight time and  $\Delta t$  is peak width. Use of a longer extraction region ( $x$ ) will require more time to fill with ions and thus a higher duty cycle. However, with a conventional two-stage Wiley and McLaren ion-acceleration system [32] such as the one employed in this instrument, the ability of space focusing to compensate for the initial spatial distribution of ions within the extraction volume is impaired as the length of the region is enlarged. Degraded space focusing results in broader spectral peaks and reduced resolving power. All studies described in this paper employed a spectral generation rate of 20 kHz and an extraction region length of 1 cm.

The final and most attractive method for the improvement of instrument duty cycle is to reduce ion velocity ( $v_s + v_o$ ) prior to the extraction region. Lower ion velocities will result in longer extraction-volume fill times and higher efficiency. As discussed previously, the initial ion velocity results from the combination of isokinetic vacuum extraction and the isoenergetic plasma offset potential. The ideal solution to produce unity duty cycle for all  $m/z$  is to generate a low, mass-independent velocity. However, as can be seen from Table 2, collisional cooling of the primary ion beam results in a relatively low mass-independent ion energy of approximately 2.0 V. Although the energy of all  $m/z$  was reduced, so improved duty cycles can be achieved, the mass-dependent velocity of the primary ion beam resulted in a greater mass bias against light ions. Fig. 4 shows the agreement between duty cycle values calculated from stopping-potential experiments (Tables 1 and 2) and predicted

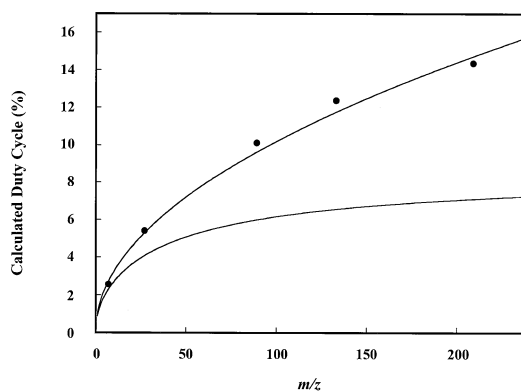


Fig. 4. Calculated instrument duty cycle as a function of  $m/z$  when the TOFMS is equipped with conventional ion optics or (●) the octopole collision cell. Data points are derived from experimentally determined ion energies obtained from stopping-potential experiments. Lines are theoretically calculated from equation 1. For conventional optics  $v_s=2350 \text{ m s}^{-1}$  and  $v_o=2.6 \text{ V}$ . With the ion guide  $v_s=0 \text{ m s}^{-1}$  and  $v_o=2.0 \text{ V}$ . Although duty cycle is enhanced for all  $m/z$  with the ion guide, a more significant mass bias is produced.

by equation 1 when the ICP-TOFMS was operated with the conventional optics or the octopole ion guide. With the conventional ion optics in place, duty cycle values range from 2.3% for lithium to 7.1% for bismuth. The octopole collision cell produces instrument duty cycles from 2.6% for lithium to 14.4% for bismuth.

From this discussion of duty cycle, it would be expected that the ICP-TOFMS sensitivity would be greater when it is equipped with the ion guide than with conventional optics. However, with the collision cell installed, sensitivity is affected by a number of factors, including duty cycle, radial focusing and/or scattering of the ion beam, and ion chemistry. For most elements, the sensitivity of the ion-guide equipped instrument was two- to tenfold poorer than with the conventional ion-optical system. This loss in sensitivity was strongly dependent on mass, with the greatest losses experienced by light ions. Lithium sensitivity dropped by up to 50-fold compared to performance with the conventional ion optics. The reasons for signal loss remain unclear, but are most likely due to a combination of ion scattering and reactions, as well as nonoptimal collisional-cell aperture diameters and ion guide acceptance.

Noise with the ion-guide equipped system was two- to sevenfold lower than with the conventional system. One of the major sources of noise in our TOFMS system arises from ions that pass through the acceleration region when the repeller electrode is at ground potential. Although these ions, mostly argon, undergo mass separation in the analyzer, their flight times are not referenced to a specific start point (the repeller pulse) and thus are detected as a continuum background. Since the extracted ion packet receives energy from the repeller pulse in addition to the acceleration potential, energy discrimination can be used to reduce this background [33]. However, charge exchange within the flight tube between the reflectron and detector produces high-energy neutrals that are unaffected by electrostatic discrimination and therefore generate noise events. Preacceleration beam modulation limits the number of excess ions that enter the mass analyzer, but to assure the highest possible sensitivity the extraction region is typically overfilled. These surplus ions undergo charge exchange in the flight tube and result in elevated background. Ion chemistry in the collision cell with a reactive gas such as hydrogen significantly suppresses the number of argon ions that are admitted to the mass analyzer and thus reduces continuum noise. Furthermore, the addition of buffer gas to the collision cell could significantly change the composition of the gas extracted into the third-stage vacuum. This altered gas mixture may affect the rate of charge-transfer reactions within the mass spectrometer.

The combination of lowered signal and noise that occurs with the octopole resulted in instrument detection limits that were within a factor of two for most elements compared with performance with the conventional optics (Table 3). The limit of detection was defined at a signal to background noise ratio of three. Light ions experienced the most significant degradation in detection limits due to the elevated difference in duty cycle and possible pressure-related scattering losses within the collision cell. As seen in Table 3, the instrumental mass bias was much greater with the octopole than with the conventional optics. Of course, different collision-cell conditions could be used to selectively enhance the performance over restricted

Table 3  
Comparison of ICP-TOFMS limits of detection<sup>a</sup>

Element	<i>m/z</i>	conventional ion optics <sup>b</sup>	octopole ion guide <sup>c</sup>
Li	7	61	4077
Mg	24	47	614
K	39	NA	367
Ca	40	NA	2211
Sc	45	25	186
Mn	55	15	49
Fe	<sup>d</sup>	2300	624
Co	59	14	25
Y	89	23	32
In	115	6	8
Cs	133	13	11
Bi	209	15	20

<sup>a</sup> Limits of detection defined at a signal-to-noise ratio of three and listed in  $\text{pg ml}^{-1}$ . Mass spectral peak area used for all calculations with a measurement integration time of 10 s; Values not corrected for isotopic abundance.

<sup>b</sup> Second stage ion optic potential:  $-564 \text{ V}$ .

<sup>c</sup> Ion guide operating conditions:  $300 \text{ V}_{\text{pp}}$  at  $6.3 \text{ MHz}$ ,  $+4.5 \text{ V}_{\text{DC}}$ ,  $0.018 \text{ Torr}$ , hydrogen collision gas.

<sup>d</sup> For conventional ion optics Fe was measured at  $m/z$  54; With the ion guide Fe was measured at  $m/z$  56.

mass ranges. For example, elevation of collision cell pressure to  $0.052 \text{ Torr}$  and the DC bias to  $+9 \text{ V}$  produced a detection limit of  $1.0 \text{ pg ml}^{-1}$  for bismuth. However, under these conditions the detection of low-mass elements was even further impaired.

Use of the collision cell resulted in the selective reduction of argon-related species through charge transfer reactions with hydrogen and extracted plasma gases. The reduction in argon-ion concentration resulted in improved detection limits for isotopes such as  $^{39}\text{K}$ ,  $^{40}\text{Ca}$ , and  $^{56}\text{Fe}$  that ordinarily suffer isobaric interferences. Under robust plasma conditions, potassium and calcium could not be detected with the normal ion optics due to the need for deflection of the intense argon signal at  $m/z$  40. Suppression of argon ions through charge exchange allowed the ICP-TOFMS to be operated with robust plasma and without the need for deflection. The calculated detection limit for  $^{40}\text{Ca}$  was worse than for other elements of similar mass due to the elevated background ( $8500 \text{ cps}$ ) caused by remaining argon ions. To a lesser extent the use of hydrogen as a collision gas sup-



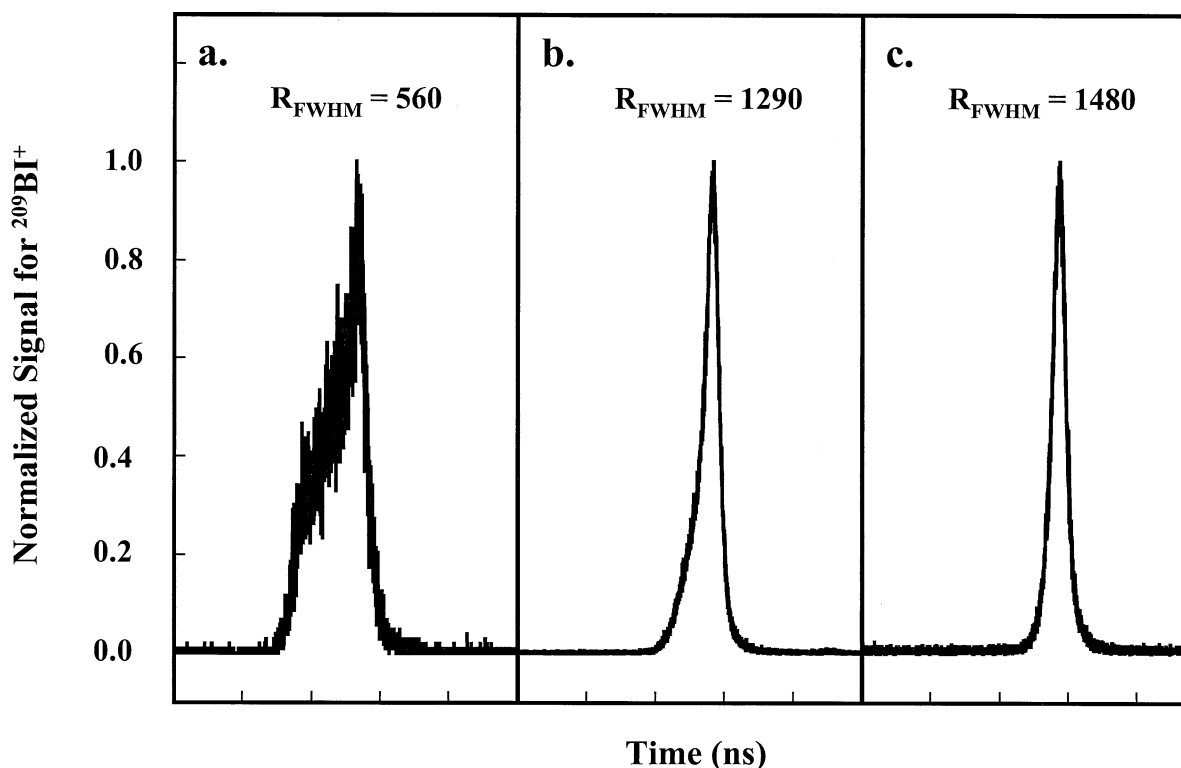


Fig. 5. Peak shapes and spectral resolution for bismuth at collision cell pressures of (a) 0.001, (b) 0.027, and (c) 0.052 Torr. Each spectral peak is normalized to its own maximum value. Divisions on the time axis represent 50 ns. Collision cell operating conditions: 300 V<sub>pp</sub> RF potential at 6.3 MHz, +4.5 V<sub>DC</sub>. Hydrogen used as buffer gas.

pressed  $^{40}\text{Ar}^{16}\text{O}^+$  and allowed the measurement of iron at its most abundant isotope ( $m/z$  56).

### 3.3. Resolution

As shown earlier, an elevated collision cell pressure greatly reduces the range of energies in the primary ion beam. This narrower energy distribution results in improved mass resolving power. A pressure increase from 0.001 to 0.052 Torr resulted in a 6-fold reduction in the FWHM of the energy profile for bismuth. Fig. 5 displays the mass spectrum of bismuth over the same collision-cell pressure range. The same ion extraction conditions were used independent of collision cell pressure. At a pressure of 0.001 Torr [Fig. 5(a)] a broad energy spread generated a relatively wide peak with a resolving power of only 560 FWHM. Although raising the collision cell pressure

to 0.027 Torr significantly improved resolving power [ $R=1290$  FWHM, Fig. 5(b)], appreciable peak fronting was still evident. At a pressure of 0.052 Torr [Fig. 5(c)] a symmetrical peak with a corresponding resolving power of 1480 FWHM was obtained.

Table 4 compares the resolving power of the ICP-TOFMS equipped with conventional electrostatic optics and with the ion guide collision cell operated under moderate conditions. The reduction in ion energy spread produced by collisional cooling within the octopole resulted in a 10 to 80% improvement in mass resolving power. Lithium, with a measured peak width of 4.7 ns FWHM, saw a relatively small improvement in resolving power with the ion guide. As suggested by Coles and Guilhaus [34], this resolution is most likely limited by detector pulse width and trigger jitter. The minor resolving power improvement noted for bismuth was a result of the peak

Table 4  
Comparison of ICP-TOFMS resolving power<sup>a</sup>

Element	$m/z$	conventional ion optics <sup>b</sup>	octopole ion guide <sup>c</sup>
Li	7	410	510
Mg	24	690	1090
K	39	NA	1360
Ca	40	NA	1220
Sc	45	790	1310
Mn	55	960	1470
Fe	<sup>d</sup>	910	1440
Co	59	810	1470
Y	89	870	1490
In	115	1080	1710
Cs	133	1030	1510
Bi	209	1140	1240

<sup>a</sup> Resolving power measured at full width half maximum.

<sup>b</sup> Second stage ion optic potential:  $-564$  V.

<sup>c</sup> Ion guide operating conditions:  $300$  V<sub>pp</sub> at  $6.3$  MHz,  $+4.5$  V<sub>DC</sub>,  $0.018$  Torr, hydrogen collision gas.

<sup>d</sup> For conventional ion optics Fe was measured at  $m/z$  54; With the ion guide Fe was measured at  $m/z$  56.

asymmetry experienced with high-mass ions at moderate pressures (see Fig. 5). Under more advantageous conditions, the resolving power for high-mass ions was significantly improved. Fig. 6 compares mass spectra of thallium, lead and bismuth collected with the conventional ion optics and with the collision cell. The octopole was operated at  $400$  V<sub>pp</sub> ( $6.3$  MHz),  $+10$  V<sub>DC</sub> with a pressure of  $0.038$  Torr. These conditions improved resolving power for bismuth to  $1870$  FWHM, a  $65\%$  enhancement.

It is important to note that at this time ICP-TOFMS resolving power is still less than the  $2500$ – $3000$  resolving power needed to separate many of the most important isobaric interferences [1].

### 3.4. New spectral interferences

Ion chemistry within the collision cell results in beneficial chemical and charge-transfer reactions that eliminate or reduce isobaric interferences [15,19]. However, similar reactions within the ion guide produce new unwanted ions that complicate otherwise simple elemental mass spectra. This uncontrolled sequential ion chemistry can follow many pathways to

produce a diverse population of species [17]. Efficient reactions will result in elevated chemical background and degraded limits of detection. Fig. 7 shows the complicated mass spectrum that is produced by the ion guide when a deionized water sample is nebulized. The clusters of ions separated by  $14$   $m/z$  are indicative of the addition or loss of  $\text{CH}_2$  groups and suggests the presence of organic contaminants (acetone from cleaning, impurities in the buffer gas, pump oil, etc.) within the collision cell.

With a low-resolution mass spectrometer, this increase in chemical background could severely hinder the measurement of trace analyte concentrations. Several methods have been developed to suppress unwanted background ions formed within the collision cell. The simplest technique, proposed by Rowan and Houk [14], requires the ion guide to be operated at a slightly less positive potential than the mass analyzer. Ions formed within the collision cell will have a lower energy than those from the ionization source so energy discrimination can be used to reduce the background. Disappointingly, in the present study all attempts to operate the octopole at a negative DC bias resulted in significant degradation of sensitivity and resolution.

Tanner and coworkers [17,18,20,21] have developed a more complex, yet very successful approach to control the transmission of unwanted ions. With their dynamic reaction cell (DRC), the ion guide is operated as a low-resolution mass filter prior to the main analyzer. Ions that are precursors to interferent species do not follow stable trajectories and are not transmitted. Removal of these precursor ions limits sequential chemical reactions within the collision cell. This technique for the elimination of unwanted ions is ideally suited for use with scanned primary mass spectrometers. However, the pseudosimultaneous multielemental capabilities of TOFMS would be impaired by the prefilter action of systems such as the DRC.

Fortunately, the resolving power of the ICP-TOFMS is sufficient to separate analytes of interest from most carbon-containing background species. Fig. 8 shows the spectral resolution of  $^{59}\text{Co}^+$  ( $m/z$   $58.933$ ) from a background ion at  $m/z$   $59.050$ . This

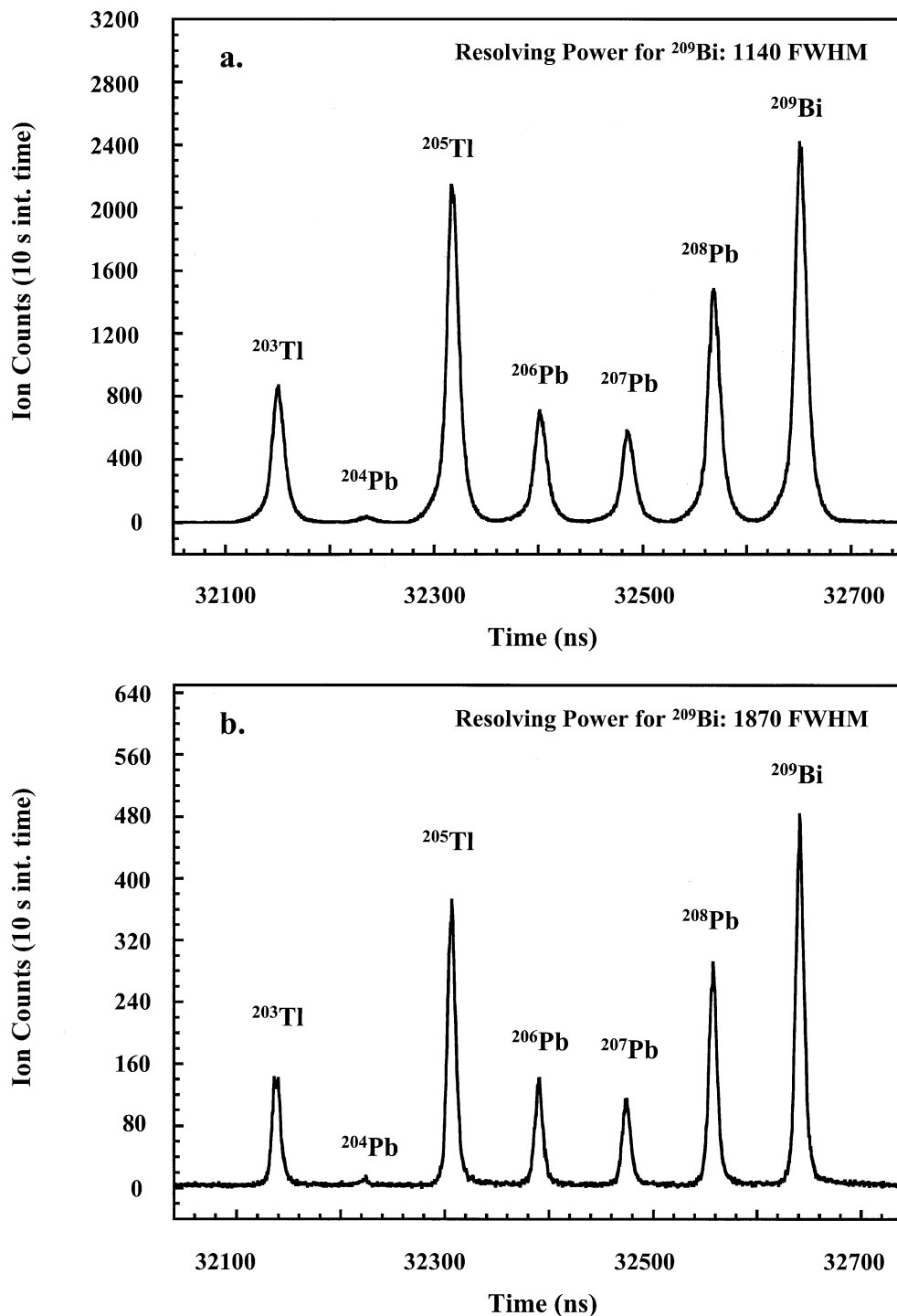


Fig. 6. ICP-TOFMS mass spectra for a  $10 \text{ ng ml}^{-1}$  thallium, lead, and bismuth solution produced by (a) conventional ion optics and (b) the octopole ion guide. Collision cell operating conditions:  $400 \text{ V}_{\text{pp}}$  RF potential at  $6.3 \text{ MHz}$ ,  $+10 \text{ V}_{\text{DC}}$ ,  $0.038 \text{ Torr}$  with hydrogen gas.

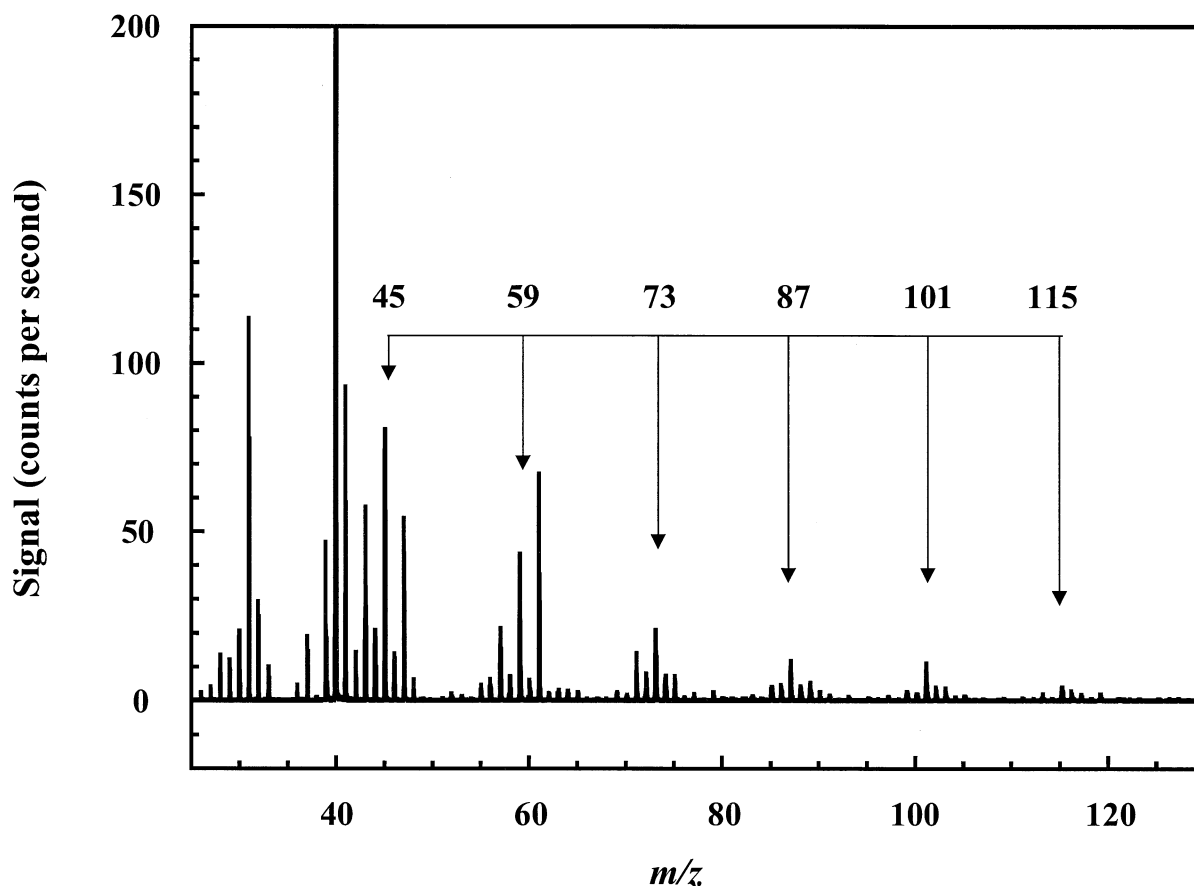


Fig. 7. Background mass spectrum produced by the nebulization of deionized water into the ICP-TOFMS equipped with the octopole ion guide. Collision cell operating conditions: 300 V<sub>pp</sub> RF potential at 6.3 MHz, +4.5 V<sub>DC</sub>, 0.018 Torr with hydrogen gas. Spectrum shows ion clusters spaced by 14 *m/z*, suggesting the successive loss of CH<sub>2</sub> groups. The hydrocarbon background arises from sequential ion chemistry within the collision cell.

separation requires a resolving power of greater than 530, which is easily achieved with the ion guide-equipped ICP-TOFMS with a resolving power of 1470 FWHM for cobalt. Based on mass calibration, the unknown peak is most likely C<sub>3</sub>H<sub>7</sub><sup>16</sup>O<sup>+</sup>. Although the exact source of this ionized species is unknown, a likely origin is acetone remaining from an earlier cleaning of the octopole [17]. Fig. 9 displays a more complex situation where three species exist with the same nominal mass. With resolving powers of greater than 1150 and 600 FWHM, <sup>45</sup>Sc<sup>+</sup> (*m/z* 44.959) is separated from <sup>12</sup>C<sup>16</sup>O<sub>2</sub>H<sup>+</sup> (*m/z* 44.998) and <sup>12</sup>C<sub>2</sub>H<sub>5</sub><sup>16</sup>O<sup>+</sup> (*m/z* 45.034), respectively. A resolving

power of greater than 1250 FWHM allows the ion guide-equipped ICP-TOFMS to differentiate the two carbon species from one another.

#### 4. Conclusions

An ICP-TOFMS has been fitted with an octopole collision cell in an attempt to improve the analytical performance of the instrument for elemental analysis. Detection limits of the ion guide-equipped system were comparable to those from the conventional instrument for most elements. Charge exchange

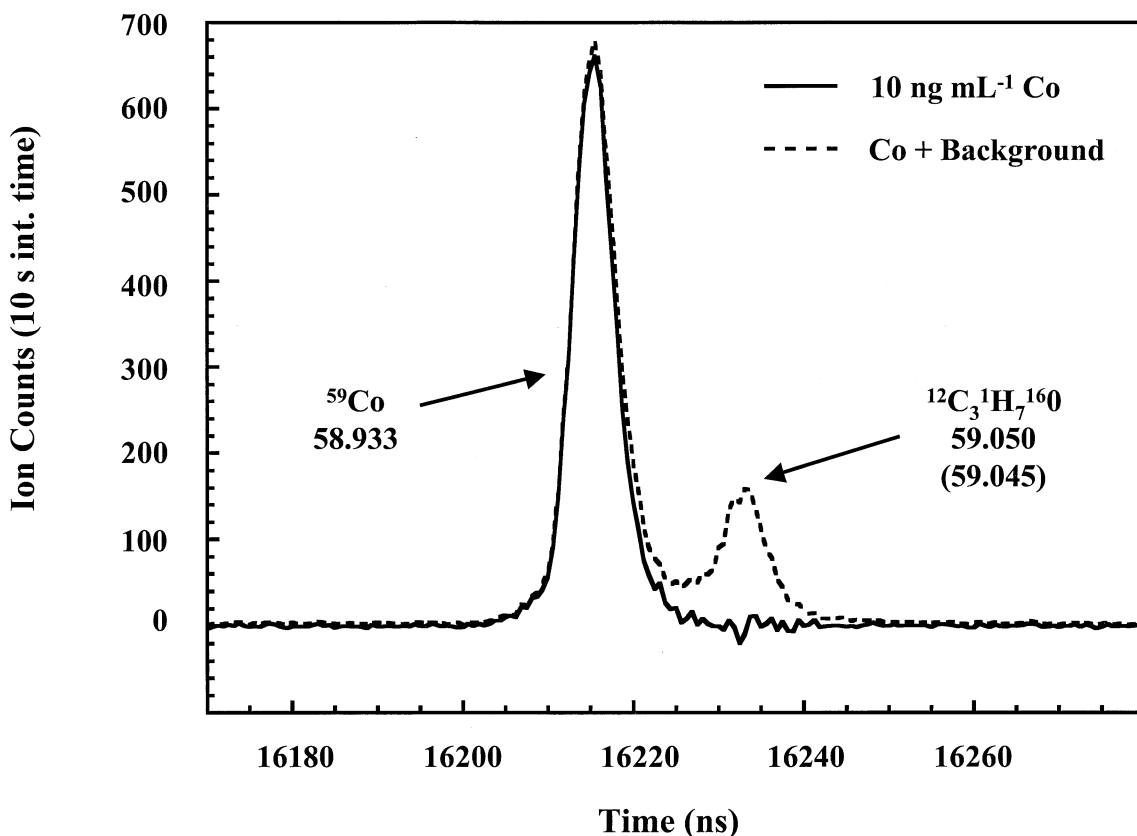


Fig. 8. Spectral resolution of cobalt and a hydrocarbon background peak with the octopole ion guide in place. Collision cell operating conditions: 300 V<sub>pp</sub> RF potential at 6.3 MHz, +4.5 V<sub>DC</sub>, 0.018 Torr with hydrogen gas. The cobalt solution concentration was 10 ng mL<sup>-1</sup>. The dashed line is the raw signal measured with the ion guide, whereas the solid line is the blank-subtracted analyte signal. The number directly below the elemental formula is the theoretical compound mass. The mass predicted by ion flight time is shown in parentheses.

with a reactive collision gas made possible the measurement of several commonly interfered isotopes. The significant gains in sensitivity expected from collisional focusing and cooling of the primary ion beam were not realized. Additionally, a significant light-mass bias was experienced when the ion guide was operated at elevated collision-gas pressure. Collisional cooling resulted in a significant reduction of both the most probable energy and isomass energy distribution of the primary ion beam. The reduction in ion-energy distribution resulted in an improvement in mass-spectral resolving power. The enhanced resolving power afforded by the ion guide significantly lowered the impact of

chemical noise produced by sequential ion chemistry involving trace organic contaminants on analyte detection.

At this time it is the authors' opinion that the incorporation of collision cells with TOFMS systems for elemental analysis will be limited to specific applications. Factors that will restrict the use of ion guides include reduced sensitivity and elevated mass bias against light ions. Further development of ion guide-equipped ICP-TOFMS systems seems likely to produce resolving powers greater than 2500–3000 and should allow the separation of many common isobaric interferences. Additionally, ion chemistry-enabled use of interfered *m/z* will drive continued

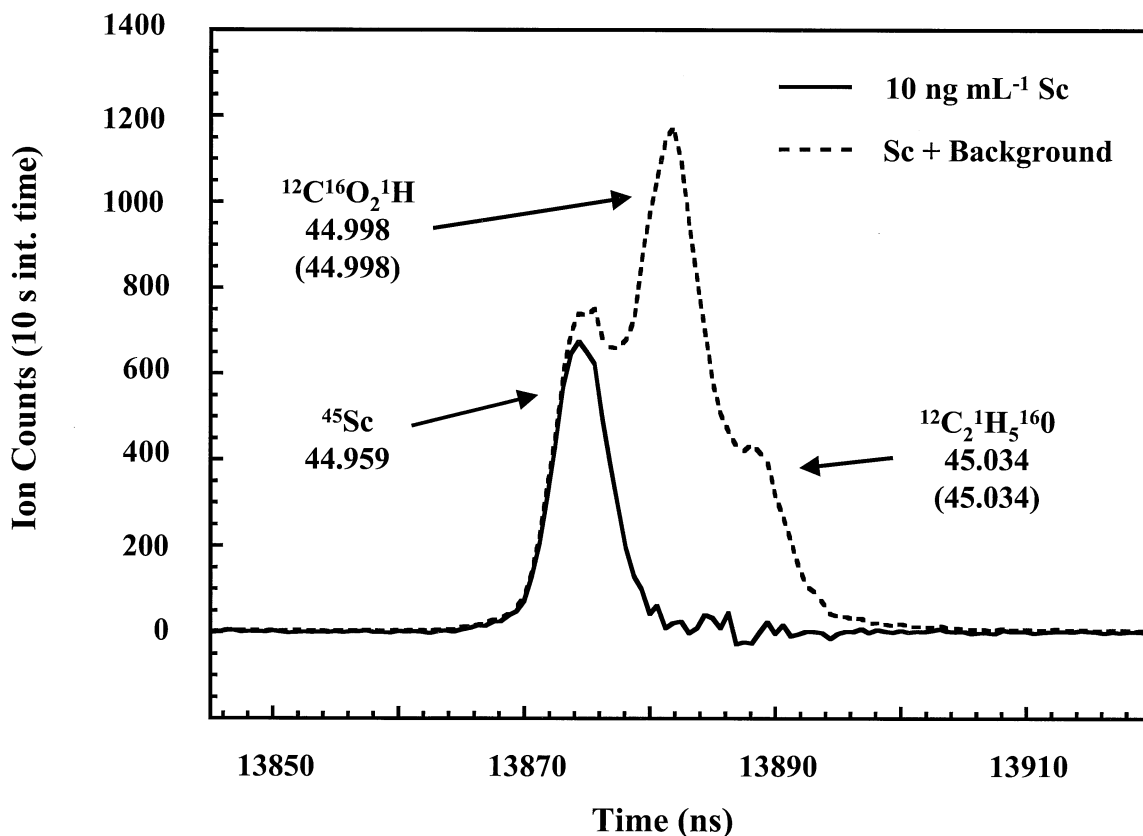


Fig. 9. Spectral resolution of scandium and hydrocarbon background peaks with the octopole ion guide in place. Collision cell operating conditions: 300 V<sub>pp</sub> RF potential at 6.3 MHz, +4.5 V<sub>DC</sub>, 0.018 Torr with hydrogen gas. The scandium solution concentration was 10 ng mL<sup>-1</sup>. The dashed line is the raw signal measured with the ion guide, whereas the solid line is the blank-subtracted analyte signal. The number directly below the elemental formula is the theoretical compound mass. The mass predicted by ion flight time is shown in parentheses.

research toward the combination of collision cells with ICP-TOFMS.

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