

# Collisional dissociation in plasma source mass spectrometry: A potential alternative to chemical reactions for isobar removal†

R. Kenneth Marcus

Department of Chemistry, Biosystems Research Complex, Clemson University, Clemson, SC 29634-0973, USA

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There has been a great deal of interest over the last half-dozen years in the use of selective chemical reactions to remove problematic species from ion beams extracted from analytical plasma sources. While these chemistries are well founded in principle, they require *a priori* knowledge of spectral contributors and all concomitant sample species. Different chemistries are required on both the analyte and matrix-specific bases. This approach has led to the generation of instrument/analysis cookbooks very much akin to those developed for graphite furnace atomization atomic absorption spectrophotometry (GFA-AAS). In addition to chemical reactions, the organic mass spectrometry community has employed kinematic (collisional) methods to dissociate molecular ions where the production of stable fragments is achieved to yield structurally significant product spectra. In this same way, collision-induced dissociation (CID) has been employed to remove molecular isobars in inductively-coupled plasma (ICP) and glow discharge (GD) mass spectrometries. Discussed here are the results of those studies, dating back over a dozen years ago, and how they compare in practical terms with the current commercial implementation of chemical reactions. Interestingly, there have been no publications that have actually compared the use of chemical and kinematic methods on the same instrumentation to achieve selective and universal analysis schemes. This “perspectives” paper seeks to present those previous CID works to a plasma source mass spectrometry community, wherein multi-quadrupole systems are becoming commonplace, in hopes of evoking substantial experimental work and scientific debate that may pay off practical benefits to the general user.

## Introduction

The first papers in the area of plasma source mass spectrometry (PSMS), both inductively coupled plasma (ICP-MS)<sup>1,2</sup> and glow discharge (GDMS),<sup>3,4</sup> clearly noted the presence of isobaric interferences in the mass spectra that could be attributed to molecular species extracted from the analytical plasmas. Most common in the spectra from ICP plasmas are ions derived from water-related species in the plasma, entrained atmospheric gases, and complexes between those entities and target analytes (usually metals). In the case of the glow discharge plasma, the observed molecular species are derived from the discharge gas, sputtered metal dimers, and in the case of refractory samples, remnant metal oxides. Each type of plasma has been studied in detail towards minimizing or alleviating problematic molecular ions. For example, in ICP-MS, variations in gas and liquid flow rates, solvent loading, and region-specific ion sampling have all been applied to varying degrees of success.<sup>5–8</sup> Similarly, various GDMS studies have been directed at optimizing discharge operation and ion sampling conditions.<sup>9,10</sup> The wealth of these sorts of studies in plasma source MS has yielded, at best, conditions that minimize isobaric interferences. In the end, isobaric overlaps are usually the predominant limiting factor in trace ICP-MS and GDMS analyses.

The first instinct, beyond limiting the production or sampling of polyatomic ions, in minimizing these deleterious effects is the use of mass analyzers with sufficient resolving power to alleviate the vast majority of problematic interferences. Interestingly, modest-resolution (up to  $m/\Delta m$  of  $\sim 7500$ ) sector-field instruments are the only commercial format of the GDMS technique that has enjoyed commercial success.<sup>11,12</sup> This is due very simply to the fact that the benchmark

instrument, the VG 9000, was developed within a company with a strong presence in the high vacuum surface science and organic mass spectrometry fields. As such, the availability of instrumentation/hardware and experienced personnel presented a rational route to a still-successful product line. High cost, complex instruments are quite normal in the laboratories of traditional GDMS users, so acceptance of these instruments has never been in question for those needing its capabilities.

Even though the presence of molecular species in ICP-MS spectra (derived from solution sample aspiration) is far more prevalent than in the GDMS spectra of solids, the early producers of ICP-MS instruments sought to produce instruments of comparable complexity (or as much as possible) to ICP optical spectrometers. Surely, the success of quadrupole-based ICP-MS instruments supports those business decisions. Nearly a decade after the commercial introduction of the VG 9000, VG/Fisons introduced an ICP-MS on a sector-field platform.<sup>13</sup> Over the last decade, the utilization of sector-field instruments in ICP-MS has continued to grow for applications wherein the spectrum produced from the target samples are simply too complex for quadrupole analyzers to be used effectively.<sup>14</sup> (The added precision and accuracy of sector instruments for isotope ratio determinations is not questioned, but is beyond the scope of the present discussion.) Unfortunately, the cost and complexity of these instruments is well beyond what the vast majority of analytical laboratories can afford; particularly since *simplicity* is a major selling point of the ICP-MS technique.

The most active area of atomic spectroscopy instrumentation development at this time (at least by the manufacturers) is the implementation of collision/reaction cell technologies as means of removing isobaric interferences that are predominantly due to molecular ions extracted from plasma sources.<sup>15–22</sup> The use of thermodynamically-favorable complexation chemistries along with atom and charge exchange reactions is being touted by most ICP-MS manufacturers as the optimum means of

† The opinions expressed in the following article are entirely those of the author and do not necessarily represent the views of the Royal Society of Chemistry, the Editor or the Editorial Board of JAAS.

achieving spectral simplification. A number of exotic reaction schemes can be employed with relatively high efficiencies, when the thermodynamics of the reactions overcome the kinetic limitations (*i.e.*, transit time) of an ion passing through a pressurized rf-only quadrupole assembly (a.k.a., the reaction cell). Use of specific reaction gases and reaction conditions (gas density and collision energy) can yield effective “isolation” of a given analyte’s signal to levels that reflect  $10^3$ – $10^6$  improvements in detectability (though not necessarily limits of detection). There are indeed decades of ion–molecule chemistry data that support the efficiencies of these reactions. There is no dispute that the basic chemistries are effective. Unfortunately, the specificity of these reactions comes with incredible amounts of instrumentation and application overhead. In essence, ICP-MS, the most powerful of multielement analysis methods on a first-principles basis, can become limited in coverage to specific elements in a sample for a given reaction strategy.

Much in the same way that the graphite furnace atomizer (GFA) was at first a liberating and powerful alternative to flame sources, the new complexities of reaction cell chemistries may far outweigh the meaningful gains that the “typical” user can afford. Every GFA manufacturer had/has its own set of “recipes” for furnace geometry and material, temperature programs, matrix modifiers, background correction approaches, analyte transitions, *etc.* This situation tended to confuse potential users and was, perhaps, a deterrent to wider use, particularly as ICP-OES and MS began to gain in acceptance. The same phenomenon is emerging with the ICP-MS manufacturers. Such an approach flies in the face of what most industries and businesses expect to gain from greater system complexity. Take the automobile industry for example. The electronic control systems present in any modern car are incredibly complex in nature, but through their growing complexity (at the board level) the operation of the vehicle (at the user level) is actually enhanced and *simplified*. The ultimate question (as in the case for the graphite furnace) is whether the greater complexity of highly selective yet efficient chemistries offers greater *simplicity* and flexibility for the end users. It may be that there are more general, though perhaps less effective, ways to attain the same goal that may be of greater utility and *simplicity* to the average PSMS user. (Note the generic use of the term plasma source mass spectrometry, as the same arguments are relevant in ICP and GDMS.)

The purpose of this article is to question the use of reaction chemistries in lieu of other (potentially more generic) approaches to the removal of isobaric (atomic and molecular) interferences in PSMS. There are in fact a number of fundamental mechanisms that can be considered for such a chore, and these should be evaluated on current state-of-the-art instruments to hopefully yield the most effective instrument configuration that retains the incredible multielement power of the techniques. In fact, at least one manufacturer seems to have adopted a more generic approach through the combination of chemistry and

energy discrimination; there are others to try as well.<sup>23</sup> Specifically, the use of collision-induced dissociation as a means of removing molecular isobars in PSMS is reviewed here. The ion species dissociated effectively to date have included the most tenacious of oxides, metal dimers, and metal argide interferences. Unfortunately, all of these studies have been performed on home-built instruments or those converted from organic MS applications.<sup>9,24–33</sup> Lack of greater quantitative results from those instruments and the fact that most of the studies were performed with GD ion sources have led to unsubstantiated assumptions of their potential and the methodology being written off as ineffective by authors in early reaction cell papers.<sup>17,22</sup> Perhaps it is time to learn from those works as a basis for true comparisons with current commercial technologies with the goal of producing approaches that yield *simpler* PSMS spectra, through simpler methodologies.

The basic idea of the use of collisional dissociation in PSMS is depicted in Fig. 1. Shown in very simple terms is an ion beam composed of various atomic and molecular species sampled from a plasma. All of the ions are passed through a collision cell (just as currently employed reaction cell instruments) where polyatomic species are dissociated and the desired atomic ions are passed to the mass analyzer. In the CID approach, there is no *a priori* requirement to know the sample composition. Simply, all molecular species are dissociated. In addition, charge exchange reactions between the target gas and discharge gas species will occur, removing them from the ion beam prior to mass analysis. Successful implementation of such a methodology would provide the end user with a very generic means of simplifying PSMS operation as there are no element/matrix specific chemistries to consider. Described in the following sections are previously published demonstrations of the use of CID to alleviate molecular and atomic interferences in PSMS. The intent is to perhaps stimulate a revisiting of the methodology in light of the current acceptance of multiple quadrupole instrumentation.

### Basics of collision-induced dissociation

For many people, the fundamental aspects of collision-induced dissociation (CID) or collision-activated dissociation (CAD) are more simple to understand than chemical reactions (*i.e.*, kinematics are more intuitive than thermodynamics). McLuckey presented a straightforward, yet thorough, review of collisional activation processes in 1992. This review, written from the point of view of organic applications for structural analysis, lays out the basic considerations of relevance in the use of CID in PSMS. There is, in fact, a wealth of literature describing the fundamentals and applications of the methodology, involving the use of beam-type (sector-field), multiple-quadrupole, and three-dimension trapping instruments.<sup>34</sup> The essence of the process is the conversion of the translational energy of the extracted molecular plasma ion into vibrational

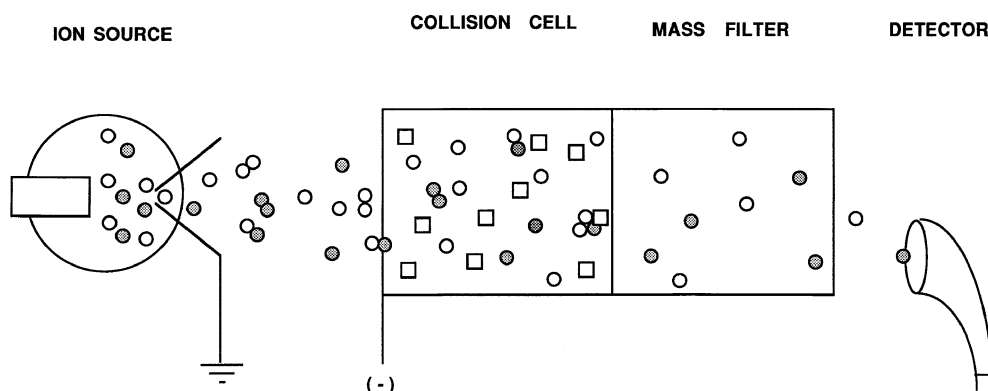


Fig. 1 Diagrammatic representation of the use of collisional dissociation for the removal of molecular isobars in plasma source mass spectrometry.

energy through collision with a target gas atom. Think of this as the reverse of a billiards break, where the polyatomic species (the rack of balls) is fired against the cue ball (gas atom/molecule). In such a collision, energy will be transferred between the moving polyatomic and the *effectively* stationary target atom (effectively because the gas phase atom does have a relatively minute thermal motion). Energy will be given to the target atom which will be carried away in the form of momentum, with a large portion of the energy being distributed among the atoms of the polyatomic species in the form of vibrations. If the incorporated internal energy is sufficient to overcome specific bond energies ( $D_o$ ), dissociation will occur. Beyond this single-collision picture, there also exists the possibility that a vibrationally excited molecule can experience multiple collisions, imparting further energy to take the molecule up the “vibrational ladder” to affect dissociation. In comparison with most organic MS applications, polyatomics in PSMS generally have only one degree of vibrational freedom, so that the conversion from translational-to-vibrational energy is far more focused.

The extent of molecular species dissociation in a collision cell (including the volume of an ion trap) is dependent on the energy coupled to the molecular ion and the effective path length over which the collision(s) occur. The maximum amount of vibrational energy that can be coupled to a molecule upon collision with a target atom is given by the center-of-mass energy ( $E_{cm}$ )

$$E_{cm} = E_{lab} (m_t / (m_t + m_p)) \quad (1)$$

where  $m_t$  and  $m_p$  are the relative masses of the target gas and the molecular ion and  $E_{lab}$  is the dc offset (bias) of the collision quadrupole with respect to the region where the ion is formed. The relationship between  $E_{cm}$  and  $E_{lab}$  reflects the controllable translational energy (at least in collision cell instruments) and its distribution between the collision partners. The translational (kinetic) energy of an ion entering a collision cell in a PSMS system is actually the potential energy difference between the birthplace of the ion (*i.e.*, the plasma potential) and the pole offset potential, inclusive of energy gains and losses due to gas dynamics and the ion transfer optics.

While there will exist a threshold  $E_{cm}$  (and thus  $E_{lab}$ ) value to affect cleavage of a given bond, the vast majority of the (primarily) diatomics extracted from plasma sources will exist in vibrational excited states during the course of their transit from the plasma to the collision cell. As such, it will seldom be the case that a bond's full dissociation energy will need to be provided. This is fortuitous, because the extent of scattering losses from the confines of the collision cell increases as  $E_{lab}$  increases. This is true for both the problematic polyatomic ions as well as the desired monatomic analyte ions. As such, one must choose collision conditions that provide efficient dissociation, while minimizing scattering losses. This is one of the strongest attributes of current reaction cell approaches, as those collisions are by definition most effective at very low, in fact thermal, energies.

The second controlling experimental parameter in achieving CID is the effective path length over which collisions occur. The path length of the cell is related to the primary ion's trajectory through Q1 (a function of mass and kinetic energy of the ion, the rf driving frequency, and the pole potentials), but the pressure of the gas in the cell controls the collision probability. Beyond the single-collision limit, the target gas density controls the path length, where the efficiency can be characterized through the reduced ion beam intensity ( $I$ ) by a Beer's Law analogy as:

$$I = I_0 e^{-n\sigma L} \quad (2)$$

where  $I_0$  is the initial intensity (without collision gas),  $n$  is the number density (pressure) of the target gas,  $\sigma$  is the cross

section for loss, and  $L$  is the path length of the ion trajectory. Higher number densities increase collision rates and, therefore, increase the CID efficiency. Unfortunately, the attenuation of the beam due to ion loss caused by elastic scattering is also proportional to the gas pressure. Thus, a trade-off exists between the atomic losses due to scattering and the polyatomic losses due to CID as the collision pressure is increased. The cross section for loss,  $\sigma$ , encompasses many possible factors affecting ion loss, including collision energy (which is proportional to the reduced mass of the collision partners), size (geometric cross section and vibrational degrees of freedom), and relative ionization potentials. The latter quantity has direct relevance in the fact that symmetric and asymmetric charge exchange are very effective means of removing many water- and air-related polyatomics and doubly-charged species that have ionization potentials much higher than desired atomic ions; a common strategy employed in PSMS reaction cells.

## Reaction and collision cells in ICP-MS

Douglas<sup>24</sup> and Houk<sup>25</sup> independently presented the original descriptions of the potential use of chemical reactions to remove molecular isobars in ICP-MS in 1989. It is important to note that these observations were derived from studies into the use of CID to alleviate molecular species. Douglas described the use of a triple quadrupole mass spectrometer (as commonly used in organic MS/MS experiments) to selectively admit ion species of interest into a collision quadrupole and a third (mass resolving) quadrupole to determine the reaction products.<sup>24</sup> Loss cross-section determinations were made for a range of atomic and polyatomic ions for collisions at a relatively high energy ( $E_{lab}$ ) of 50 eV using argon as the target gas. The obtained values for the polyatomics were only a factor of 2 or so higher than those for atomic ions, suggesting large scattering and charge exchange losses by the latter. Clearly this situation could not be expected to yield large gains in spectral simplicity. A more telling experiment involved the use of air as the collision gas for determinations of rare earth species. Neutral addition scans with the third quadrupole passing a mass 16 u (oxygen addition) above the first, showed that atomic  $Ce^+$  and  $Tb^+$  were effectively converted to their monoxide forms, while the primary oxides did not add a second oxygen atom. Thus the plasma-formed oxides did not show up in the final spectrum. This experiment serves as the basis for many of the existing approaches used in present-day reaction cell ICP-MS.

Houk demonstrated that  $Fe^+$  and  $Co^+$  analyte count rates were depressed by only ~25% when Xe was used as a target gas, with those of  $As^+$  and  $Se^+$  depressed by ~35% in the presence of  $CH_4$  as the target species at relatively low collision (~5 eV) energies.<sup>25</sup> At higher energies more typical of those used in organic MS, extensive scattering from the Xe target atoms led to little preferential loss of the argon dimer ( $Ar_2^+$ ) over atomic  $As^+$ . This of course is to be expected as scattering losses increase with both the ion kinetic energy and the mass of the target gas. The authors noted that while CID was likely a contributor to loss of molecular ions, the possibility of charge exchange and chemical reactions were of high probability. Such reactions are most efficient at low collision energies (where scattering losses were minimized) and where the thermochemistry ( $\Delta H$ ) for reaction was exothermic. As a final indication of the potential utility of double-quadrupole geometries, Houk pointed to, and demonstrated, the use of selective energy filtering between reaction products and primary ions.<sup>25</sup>

The basic concepts in the current use of reaction cells in conjunction with ICP-MS have been thoroughly and exceptionally, described by Tanner and associates.<sup>17,22</sup> It is beyond the scope of this paper to go through the underlying principles of the use of reaction chemistries in ICP-MS, but it is

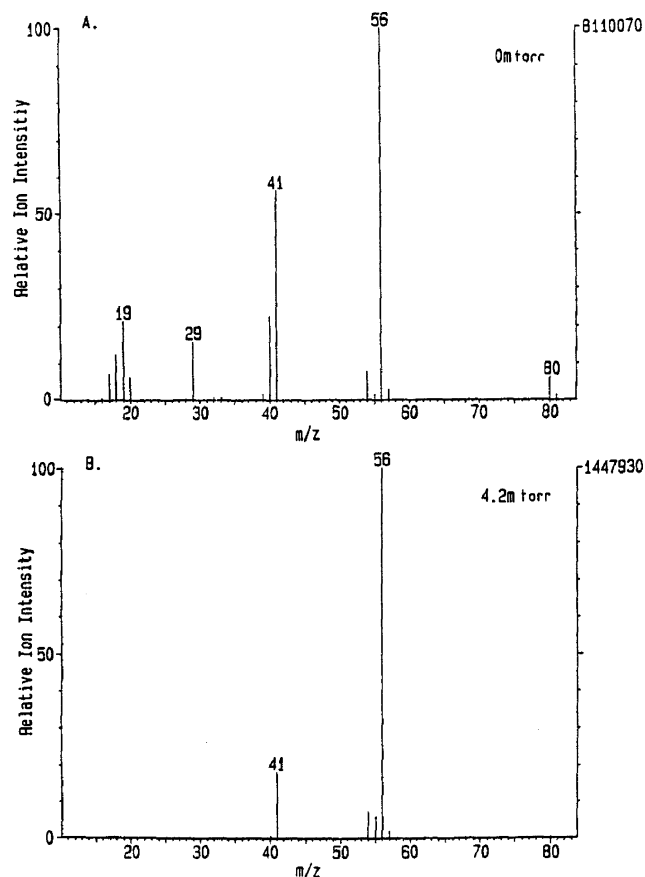
instructive to list some of the critical criteria as presented in those works. Principally, three types of reaction have been employed to alleviate isobaric interferences: (1) charge exchange from the interferent to the target gas, (2) atom transfer to the analyte to move it to a new  $m/z$  value, and (3) selective reaction with the molecular isobar to remove it from the "analyte"  $m/z$  value. In each of these cases, one is relying on the fact that the reaction rates for the analyte and isobar with the target gas species are sufficiently different to render a large disproportionality in the responses of the two isobars. Charge exchange to a target gas atom of usually lower mass than any desired analyte provides ready remediation of an interferent condition. For example, use of  $\text{NH}_3$  as a target is very effective in removing the  $^{40}\text{Ar}^+$  species from the ion beam to expose buried  $^{40}\text{Ca}^+$ , simply producing a new ion at  $m/z = 17$  u. Fortunately, most of the argon-related isobars have much higher ionization potentials than analyte species, and so this is an incredibly versatile removal process.

On the other hand, the second and third "shifting" processes *de facto* complicate the product mass spectra by the introduction of new ions to the spectrum. Here is where life begins to get complicated. In the demonstration by Douglas,<sup>24</sup> there are a number of scan modes for triple-quadrupoles wherein mass shifting is easily monitored, while maintaining overall spectral simplification. In the case of commercial double-quadrupoles, all surviving primary ions and new products can be seen without regard to formation mechanism. As demonstrated by Houk, the use of selective energy filtering to bias against lower-energy product ions is a very effective means of rejecting potential new interferents.<sup>25</sup> It must be remembered that it is difficult to energy-resolve the desired atomic species from potential reaction products if the primary "collision" energy is  $< 1$  eV as used in the "reaction cell" mode.

## Reaction and collision cells in GDMS

While the GD and ICP are very different ion sources, the types of interferent species (both atomic and molecular) are very similar in nature (*e.g.* argon dimers, metal oxides, *etc.*) and thus illustrative of the potential of the method across PSMS. In the year before the publication of the oft-cited papers of Douglas and Houk,<sup>24,25</sup> Harrison and co-workers first reported the use of a triple-quadrupole mass spectrometer to effect collision-induced dissociation of a wide variety of glow discharge plasma species,<sup>9</sup> followed by a more detailed report in 1989.<sup>29</sup> In the initial paper, the authors showed that use of  $\sim 4$  mTorr of argon as the collision gas could effectively negate the deleterious effect of the presence of the common  $\text{Fe}_2^+$  (dimer) and  $\text{FeAr}^+$  (argide) species derived from the sputtering of a steel specimen on the *apparent* isotopic distribution of the minor Mo constituent. In fact, both species were reduced to undetectable levels.

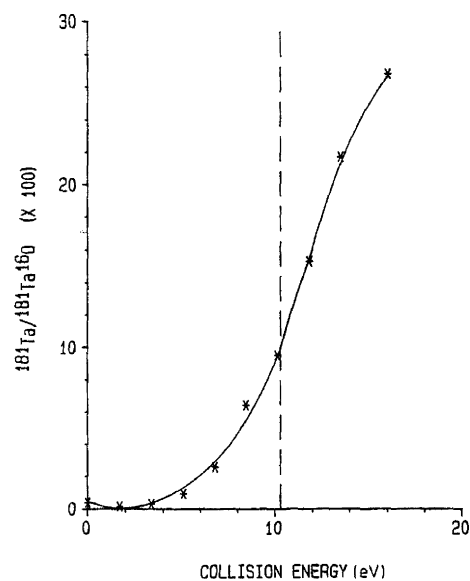
More detailed investigations of the use of the non-linear collision cell revealed that the off-axis geometry is quite effective in minimizing photon and fast-neutral sources of detector noise.<sup>29</sup> The system was quite efficient in its transport of the desired atomic species, exhibiting a suppression of only a factor of 7 (in the worst case), while the limits of detection were degraded by only a factor of 3, *i.e.*, the loss in intensity is compensated to a large extent by lower background noise. The roles of collision gas (argon) pressure and the respective pole bias values on the extent of molecular species dissociation were examined. Fig. 2 illustrates the basic aspects of the CID spectral simplification in the mass spectra obtained from NBS NIST 1264a stainless steel. The top spectrum shows the presence of water and nitrogen-related species (from discharge gas contaminants) in the region of 20 and 30 Da, argon and argon hydride (40 and 41 Da), and the argon dimer (80 Da). Use of an argon collision gas pressure and a *very low* collision



**Fig. 2** Low gain glow discharge mass spectra of NIST SRM 1264a stainless steel. (a) Baseline spectrum without the presence of collision gas. (b) Resultant spectrum upon introduction of 4.2 mTorr of argon in Q2. Pole offset ( $E_{\text{lab}}$ ) = 4.2 eV in both cases.<sup>29</sup>

energy ( $E_{\text{lab}}$ ) of 4.4 eV, removes the water, nitrogen, argon, and argon dimer species to undetectable levels. (In hindsight, the  $\text{ArH}^+$  may have been formed in the cell due to impurities in the collision gas.) The authors demonstrated the counteracting effects of increasing collision energy: added atomic losses due to scattering and increased collisional dissociation. In general, the scattering losses were minimal up to  $E_{\text{lab}}$  values of 30 eV.

Fig. 3 illustrates the ability of simple CID to dissociate one



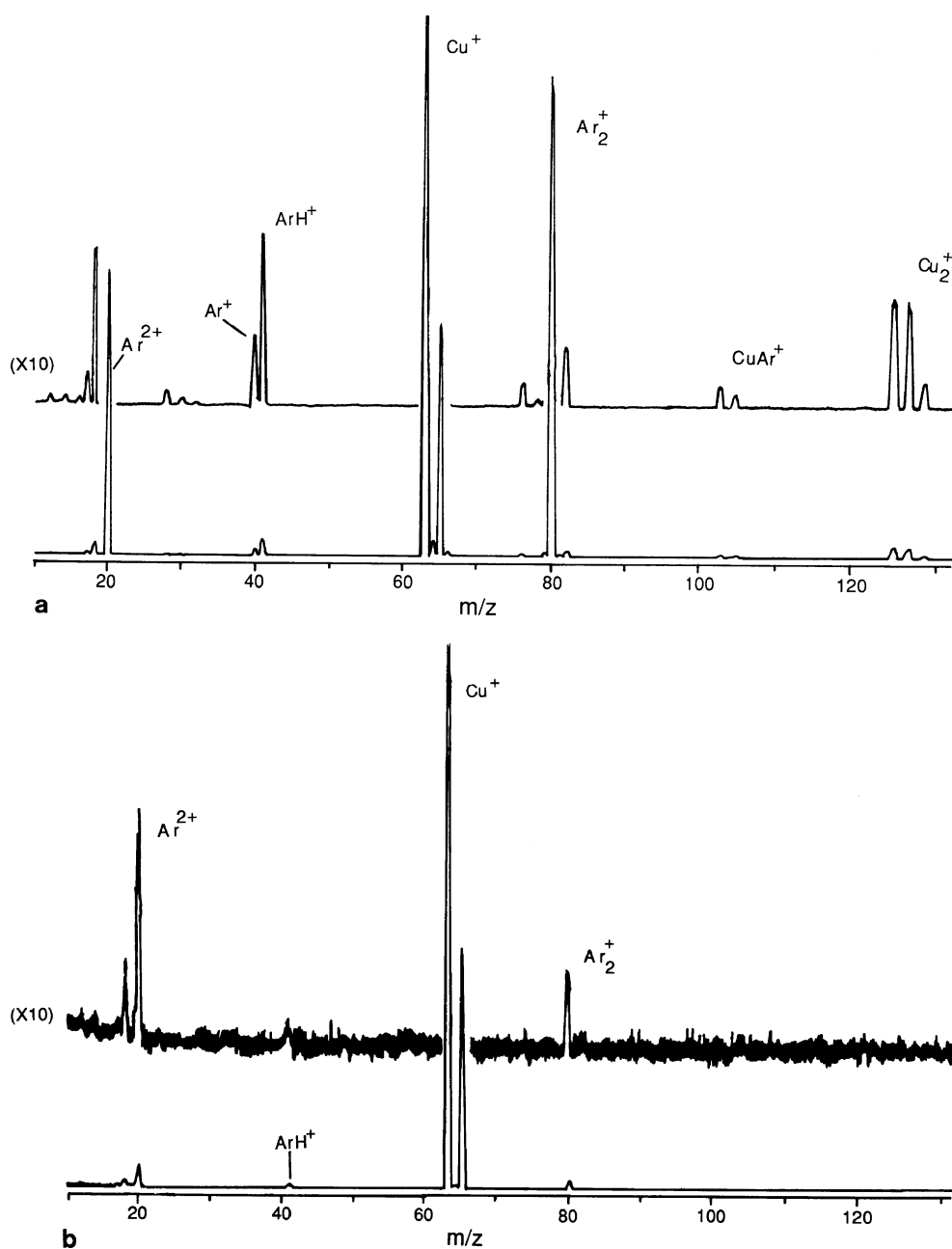
**Fig. 3** Plot of the  $\text{Ta}^+$ -to- $\text{TaO}^+$  ratio as a function of collision energy ( $E_{\text{CM}}$ ) for depicting the dissociation of  $\text{TaO}^+$ . Argon target pressure = 2.1 mTorr.<sup>29</sup>

of the most tenaciously bound polyatomic species,  $\text{TaO}^+$  ( $D_0 \approx 10.3 \text{ eV}$ ).<sup>29</sup> The plot of the relative intensities of  $\text{Ta}^+$ -to- $\text{TaO}^+$  (formed by the presence of background water while sputtering a Ta target) as a function of the center-of-mass energy reveals very effective dissociation. The onset of dissociation at energies below  $D_0$  is an indication of the existence of vibrationally excited  $\text{TaO}^+$  in the beam. Based on the shape of the curve, it appears that the degree of dissociation is beginning to maximize at the upper end of the energy range. The authors conclude that the results are indeed very promising and worthy of future instrumentation development. They further suggest that charge exchange reactions could be employed to advantage to reduce doubly-charged species in particular.

In 1990, Duckworth and Marcus described the use of a home-built, double quadrupole spectrometer to effect non-discriminant dissociation of molecular species sampled from a radiofrequency (rf) glow discharge source.<sup>26</sup> The principal motivation for this approach was to provide a simpler platform than a triple-quadrupole analyzer. In short, all plasma species

were passed to the rf-only collision cell, with the desire of having the atomic analyte species proceed with minimal scattering losses while subjecting problematic molecular species to collisional dissociation. In addition, those species having higher ionization potentials than the target gas could be removed from the ion beam through charge exchange reactions. The metallic element having the highest ionization potential, Hg, 10.4 eV, is readily preserved in lieu of the common argon discharge gas and other molecular ions by each of the common target gas species. The fact that an rf source was used here presents the added challenge in the presence of oxide ions in the extracted mass spectra by virtue of the ability to directly sputter oxides and other refractory materials.

Shown in Fig. 4 are the respective rf-GDMS spectra from the sputtering of a copper target, for the cases of the evacuated collision cell and pressurization with argon to a value of  $4 \times 10^{-4} \text{ Torr}$  as measured in the mass analyzer region. (The actual value was probably a factor of ten higher.) Seen in the top traces are spectra that are dominated by  $\text{Ar}^{2+}$ ,  $\text{Cu}^+$ , and  $\text{Ar}_2^+$ .

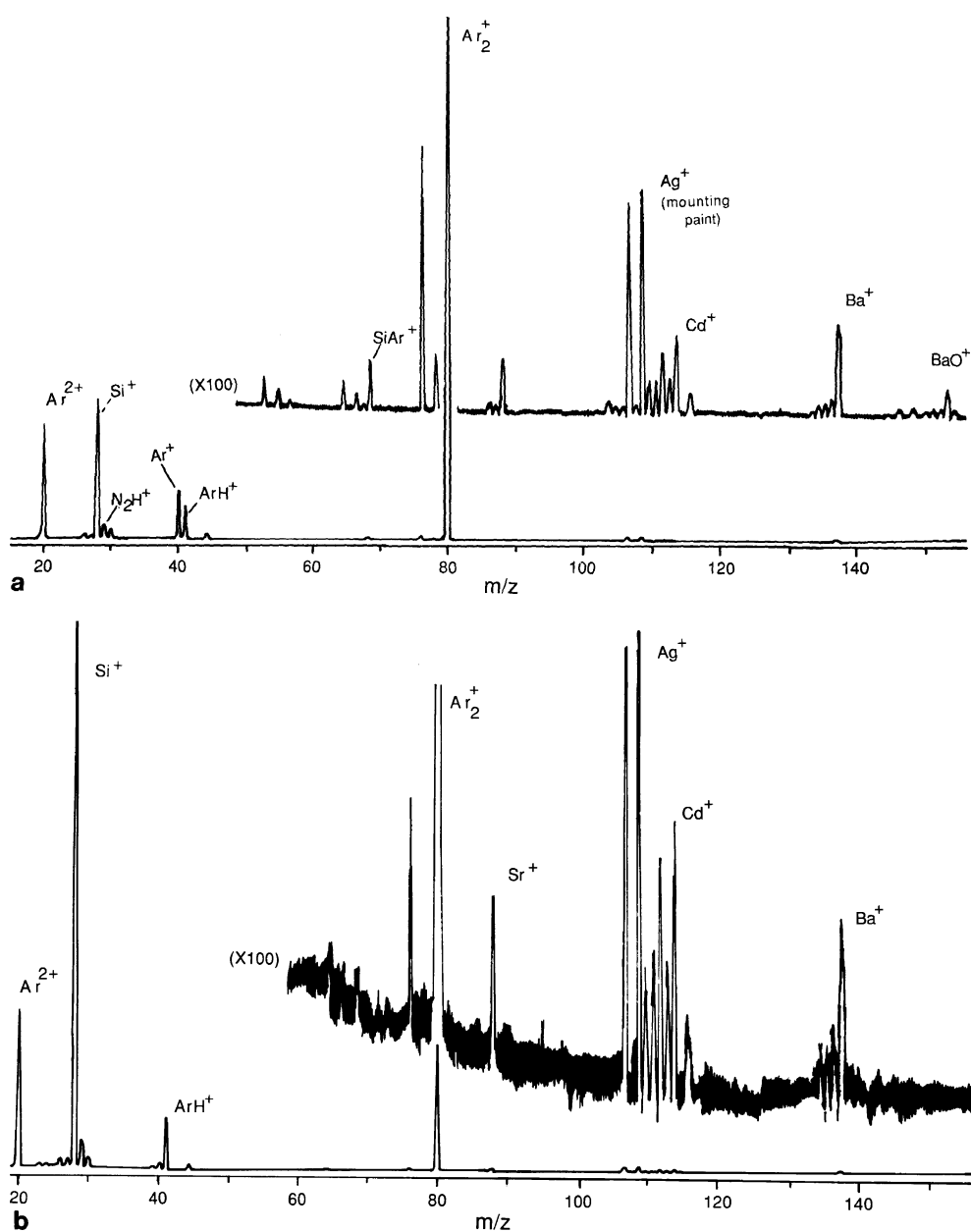


**Fig. 4** Rf-glow discharge mass spectra of a stock copper cathode. (a) Baseline spectrum without the presence of collision gas. (b) Resultant spectrum upon introduction of  $4 \times 10^{-4} \text{ Torr}$  Ar as measured in the analyzer chamber (scale expansion  $\sim 15 \times$ ). Pole offset ( $E_{\text{lab}}$ ) = 40 eV in both cases.<sup>26</sup>

Scale expansion reveals contributions from  $\text{Ar}^+$ ,  $\text{ArH}^+$ ,  $\text{CuAr}^+$  and  $\text{Cu}_2^+$  at single-percent levels relative to the atomic copper signals. The bottom set of traces clearly demonstrates the effective reduction of the argon, argide, and copper dimer ions to undetectable levels, while the scattering losses of the  $\text{Cu}^+$  were less than a factor of 10 in comparison to the empty collision cell. It must be stressed that the instrument used in this work had a useful dynamic range of only  $\sim 100\text{--}300\times$  because it employed no photon stop between the ion source and continuous dynode detector. The data acquisition was limited to single scans, and the actual output was to a flatbed  $X\text{--}Y$  recorder. As such, determinations of the absolute removal efficiencies of potentially interfering ions were not practical.

Fig. 5 depicts what is a most remarkable result (and of greatest relevance) in demonstrating the possible utility of CID as a generalized removal strategy for all forms of PSMS.<sup>26</sup> Taking advantage of the versatility of the rf-GD source, the mass spectrum extracted in the course of sputtering a NIST SRM 1412 multicomponent glass presents a number of different spectral interferences. The spectrum is virtually dominated

by the argon dimer signal at 80 Da, with the matrix  $\text{Si}^+$  species being present at a relative abundance of  $\sim 25\%$ . (This early generation rf-GD source was far from optimal.) Scale expansion reveals contributions from a number of other species, including  $\text{Ar}^{2+}$  and  $\text{Ar}^+$ , along with the isotopic signatures representative of the Ag sample mounting paint and the Sr, Cd, and Ba glass components (nominally 4.5% by wt for each oxide). Of course, the most daunting spectrum component is  $\text{BaO}^+$ , which is not surprising given the nature of the sample and the tenacity of the Ba–O bond. By use of the same CID conditions as in Fig. 4, the product spectrum is dramatically simplified in a number of ways, again with atomic scattering losses of less than an order of magnitude. First, the Si matrix signal is now the dominant feature. Second, the single-scan Si isotope errors are reduced from  $\sim 40\%$  down to  $\sim 2\%$  (both of which were reproducible values). The improvement here is due to the collisional removal of nitrogen-related species  $\text{N}_2^+$ ,  $\text{N}_2\text{H}^+$ , and  $\text{NO}^+$  at masses 28, 29, and 30 Da, respectively. Third, the intensity distributions of species in the region of 40 Da are changed to reflect the previously obscured Ca and K sample components. Fourth, even with the use of a modest pole

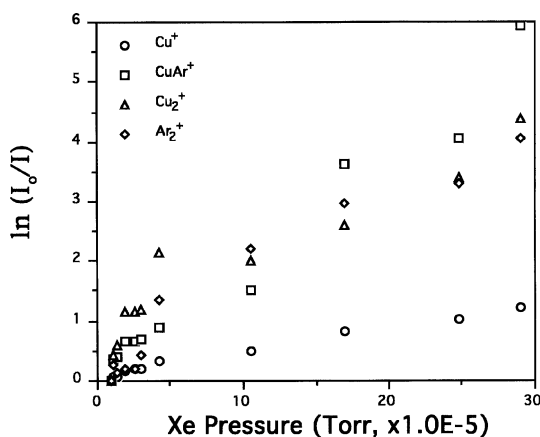


**Fig. 5** Rf-glow discharge mass spectra of a NIST SRM 1412 multicomponent glass. (a) Baseline spectrum without the presence of collision gas. (b) Resultant spectrum upon introduction of  $4 \times 10^{-4}$  Torr Ar as measured in the analyzer chamber (scale expansion  $\sim 10\times$ ). Pole offset ( $E_{\text{lab}} = 40$  eV in both cases).<sup>26</sup>

bias of 40 eV, the  $\text{BaO}^+$  species are removed to undetectable levels. Fifth, the relative relationships for the intensities of the Sr, Cd, and Ba atomic ions are virtually unchanged. Finally, all of the above results are achieved under a single set of dissociation conditions (*i.e.*, both the copper and glass analyses). Based on comments in the ICP-MS literature, one would be led to believe that these basic observations are not attainable with double-quadrupole systems of the sorts employed in current ICP-MS literature. Surely, this cannot be the case given the simplicity of the apparatus employed here.

The double-quadrupole rf-GDMS studies were extended by Marcus and co-workers to evaluations of the use of different target gases (Ar, Xe, and  $\text{N}_2$ ) and a range of collision energies.<sup>27</sup> These gases provide a range of target masses, ionization potentials and, in the case of  $\text{N}_2$ , a larger physical cross-section at the expense of added degrees of vibrational freedom. A new direct insertion probe (DIP) source design was implemented with a copper sample disk employed in all of the studies.<sup>35</sup> To remove potential experimental biases, the collision conditions were optimized for each gas. Attenuation factors ( $\ln I_0/I$ , where  $I_0$  is the intensity without gas and  $I$  is the intensity measured with the cell pressurized) were determined as a function of collision cell pressure for the different target gases. Fig. 6 is a plot of attenuation factors as a function of cell pressure for the studied analyte and interferent species with the use of xenon as the target gas. Clearly seen is the fact that the slope of the  $\text{Cu}^+$  response function is far lower than those for  $\text{CuAr}^+$ ,  $\text{Ar}_2^+$ , and  $\text{Cu}_2^+$ , revealing multiple orders of magnitude improvements in relative analyte contributions in the product spectra. The extent of the improvements was limited again by the dynamic range of the detection system. Not shown in the plot, but evidenced in “energy discrimination” experiments of the sort used in ICP-MS, was the successful removal of  $\text{Ar}^+$  from the primary ion signal through asymmetric charge exchange with the Xe target gas. Of the three gases, xenon provided far better performance as a target gas, providing efficient CID, removal of high ionization potential species *via* charge exchange, and lower than expected scattering losses ( $<1$  order of magnitude under efficient CID conditions). Given the flow rates of  $<1 \text{ mL min}^{-1}$ , the higher cost of xenon as compared with argon was not seen as a limitation to its use in PSMS.

The early work in multiple quadrupole GDMS should be of direct relevance to current applications of collision/reaction cells in ICP-MS. Of particular importance are the demonstrated removal of argon-associated species and the dissociation of rare-earth oxides. There are no fundamental reasons why the same sorts of experiments, evaluating the use of combined CID, charge exchange, and energy discrimination, could not be performed on those modern instruments. There

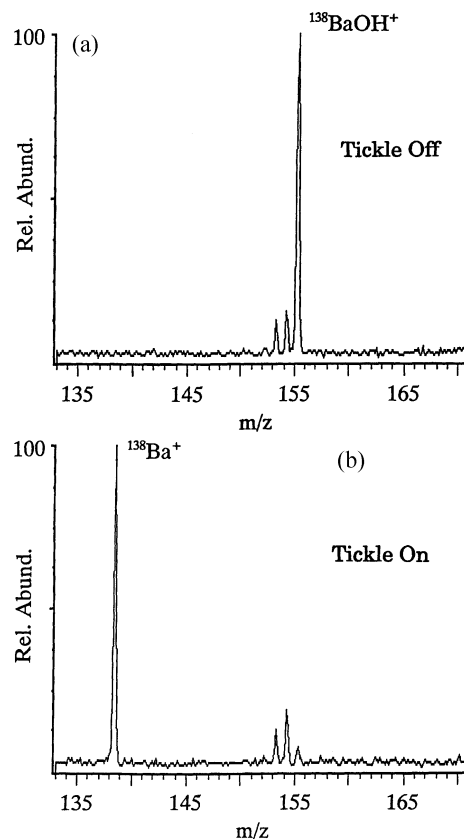


**Fig. 6** Attenuation factors for different plasma species present in the rf-GDMS spectra of a stock copper cathode as a function of target gas pressure. ECM values range from 4.7 eV for  $\text{Cu}^+$  to 3.6 eV for  $\text{Cu}_2^+$ .<sup>27</sup>

are, in fact, other approaches to effecting CID on instruments that are also amenable to PSMS sampling and analysis.

Predating the benchmark studies of Koppenaal *et al.* in the use of ion trap mass spectrometry (ITMS),<sup>36,37</sup> McLuckey and co-workers at Oak Ridge National Laboratory demonstrated the effective sampling of an rf-GD source with an ion trap instrument.<sup>28</sup> A DIP source mounted in a six-way cross was mated to an instrument previously employed with a gas sampling glow discharge (GSGD). These experiments first demonstrated the potentially attractive feature of adventitious water as a means of removing argon-related ions from the recorded spectra *via* charge exchange and proton transfer reactions, yielding  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$ . These species are effective at “shuttling” charge out of the trap when a low mass cut-off below 20 Da is employed. Koppenaal’s studies of ICP-ITMS expanded on this phenomenology using  $\text{H}_2$  as a bath gas, forming the basis of the current reaction cell chemistries employed in many ICP-MS laboratories on double-quadrupole instruments.<sup>38</sup>

The work of the Oak Ridge group has demonstrated very elegantly the usefulness of performing CID of tightly bound metal oxides extracted from rf-GD ion sources.<sup>28</sup> Fig. 7 presents the rf-GD-ITMS spectra for barium-related species from the sputtering of NIST SRM 1412. In this case, the extracted  $\text{BaO}$  ions (also seen in Fig. 5), further react within the trap with adventitious water to form the hydroxide species seen here. (Other species present within this mass window were selectively ejected from the trap to simplify the spectrum.) The bottom scan illustrates the selective dissociation of  $^{138}\text{BaOH}^+$  through the use of resonant excitation. The product mass spectrum shows that the barium hydroxide at 155 Da is converted with near-unit efficiency down to the atomic  $^{138}\text{Ba}$  ion. In this case, the 100 ms excitation is seen to be very effective (and selective) in breaking the  $\sim 5.5 \text{ eV}$  Ba–OH bond.



**Fig. 7** rf-GD ion trap mass spectra of NIST SRM 1412 multi-component glass. (a) Spectrum acquired following ejection of all plasma ions except those attributed to BaOH isotopes. (b) Product spectrum following selective excitation of only the  $^{138}\text{BaOH}^+$  species.<sup>28</sup>

Note in fact that the non-excited  $\text{BaOH}^+$  species (*i.e.*, the other Ba isotopes) do not experience scattering losses while still undergoing collisions with the helium bath gas atoms. This efficient retention is not surprising as the three-dimensional IT structure does indeed “trap” ions in the developed potential energy well. Of course, the relatively low kinetic energy of the ions and the resultant “cooling” *via* collisions with low-mass He atoms are also advantageous in minimizing scattering from stable orbits.

The simplified picture of CID within an IT structure involves a combination of ion acceleration by the applied excitation potentials, and collisions with helium atoms, to effectively promote the molecular ion up the vibrational energy ladder in small steps until the bond dissociation energy has been reached. A model to this effect has been verified experimentally using a GD ion source.<sup>31</sup> In essence, dissociation within the ion trap can be thought of first as an increase in the effective collision path length while also adding the trapping and cooling aspects to help retain the desired atomic ions.

Duckworth and co-workers<sup>33</sup> have recently demonstrated a methodology that might be thought of as analogous to the collision/reaction cell approach as practiced in the Agilent Technologies instruments. The essence of the resonance excitation experiment is that each unique  $m/z$  value has a unique secular frequency for selective excitation, regardless of the chemical identity of the ion at that mass. As in the case of the use of energy discrimination in double-quadrupoles to differentiate molecular ions of high collision cross-section from atomic ions of low cross-section, they demonstrated that resonance excitation of molecular and atomic ions of the same nominal mass can be differentiated in the same way. Specifically, selective removal of one of the most tenaciously bound metal oxides ( $\text{TaO}^+$ ,  $D_0 \approx 10.3$  eV) while retaining the atomic  $^{197}\text{Au}^+$  was achieved. Fig. 8 illustrates the gradual loss of ion signal at  $m/z = 197$  Da as a function of excitation time for the case where just  $\text{Ta}^+$  (which is reacted with introduced  $\text{O}_2$  to form  $^{197}\text{TaO}^+$ ) and both  $\text{Ta}^+$  and  $\text{Au}^+$  are stored in the trap. As can be seen, unit removal of the molecular species is achieved after just 30 ms of reaction time. Very simply, this result reflects the fact that the loss rate for the oxide is far greater than that for the atomic ion. In fact, the measured loss rates are  $68 \text{ s}^{-1}$  for  $\text{TaO}^+$  and  $<5 \text{ s}^{-1}$  for  $\text{Au}^+$ . The authors also illustrated different scan modes to effect the selective removal of a rare-earth oxide in the presence of an isobaric atomic ion ( $\text{GdO}^+$  *versus*  $\text{Yb}^+$ ) and metal dimer ions in the presence of atomic metal ions ( $\text{Cu}_2^+$  *versus*  $\text{Te}^+$ ). The authors note that while there is work to be done to refine PSMS-ITMS methods, they hold the basic capabilities necessary to be effectively employed as a complement to chemical resolution approaches, as demonstrated by Koppenaal and co-workers.<sup>36,38</sup>

## Method development for collision-induced dissociation

The initial reason for pursuing CID strategies for removal of polyatomics in PSMS is the experimental simplicity. The discussion above might suggest, though, that this is not the case. As is the case with reaction cell methods, there exist a number of parameters that must be evaluated to properly implement CID in PSMS. What is different, though, is that CID can be used in a very generic sense. Olesik has recently described a flow chart approach to parameter optimization for reaction cell chemistries.<sup>39</sup> Relevant considerations in the choice of reactant gas include chemical thermodynamics and kinetics, creation of new isobars at higher masses through complexation/condensation reactions, atomic ion loss cross sections, the relative ionization potentials between the analytes and the reagent gas, and the  $q$ -value (band pass) of the cell. It cannot be stressed enough that this choice is *element (analyte) specific*. Other parameters to be optimized include the reaction cell pressure, the collision cell bias potential, and the relative dc off-set potentials between the collision and analyzer quadrupoles (hexapole/octapoles).

In the case of CID optimization, there are analogous parameters that need to be considered, but to a much more general extent. The goal in all PSMS methods should be *simplicity*. For example, use of a reagent gas having an IP less than that of argon will affect loss of the most common of plasma gases as well as many air- and water-related molecular ions *via* charge exchange. Collision conditions (energy and gas density) can be optimized based on the dissociation of the most problematic of expected molecular species. For example, if you can dissociate  $\text{TaO}^+$ ,  $\text{FeO}^+$  is easy, and they are both dissociated under the same conditions! Granted, the lowest practical cell pressure and collision energy will preserve greater fractions of the desired atomic ions. Simple attenuation factor determinations (as in Fig. 5) are straightforward to perform with respect to pressure and  $E_{\text{lab}}$ , and they are not sample specific! While the use of non-reactive target gases greatly minimizes the potential for creation of new species *via* complexation or condensation, the implementation of energy-resolved mass analysis is potentially more powerful in cases where 10s of eV accelerating potentials are employed. As suggested by Marcus and co-workers,<sup>27</sup> and to a lesser extent by Houk for ICP-MS,<sup>25</sup> Xe presents a very attractive option based on its mass (good for energy transfer), its ionization potential (12.1 eV), and inert chemical nature. The costs involved would be minimal for typical collision/reaction cell systems. Indeed, the savings in not having to maintain a stock of different gases and the associated hardware and the time required to perform specific reaction strategies may be significant.

It must be confessed that the situation is more complicated if one chooses to use three-dimensional ion traps to achieve

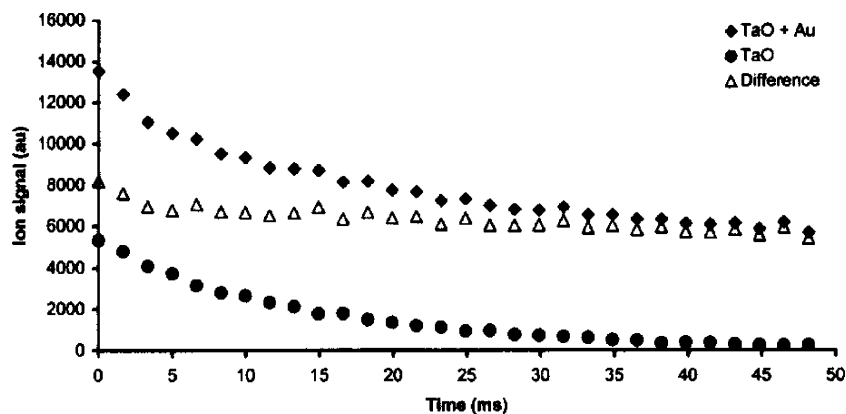


Fig. 8 Plot of measured ion signal *versus* excitation time illustrating the dissociation of  $^{181}\text{TaO}^+$  in the presence of  $^{197}\text{Au}^+$ .<sup>33</sup>



molecular dissociation and mass analysis. In such a case, the CID process is controlled by the selective excitation of the parent molecular ion at its respective secular frequency. Use of broadband excitation can limit somewhat the extent of needed *a priori* knowledge of the presence of each interferent. This complication, though, is treatable at the software level without the further need to apply species-specific chemistries. There would also be complexities dealing with the relationships between electrode powering modes for trapping, CID, and mass analysis. Perhaps the best use of an ion trap is as a “stand alone” dissociation cell, coupling it to another mass analyzer such as a linear quadrupole or better yet a time-of-flight analyzer.<sup>40</sup> In this way, separate control of the two steps in the analysis can be achieved. In actuality, the best overall configuration for performing CID in PSMS is the use of a linear ion trap to increase the collisional path length, alleviate the need for selective excitation strategies and overcome limitations of trap storage capacity.<sup>41</sup>

## Conclusions

Now that the potential complexities of multiple-quadrupole instruments have become accepted by the PSMS manufacturers, it is reasonable to wonder whether or not the use of reaction chemistries presents the most generic and simple means of performing *multielement* analysis. This, in combination with high sensitivity, is the most overwhelming reason for any laboratory to have incorporated the technique to begin with. The presentations and publications in collision/reaction cell ICP-MS reveal incredible levels of selectivity, but this is not the question. A number of refereed publications have illustrated the potential uses of CID/CAD strategies to simplify the product mass spectra from GD ion sources (and in fact to a lesser extent ICP sources). Efficient removal of problematic species *via* a combination of CID, charge exchange, and energy-resolution has been demonstrated on home-built quadrupole and ion trap instruments. Admittedly, those works were performed on what might be viewed as inferior instruments by current ICP-MS standards: this should be all the more reason to revisit the basic concept. The results would certainly be better in terms of analyte retention with modern hexapole and octapole geometries. Perhaps a linear ion trap is the best platform for CID in terms of increasing path length and improved atomic ion retention as lower gas pressures and collision energies would be required.<sup>41</sup> Rather than accept the common mantra that CID is a very inefficient process, owners of the commercial instruments are well positioned to determine whether these approaches present practical advantages in terms of generality and simplicity. Perhaps they do not, but someone needs to *run the reaction* and publish the results. The author would be happy to discuss such a project with any interested manufacturers.

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