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**A Glow Discharge Ion Source with
Fourier Transform Ion Cyclotron Resonance
Mass Spectrometric Detection**

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ABSTRACT

A glow discharge ion source has been coupled to a Fourier transform ion cyclotron resonance mass spectrometer using a series of four electrostatic lenses to accelerate and focus ions generated external to the instrument's high magnetic field into its analyzer cell. Like other glow discharge mass spectrometers, glow discharge-Fourier transform ion cyclotron resonance can provide a quantitative measure of bulk analyte concentration with good precision and accuracy. Although detection limits currently attainable are several orders of magnitude higher than the commercially available magnetic sector based instrument, this approach holds promise for ultra high mass/ultra high resolving power mass analysis. Several schemes are proposed to lower the detection limits of the technique while still providing high enough resolution to resolve isobaric interferences.

Techniques of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry [1-4] have been applied to a wide range of chemical problems, from ion photodissociation [5-7] to comparisons of gas phase and solution reactivity [8,9] to analyses of polymers and biopolymers [10-12]. With the exception of conventional electron impact ionization, laser desorption (LD) ionization has been the most widely applied means of ion formation in FTICR experiments [13-15]. However, the susceptibility of many compounds to physical damage induced by laser desorption has imposed an inherent limitation on LDFTICR use and has prevented its widespread acceptance. Concurrently, other ionization methods, such as fast-atom bombardment or supersonic expansion/photoionization, have proven difficult to implement because the relatively high background pressures accompanying them are not compatible with ultra high mass/ultra high resolution FTICR analysis.

Efforts to reduce the effects of high pressures from alternative ionization sources have involved two different approaches. The first makes use of a dual cell configuration [16], in which ion formation takes place in a high pressure source region, with ions subsequently transferred through a small conductance limit to a lower pressure analysis region. In the second approach, the ions are generated in a region external to the magnetic field associated with the FTICR experiment, and are then injected into the analyzer cell through several stages of differential pumping. Successful external ion generation followed by FTICR analysis was first reported by McIver and coworkers [17]. They employed an RF-only quadrupole ion guide to transport ions from a high pressure external ion source into an ICR cell maintained at several orders of magnitude lower pressure; there the ions were trapped and mass analyzed. Several other groups [18-23] have used this or other approaches

not involving quadrupoles to transport ions generated by a variety of alternative ionization sources into FTICR analyzer cells.

One means of external ionization that has not yet been used with FTICR mass spectrometers is the glow discharge (GD): a type of gaseous plasma, as exemplified by a common neon light. The glow discharge, whose name arises from the bright central glow produced by the emission from excited gaseous atoms, is a partially ionized gas consisting of an equal number of positively and negatively charged species and a larger number of neutral species [24]. The source consists of two electrodes typically operating in a low pressure (0.1 -10 Torr) rare gas environment. A representative analyte population is produced by cathodic sputtering, and the atoms are subsequently excited and ionized in the negative glow region of the discharge.

Glow discharge mass spectrometry (GDMS), which combines the design simplicity of the glow discharge ion source with the high sensitivity and selectivity of mass spectrometric analysis [25-27], has been shown to compare well with other types of plasma source mass spectrometry, such as ICP-MS (inductively coupled plasma) [28]. The ion source is compact and relatively inexpensive to build and maintain, and it operates at modest gas consumption rates (cc/min) and low wattage. Specific analytical problems have arisen, however, where more versatility than provided by commercially available instrumentation is necessary. Radio frequency discharges, as well as thermal atomizers have been coupled to magnetic sector instrumentation to provide for nonconductor and solution analysis [29], and other efforts have utilized conventional d.c. glow discharges as sources for more specialized mass analyzers [30]. We report in this paper the successful coupling of a

glow discharge ion source to an FTICR mass spectrometer. The results of initial experiments are presented, and possible applications based on the high mass resolution provided by FTICR mass analysis are discussed.

EXPERIMENTAL

The positive ions generated in the negative glow region of a coaxial cathode glow discharge were mass analyzed by a home-built FTICR mass spectrometer described in more detail elsewhere [31]. The instrument employed a Nicolet FTMS-1000 [32] electronics console to control a 4.50 cm x 2.54 cm x 2.54 cm ion analyzer cell. Figure 1 illustrates modifications necessary to interface the FTICR mass spectrometer to the glow discharge source. A 1" Cajon Tee (Cajon Company, Macedonia, OH) served as the housing for the glow discharge, that was formed about a machined 2.0 mm diameter pin cathode positioned on the end of a direct insertion probe (DIP) for manipulation in the high vacuum system. The ion injection method was similar to the approach of Kofel and co-workers [18], in that no quadrupole ion guide was used to focus and transport ions into the cell. Instead, a series of four electrostatic lenses accelerated and focused ions sampled from a 1.0 mm diameter ion exit orifice. In these initial studies, only one stage of differential pumping was employed, facilitating the need for a 150 L/s turbomolecular pump at the ion source, in tandem with two 300 L/s and one 700 L/s diffusion pumps at the analyzer. In this manner the analyzer pressure could be maintained at 2×10^{-6} Torr (discharge pressure = 1.0 Torr), but to obtain higher resolution mass spectra, the collision frequency in the ion cell was further reduced by placing a second 1.0 mm diameter orifice between the electrostatic lenses

and the FTICR analyzer cell (Figure 1B). In this configuration the analyzer could be maintained at 9×10^{-8} Torr, but with a concomitant loss in signal intensity. The glow discharge was operated with a constant current of 2.0 mA at 1500 V d.c.

A typical pulse sequence involved dropping the analyzer cell trapping plates from +2V to ground for a period of 0.1 - 5.0 seconds to allow ions to be "injected" into the cell, and then raising the plates back to +2V for the detection phase. In order to obtain optimum sensitivity, ions at m/z 18, 19, 20, 28, 29, 40, and 41 (H_2O^+ , H_3O^+ , Ar^{+2} , N_2^+ , N_2H^+ , Ar^+ , and ArH^+ , respectively) were selectively ejected from the cell via a swept frequency ejection pulse. In typical experiments ions with frequencies from 10 kHz to 2.667 MHz were excited and detected with a bandwidth of 2.667 MHz. Fifty time domain signals of 16 K data points each were accumulated, and the average time domain signal was apodized by a modified Blackman-Harris window function [33] and zero-filled once prior to Fourier transformation. For higher resolution analysis, fifty time domain signals of 64 K data points each were averaged, and a standard heterodyne approach was employed [2].

RESULTS AND DISCUSSION

GD-FTICR Mass Spectra

Figure 2 shows the mass spectrum obtained when a Cu pin was used as the cathode in an argon discharge. The copper isotopes at m/z 63 and 65 are the major peaks, along with "interference" peaks from Ar^+ and ArH^+ , formed from trace levels of water in the argon discharge gas. Isotopic ratios agree with known values to about $\pm 0.25\%$. Figure 3 shows the results obtained for a National Institute of Standards and Technology (NIST)

stainless steel sample, 1261a, with the Ar^+ and ArH^+ ions ejected. Interfering peaks at mass 18, 19, 28, and 29 result from H_2O^+ , H_3O^+ , N_2^+ , and N_2H^+ , respectively. Minor components of the sample at the 0.5 - 2% level are easily detected, and the isotopic ratios agree with known values to about $\pm 5\%$.

Detection Limits

The detection limit for nickel in an NIST 1261a standard reference material was calculated for 50 scans accumulated over a 10 - 100 a.m.u. mass range. The standard deviation of the mean [34] for 5 background measurements was 15090 counts. The ^{60}Ni isotope, present at 0.52% in Figure 3, yielded an ion signal of 3.5 million counts, and the detection limit, calculated by multiplying the inverse of the sensitivity (1.5 ppt/count) by 3 times the mean standard deviation of the background [35], was 68ppm. The latter results are rather high when compared with other GDMS instruments, for which the detection limits are on the order of 1 part in 1 billion [36]. However, improvements in our relatively simple ion injection scheme (for instance the addition of a Bessel Box energy analyzer and quadrupole ion guide) should lower the limit of detection by several orders of magnitude.

Quantitative Analysis

One of the main advantages of GDMS analysis is its ability to provide a quantitative measurement of analyte concentration. It is common in elemental mass spectrometry to employ a reference sample and normalization factors to correct for the sensitivity variations from element to element. These relative sensitivity factors (RSF) have been shown to

depend upon the discharge conditions (pressure, current, etc.), as well as the source geometry and the ion optics [37, 38], and are usually evaluated prior to analysis. The RSF value can be calculated from a standard sample by the relationship:

$$RSF_x = (I_r/C_r) / (I_x/C_x) \quad (1)$$

where I_x is the signal intensity for species x at a known concentration C_x , and I_r is the signal intensity of the reference, r , at a known concentration C_r . The RSF value is then used as the normalization factor in conjunction with an internal standard of the reference species for the analysis of an unknown analyte ion of species x in a different sample. Since peak area has been shown to be superior to peak height for measuring relative abundances in FTICR [39], all quantitative measurements incorporated peak area values.

The RSF values of ^{60}Ni and ^{52}Cr for an NIST 1263a stainless steel sample were calculated relative to the concentration of ^{55}Mn as the reference from data obtained for ten repetitive trials of 50 scans each. For the ^{60}Ni and ^{52}Cr species the mean RSF values were 2.34 and 1.13, with a standard deviation of the mean of the ten trials being ± 0.12 and ± 0.02 , respectively. These values were then used to determine the concentration of nickel and chromium in a different stainless steel sample (NIST 1261a) by:

$$C'_x = (RSF_x)[(I'_x)(C_r) / (I_r)] \quad (2)$$

Table 1 lists the certified concentrations, as well as the concentrations calculated with the

RSF values and those calculated by direct ratioing of the peak areas (i.e., by assuming RSF's of unity). For both analytes, the application of the RSF value improved the accuracy of the analysis and produced a percent error comparable with literature values [40].

Polyatomic Interferences

Isobaric interferences have been shown to be a universal problem in elemental mass spectrometry, regardless of ion source type. In the glow discharge, isobaric interferences arise from several sources including overlapping isotopes, doubly charged species, and polyatomic ions. This last category is the most common, with interfering species originating from: 1) ionized vacuum system impurities, 2) ionized sputtered polyatomic species, and 3) polyatomic ions generated by ion/molecule reactions.

Two schemes have been proposed to overcome isobaric interferences: discrimination and suppression/elimination [37]. The first of these, discrimination, is the approach used when the glow discharge source is coupled to a high resolution magnetic sector mass spectrometer. Some typical diatomic ion interferences are dimers, oxides and argides. The required resolution necessary to effect separation of these species from an analyte of the same nominal mass varies from a few thousand to an excess of 60000 [37]. It should be noted that at present the commercial magnetic sector instrument has resolution of ca. 10000 and would only be able to effect separation of a fraction of these species.

The second method, recently reported by King and Harrison [30] involves elimination of polyatomic species by collision induced dissociation (CID) in the RF-only section of a triple stage quadrupole (TSQ). Elimination should be a more effective approach to the

problem of isobaric interferences, because the need for ultra high resolution is no longer a factor. However, several limitations of this approach, most notably the inability to obtain collision energies high enough to dissociate tenacious bonds such as M-O, have prevented it from gaining commercial success.

The FTMS approach holds the potential for both discrimination (with ultra high resolving power) and elimination (with a greater probability for collisional dissociation than the TSQ approach) of isobaric interferences. In a series of precursory studies, moderate resolution mass spectra were generated from a brass cathode in an argon discharge. Figure 4A illustrates the 39.5 - 41.5 a.m.u. region of the spectrum with Ar^+ and ArH^+ indicated at nominal masses of 40 and 41. The observed resolution for Ar^+ is 6158 at full width half maximum. Figure 4B shows the copper and zinc species in the mass range 62 - 67 a.m.u.; the $^{63}\text{Cu}^+$ ion has resolution of 7696. To date, the highest resolution obtained with GD-FTICR has been for an $^{40}\text{Ar}^+$ ion: $m/\Delta m = 41056$. Although these results are preliminary, they demonstrate the possibility of ultra high resolution GDMS. Studies are continuing to exploit the unique capabilities of the FTICR technique to resolve/eliminate glow discharge isobaric interferences.

CONCLUSIONS

A glow discharge ion source has been successfully interfaced to a Fourier transform ion cyclotron resonance mass spectrometer. Preliminary results indicate detection limits are on the order of 68 ppm, and that improved limits of detection will result from increasing the ion throughput, while simultaneously reducing the analyzer pressure. Quantitative analysis at the 0.5% level is accomplished through the use of NIST standard reference materials and relative sensitivity factors to account for sputtering and ionization differences between different elements in various materials. Moderate resolution of $m/\Delta m \sim 10000$ and high resolution of $m/\Delta m \sim 40000$ indicate that GD-FTICR holds the potential for solving the problem of isobaric interferences in elemental mass spectrometry.

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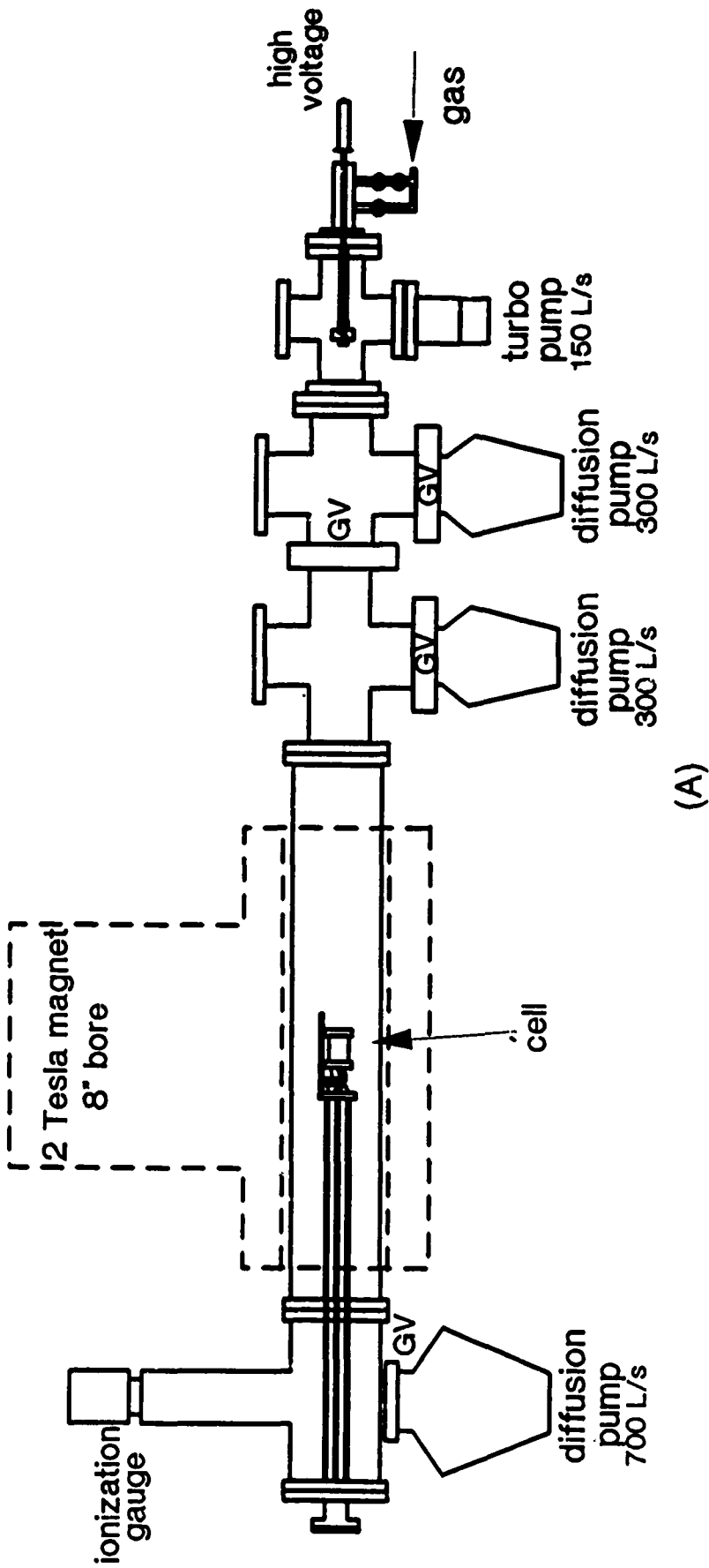
Table 1. Concentrations in an NIST 1261a standard reference sample (percent)

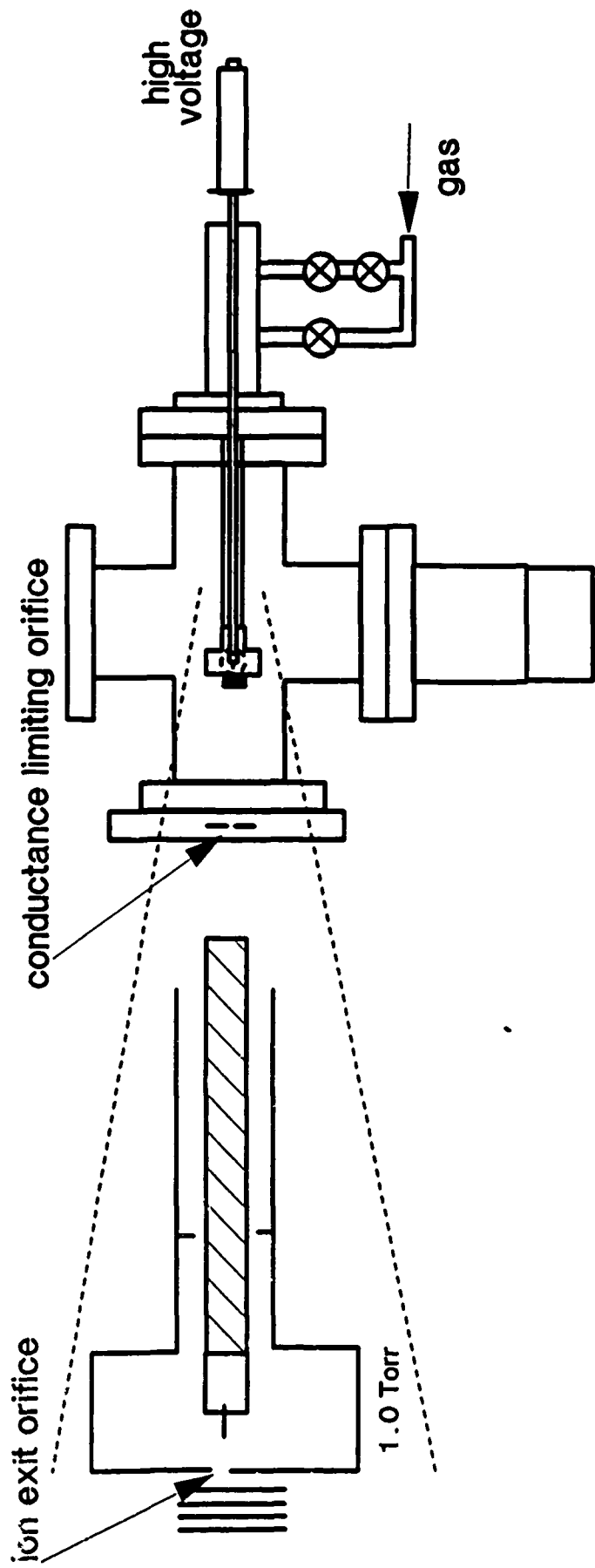
<u>Isotope</u>	<u>Certified</u>	<u>Without RSF</u>	<u>With RSF*</u>
⁵⁵ Mn	0.66 ± 0.01	-----	-----
⁵² Cr	0.58 ± 0.01	0.49 ± 0.01	0.55 ± 0.02
⁶⁰ Ni	0.52	0.25 ± 0.01	0.58 ± 0.03

*RSF values obtained from the analysis of an NIST 1263a standard reference sample (see text).

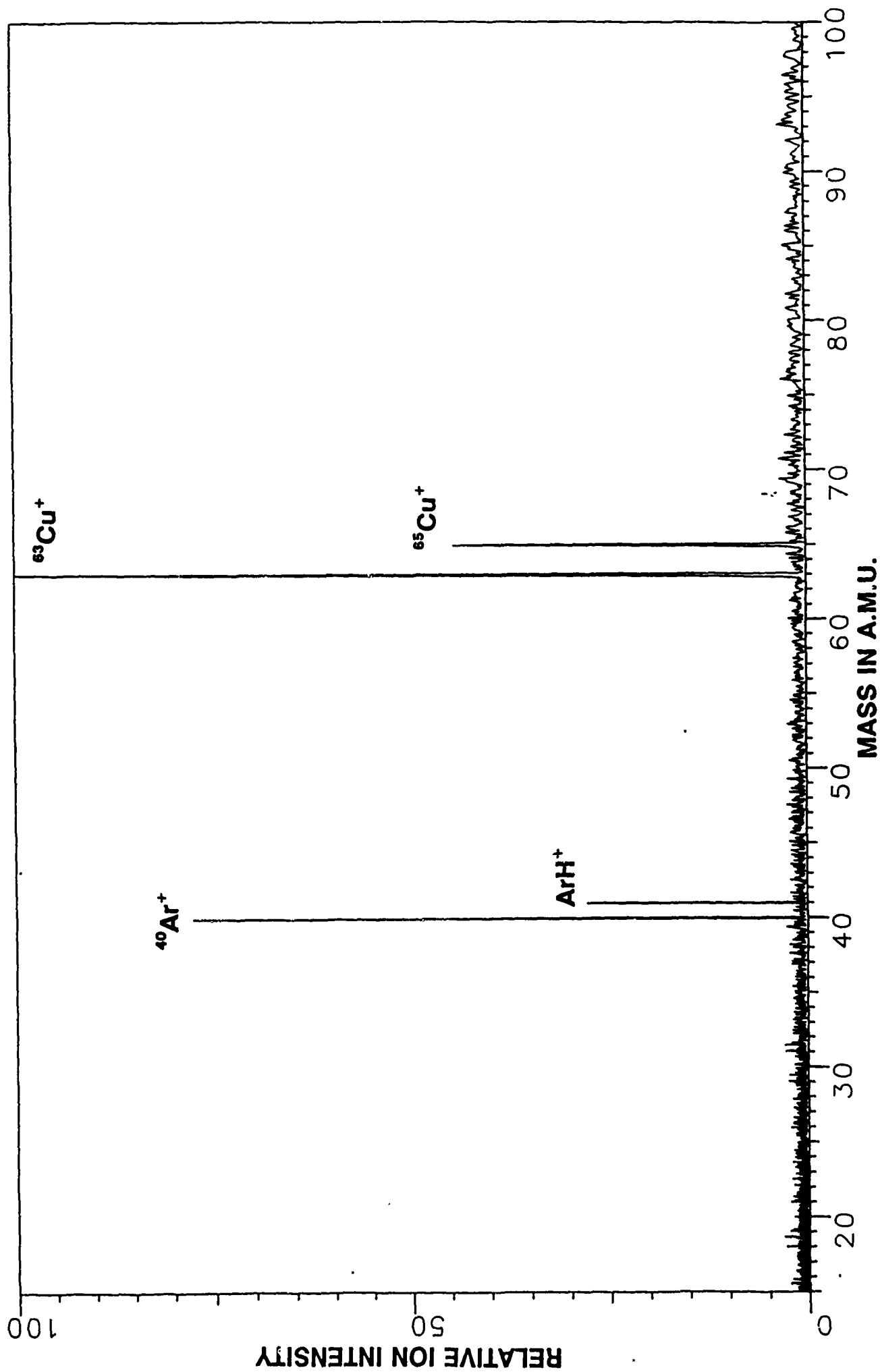
FIGURE CAPTIONS

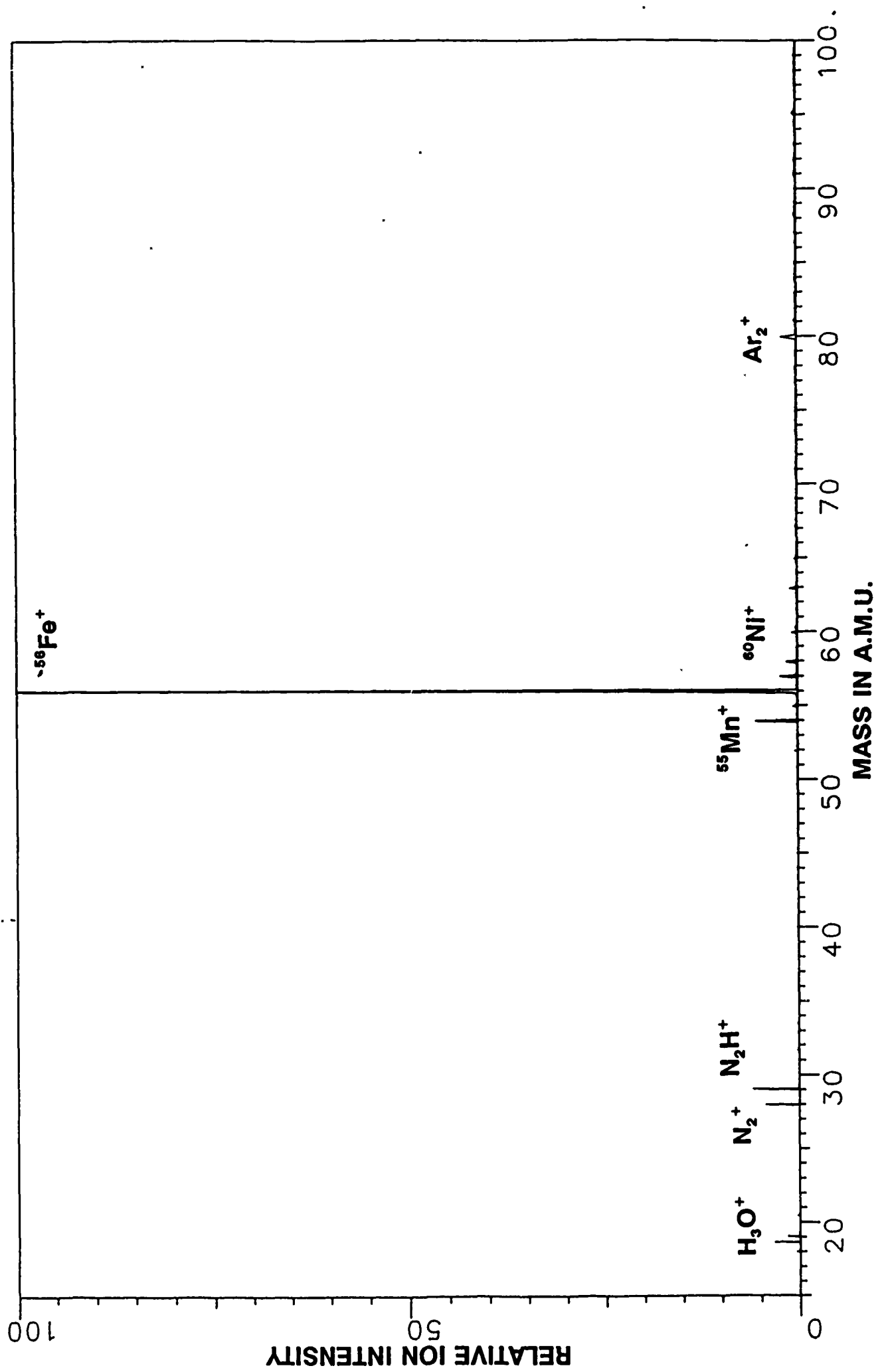
- Figure 1. (A) A 2 Tesla Fourier transform ion cyclotron resonance mass spectrometer modified to accommodate a glow discharge ion source. (B) An expanded view of (A) showing the glow discharge ion source region in detail.
- Figure 2. Low resolution GDFTICR mass spectrum of a copper cathode. 1.0 Torr argon; 1500V d.c. discharge.
- Figure 3. Low resolution GDFTICR mass spectrum of an NIST 1261a stainless steel cathode. 1.0 Torr argon; 1500 V d.c. discharge; $^{40}\text{Ar}^+$ and ArH^+ ejected.
- Figure 4. (A) Moderate resolution GDFTICR mass spectrum of a brass cathode in the mass range 39.5 - 41.5 amu; $m/\Delta m = 6158$ at nominal mass $^{40}\text{Ar}^+$. (B) Moderate resolution GDMS spectrum of a brass cathode in the mass range 62 - 67 amu; $m/\Delta m = 7696$ at nominal mass $^{63}\text{Cu}^+$. 1.5 Torr argon; 1000 V d.c. discharge.

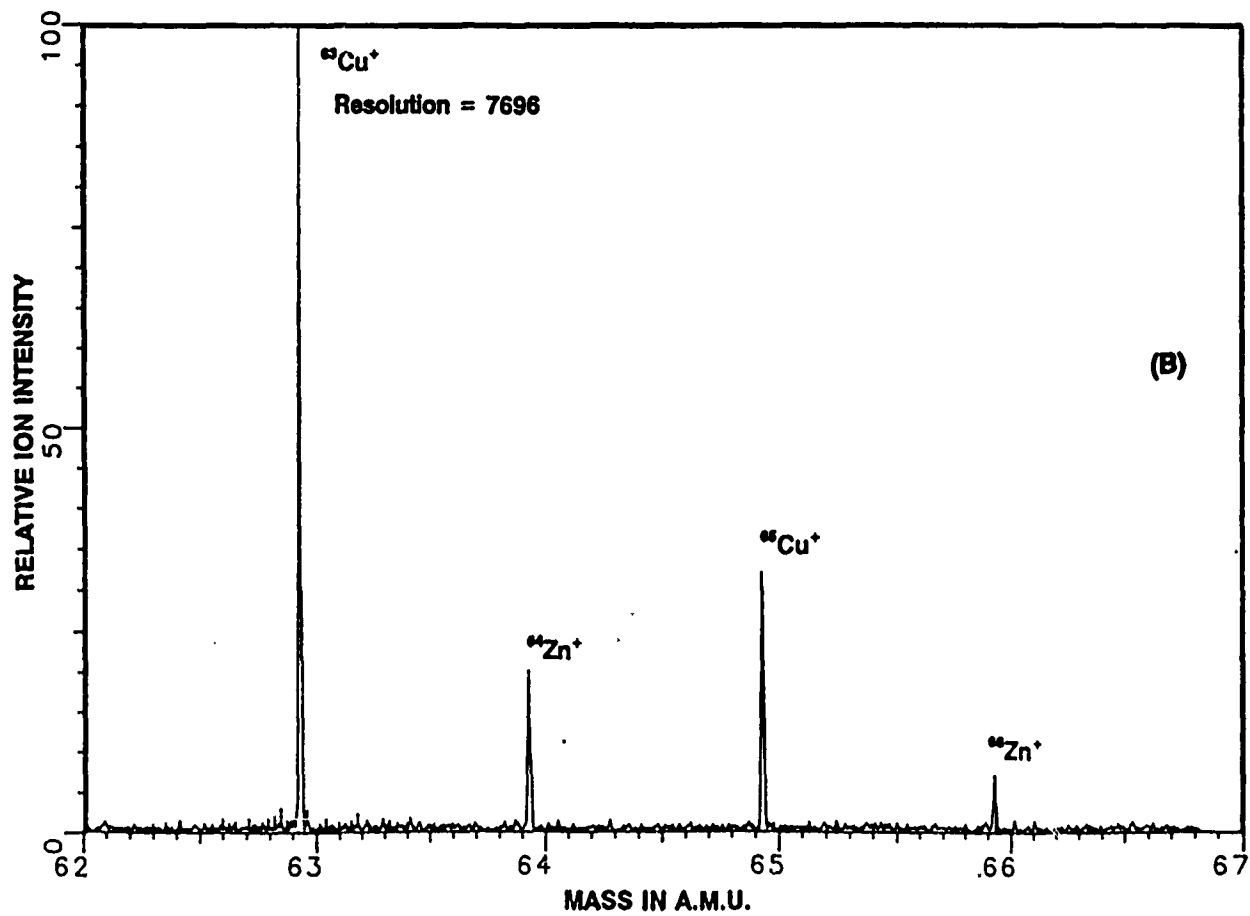
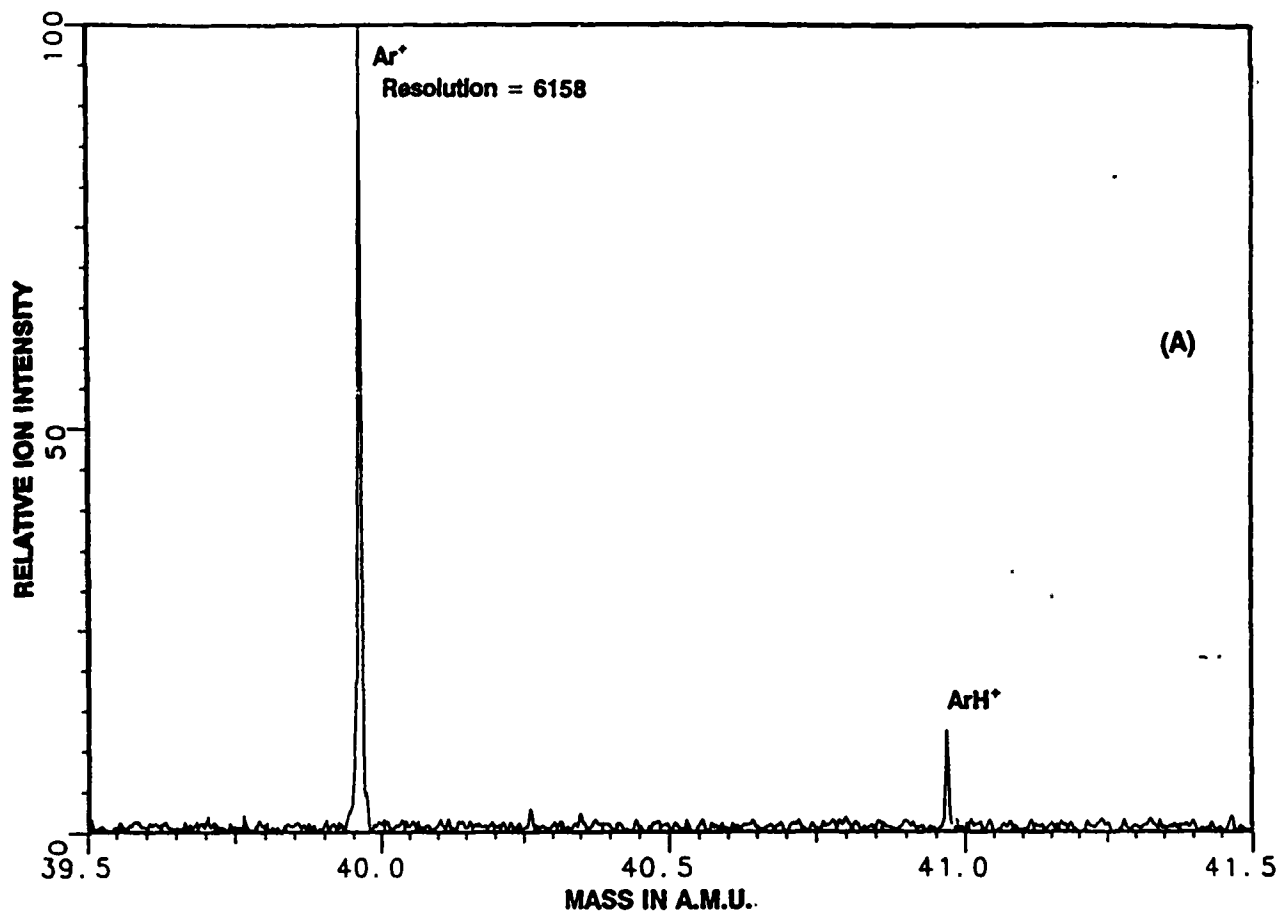




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