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Using an External Ion Source FT-ICR Mass Spectrometer

by

C.H. Watson, J. Wronka, F.H. Laukien, C.M. Barshick and J.R. Eyler

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High Mass Resolution Glow Discharge Mass Spectrometry using an External Ion Source FT-ICR Mass Spectrometer

Clifford H. Watson,¹ John Wronka,¹ Frank H. Laukien,¹ Christopher M. Barshick,² and John R. Eyler³

¹Bruker Instruments, Inc., Manning Park, Billerica, MA 01821.

²Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375.

³Department of Chemistry, University of Florida, Gainesville, FL 32611-2046.

*To whom correspondence should be addressed.

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Abstract:

A glow discharge source has been adapted for use with a commercial external ion source Fourier transform ion cyclotron resonance mass spectrometer. This combination shows promising analytical usefulness. Results on National Institute of Standards and Technology stainless steel standards showed that peaks due to nominally isobaric atomic isotopes can be observed with high mass resolution ($m/\Delta m_{1/2} \geq 290,000$). Detection limits in the high parts per billion to low parts per million range were achieved for analysis of trace metals in the standards, and concentrations of the trace elements were determined with good accuracy (better than 15%).

INTRODUCTION

Glow discharge mass spectrometry (GDMS) provides a useful method for the elemental analysis of a variety of conductive and non-conductive materials.¹ Previous analytical applications of glow discharges have made use of conventional quadrupole or magnetic sector mass analyzers,²⁻⁴ each of which has a number of advantages and limitations which must be considered when developing a practical analytical protocol for elemental analysis. Both the quadrupole and magnetic sector instruments offer high sensitivity and a large dynamic range; unfortunately, the quadrupole mass filter is inherently a low mass resolution device, and magnetic sector instruments, while capable of moderate mass resolution, lose sensitivity as mass resolving power is increased. Neither quadrupoles nor magnetic sector instruments are capable of routinely resolving closely spaced overlapping isotopic species, or other interfering mass peaks due to oxides, argides, etc., with mass resolution requirements in excess of 40,000.

Barshick and Eyer⁵ have recently demonstrated that a high pressure (133.3 Pa) glow discharge can be coupled with a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The key benefit of using FTICR for mass analysis in GDMS is the extremely high mass resolution that can be achieved.⁶ However, the FTICR mass spectrometer requires extremely low pressure in the analyzer region ($<10^{-6}$ Pa) to obtain ultra-high mass resolution. For most FTICR instruments the 133 Pa background of argon present in the GD source can severely limit the base pressure in the FTICR analyzer region and degrade the mass resolution. A resolution of only 40,000 was obtained in the previous work⁵ because pressure in the analyzer cell region could not be reduced below 1×10^{-5} Pa.

The method most commonly used in FTICR mass spectrometry to eliminate the gas load associated with GD or other high pressure sources is to separate physically the ionization and detection regions with one or more stages of differential pumping.⁷⁻¹⁴ Although the previous work⁵ used this approach to a limited extent, commercial instrumentation is available with two-stages (or more) of differential pumping. The instrument used in this report utilized 3 kV electrostatic ion focussing to transfer ions from the source (external to the magnet) through two conductance orifices and into the ICR analyzer cell while maintaining a pressure differential of $> 10^8$. In addition to alleviating the high analyzer pressure problems, an external ion source provides for quite facile sample replacement and GD source cleaning.

Another important feature of FTICR mass analysis is that, unlike magnetic sector-based instruments, sensitivity increases with mass resolution.¹⁵ This is because resolution increases as the coherent ion signal is observed for longer and longer time periods. In the absence of collisional dephasing and subsequent loss of the time domain signal, as peak widths narrow peak heights are increased, so sensitivity is enhanced with increasing mass resolution. Such enhancement provides a considerable advantage for the glow discharge/FTICR combination; high mass resolution spectra can be obtained without sacrificing sensitivity.

The results reported in this paper demonstrate the benefits of coupling a glow discharge source to a FTICR mass spectrometer optimized for external ion injection.

Initial results have far exceeded mass resolution specifications on any previous glow discharge instrument. Detection limits determined for a series of elements in National Institute of Standards and Technology (NIST) steel samples, ultra-high mass resolution, and concentration determinations of trace elements in the standard samples are all reported and discussed.

EXPERIMENTAL

An illustration of the glow discharge/external ion source FTICR instrument is shown in Figure 1. The glow discharge source was mounted in the normal source housing of a Bruker APEX 47e external ion source FTICR mass spectrometer. The instrument was pumped by turbomolecular pumps with separate pumps for the source region (330 l/s), ion optics and transfer region (50 l/s), and analyzer region (330 l/s). No additional pumping or modification of the instrument, other than removal of the standard electron ionization/chemical ionization source, was required to configure the instrument with the glow discharge source.

The glow discharge source was mounted on a standard source flange that mates with the external ion source housing. Although the source design has been previously described,⁵ in short, the glow discharge was formed within an enclosed high pressure compartment, much like a chemical ionization (CI) source housing, maintained at a 133.3 Pa pressure of argon. Ions extracted from a 1 mm ion exit orifice, located 6 mm from the standard external source lens stack, were accelerated toward the analyzer cell by a -3 kilovolt potential. The source pressure outside the glow discharge body was maintained at 1.1×10^{-1} Pa and an analyzer pressure of 9.3×10^{-7} Pa (uncorrected ionization gauge reading) was achieved.

Samples were mounted directly on a glow discharge direct insertion probe and introduced into the source housing by means of a standard probe port (Fig. 1). The samples, usually consisting of metallic rods 1 to 3 mm in diameter and 10 to 15 mm long, were held at a potential of -1000 to -1500 volts at a distance of 5-10 mm from the (grounded) ion exit orifice plate and sputter/ionized in the argon atmosphere. Ions exiting from the 1mm orifice in the high pressure source body were accelerated to 3 kV and focused (using the instrument's standard ion optics) into the center of a 4.7 T superconducting magnet. A set of ion deflection plates (used for x- and y-deflection) were pulsed to allow ions to enter the cell. Before entering the analyzer cell the ions were de-accelerated.

An ion injection/accumulation¹⁶ time of 20 - 100 ms was followed by resonant ion excitation using either a series of RF pulses for broadband detection or a narrow single frequency pulse for high resolution detection. Broadband data were acquired by digitizing the time-domain spectrum to cover a mass range of 15 to 1500 amu. High mass resolution measurements were made by digitizing the time-domain spectrum for 500 ms over a 1 amu window. For both broadband and high resolution measurements, 256 time-domain transients were averaged prior to Fourier transformation.

The glow discharge/FTICR mass spectrometer achieved a pressure differential of

$> 10^8$ between the source and analyzer vacuum regions. Thus, at a base pressure of 9.3×10^{-7} Pa in the cell, the ions can be estimated to have a mean time between ion/molecule interactions of 4.3 seconds, assuming a rate constant of 1×10^{-9} cm³/s.¹⁷ Since the duration of the digitized transient response necessary to obtain a good working resolution ($> 290,000$ full width at half maximum, FWHM) is < 5 s, few collisions which damp out the FTICR signal occur at this analyzer pressure and high resolution spectra can be obtained.

RESULTS AND DISCUSSION

Qualitative Analysis. A broadband spectrum of the NIST standard 1261a steel, shown in Figure 2, demonstrates the type of information available from a quick survey analysis. This spectrum was obtained by summing 256 transient signals covering the mass range from 15 to 1500 amu. The y-scale has been expanded in the upper mass region to permit observation of the lower concentration components. No ion ejection techniques were used to enhance the abundance of minor components. Here, even in the less sensitive broadband mode, the isotopic peaks of W, present at the 53 ppm level, are easily seen.

To demonstrate the high mass resolution of this technique, two spectra with $m/\Delta m = 290,000$ (FWHM) were obtained for the m/z 50 (Fig. 3) and m/z 58 (Fig. 4) regions of a NIST 1263a steel standard. These spectra demonstrate the ease with which the FTICR detection technique can resolve the closely spaced metal isotopes at m/z 50 (^{50}Ti , ^{50}Cr , ^{50}V) and m/z 58 (^{58}Fe and ^{58}Ni). Even though ions produced from these isotopes have masses which differ by only 1 to 3 millimass units, the corresponding peaks do not exhibit any spectral overlap.

Figure 3a shows an expanded portion of the mass spectrum around m/z 50 with peaks due to $^{50}\text{Ti}^+$ (26 ppm), $^{50}\text{Cr}^+$ (570 ppm), and $^{50}\text{V}^+$ (0.8 ppm). To show clearly the minor isotopic peaks in this spectrum, 4000 transients were averaged to yield a better signal-to-noise ratio. In order to better show peaks from the isotopes with lower abundance, the y-axis has been expanded by a factor of 5 in Figure 3b. Although ^{50}Ti (26 ppm) and ^{50}V (0.8 ppm) are relatively small components of the 1263a standard sample, peaks due to these ions are easily observed and clearly separated from that of the much more abundant ^{50}Cr (570 ppm) isotope. For extremely low level components the signals can be further averaged to provide enhanced signal-to-noise ratios. Extensive signal averaging is feasible because the glow discharge source provides stable signals for several hours from a single sample.

The region around m/z 58 for the NIST 1263a steel standard is shown in Figure 4. This high mass resolution mass spectrum was obtained by averaging 256 spectra covering a 1 amu region centered at m/z 57.935. The signals from the $^{58}\text{Fe}^+$ and $^{58}\text{Ni}^+$ ions are shown with a mass resolution of 290,000 (FWHM). Both of these isotopes normally have a high concentration in steel samples and could interfere with quantification unless there is sufficient resolution to separate them. With $>250,000$ resolution, a modest resolution by FTICR standards, these common isotopes no longer interfere with one

another.

Quantitative Analysis. To evaluate the analytical merit of this approach the detection limits for 9 common elements in a NIST 1261a stainless steel sample were determined. Results are listed in Table I. The ion signals for each of the 9 elements were measured three times in high resolution mode as described above. The detection limits were calculated by multiplying the inverse of the sensitivity by three times the mean standard deviation of the background.¹⁸ Typical detection limits ranged from 100 ppb for Cu to 6.3 ppm for Cr.

Although these detection limits are a significant improvement over previously reported GD/FTICR values (ca. 70 ppm for nickel in a NIST 1261a stainless steel sample⁵) and are comparable to results obtained using quadrupole mass analyzers, they are still 10^3 higher than those obtained with magnetic sector based instruments.¹⁹ Several studies are presently underway to improve the dynamic range of the technique; one such scheme is to improve the transport efficiency between the source and the analyzer cell. It may be more important in future experiments to concentrate on trapping only the low abundance ions in the analyzer cell and discriminating against the discharge gas and the matrix species by using a variety of methods that could include tailored ion ejections, pre-mass filtering, or some other time or energy discrimination scheme.

A three-point calibration curve for each of the elements listed in Table I was generated from the analysis of NIST 1261a, 1263a, and 1264a steel standards. To estimate typical errors associated with measuring concentrations of individual elements a fourth standard, NIST 1262a, was analyzed as an "unknown" and the concentration of each of the nine elements was determined using the calibration curves and compared to its certified value in the standard. Figure 5 shows calibration curves for the nine elements. In most cases an approximately linear fit to the calibration curve was obtained. The correlation coefficients for a linear fit to results from the three calibration points and the percent error ($| \text{predicted concentration} - \text{certified concentration} | / \text{certified concentration}$) are given in Table II for all nine elements.

Although the results in Table II show an average error greater than that previously obtained with GD/FTICR,⁵ they are encouraging because the present analysis is the first to provide both ultra-high mass resolution and quantitative analysis for minor and trace constituents. Further improvements in the instrumentation such as the use of the "Infinity"²⁰ analyzer cell, optimization of the ion extraction optics/GD source housing geometry, and cryo-cooling of the GD source should also lead to improved accuracy of the analysis.

CONCLUSIONS

Coupling of a glow discharge ion source with an external ion source FTICR mass spectrometer offers high mass resolution that can separate closely spaced isotopic peaks, provides stable mass calibration, and leads to detection limits in the 100 ppb to low ppm range. Unlike conventional mass spectrometers, the FTICR technique has the unique advantage that sensitivity is improved with increasing mass resolution. In addition to

analytical applications, the ICR ion trapping ability combined with the glow discharge source is capable of providing a variety of metal ions for subsequent analysis by ion/molecule reactions or other means.

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LITERATURE CITED

- (1) Harrison, W.W. *J. Anal. At. Spectrom.* **1988**, *3*, 867.
- (2) Bruhn, C.G.; Bentz, B.L.; Harrison, W.W. *Anal. Chem.* **1978**, *50*, 373.
- (3) Sanderson, N.E.; Hall, E.; Clark, J.; Charlabous, P.; Hall, D. *Mikrochim. Acta* **1987**, *1*, 275.
- (4) Duckworth, D.C.; Marcus, R.K. *Appl. Spectrosc.* **1990**, *44*, 649.
- (5) Barshick, C.M.; Eyler, J.R. *J. Am. Soc. Mass. Spectrom.* **1992**, *3*, 122.
- (6) Marshall, A.G.; Alber, G.M.; Gorshkov, M.V.; Grosshans, P.B.; Guan, S.; Limbach, P.A.; May, M.A.; Ricca, T.L.; Schweikhard, L.; Wood, T.D. *Proc. 40th ASMS Conf. on Mass Spectrom. Allied Top.* **1992**, *1*.
- (7) Cody, R.B.; Kinsinger, J.A. In *Fourier Transform Mass Spectrometry: Evolution, Innovation, and Applications*, ACS Symp. Ser.; Buchanan, M.V., Ed.; American Chemical Society: Washington, 1987; 359, p 59.
- (8) McIver, R.T., Jr.; Hunter, R.L.; Bowers, W.D. *Int. J. Mass Spectrom. Ion Processes* **1985**, *64*, 67.
- (9) Kofel, P.; Allemann, M.; Kellerhals, H.; Wanczek, K.P. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 97.
- (10) Alford, J.M.; Williams, P.E.; Trevor, D.J.; Smalley, R.E. *Int. J. Mass Spectrom. Ion Processes* **1986**, *72*, 33.
- (11) Hunt, D.F.; Shabanowitz, J.; Yates, J.R.; Zhu, N.Z.; Russell, D.H.; Castro, M.E. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 620.
- (12) Ijames, C.F.; Wilkins, C.L. *J. Am. Soc. Mass. Spectrom.* **1990**, *1*, 208.
- (13) Henry, K.D.; McLafferty, F.W. *Org. Mass Spectrom.* **1990**, *25*, 490.
- (14) Kofel, P.; McMahon, T.B. *Int. J. Mass Spectrom. Ion Processes* **1990**, *98*, 1.
- (15) White, R.L.; Ledford, Jr., E.B.; Ghaderi, S.; Wilkins, C.L.; Gross, M.L. *Anal. Chem.* **1980**, *52*, 1525.
- (16) Caravatti, P. U.S. Patent # 4,924,089.
- (17) McDaniel, E.W. *Collision Phenomena in Ionized Gases*, John Wiley & Sons: New York, 1964, Chapter 3.
- (18) Long, G.L.; Winefordner, J.D. *Anal. Chem.* **1983**, *55*, 712A.
- (19) Cantle, J.E.; Hall, E.F.; Shaw, C.J.; Turner, P.J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 11.

(20) Caravatti, P.; Allemann, M. *Org. Mass Spectrom.* **1991**, 26, 514.

Table I. Detection Limits Determined for Selected Elements in NIST 1261a Stainless Steel Standard

Element	Cu	Ni	Cr	V	Mo	W	Co	Ti	Mn
concentration/ppm	0.1	2.6	6.3	0.4	0.3	1.6	1.8	3.4	0.8

Table II. Concentrations of Selected Elements in NIST 1262a Stainless Steel Standard Determined Using NIST 1261a, 1263a, and 1264a Standards for a Calibration Curve.

Element	Correlation coefficient for 3 point calibration curve	Concentration predicted from calibration curve/ppm	Certified Concentration in 1262a/ppm	Percent Error
Cu	0.968	3014	3208	6.0
Ni	0.987	3122	4098	23
Cr	0.968	2929	2514	17
V	0.948	407	399	2.2
Mo	0.989	170	169	1.0
W	0.983	640	645	0.8
Co	0.995	3057	3000	1.9
Ti	0.906	926	619	49
Mn	0.900	7915	10500	25

FIGURE CAPTIONS

- Figure 1. Cross-sectional view of the external ion source GD/FTICR instrument showing the position of the source in relation to the analyzer cell and the two stages of differential pumping.
- Figure 2. Wide mass range survey spectrum of a NIST 1261a steel sample (with portions of the y-axis expanded) showing the major components and trace constituents of elements with concentrations in the low ppm range.
- Figure 3. a) Narrow mass range spectrum of the m/z 50 region of a NIST 1263a steel sample. b) Same as a) but with the y-axis expanded by a factor of five.
- Figure 4. Narrow mass range spectrum of the m/z 58 region of a NIST 1263a steel sample.
- Figure 5. Calibration curves for: a) Co, Cu, and V; b) Mo, Ti, and W; and c) Cr, Mn, and Ni generated using NIST 1261a, 1263a, and 1264a samples as standards (open points). Results for a NIST 1262a sample are shown as solid points in each curve.

Fig. 1

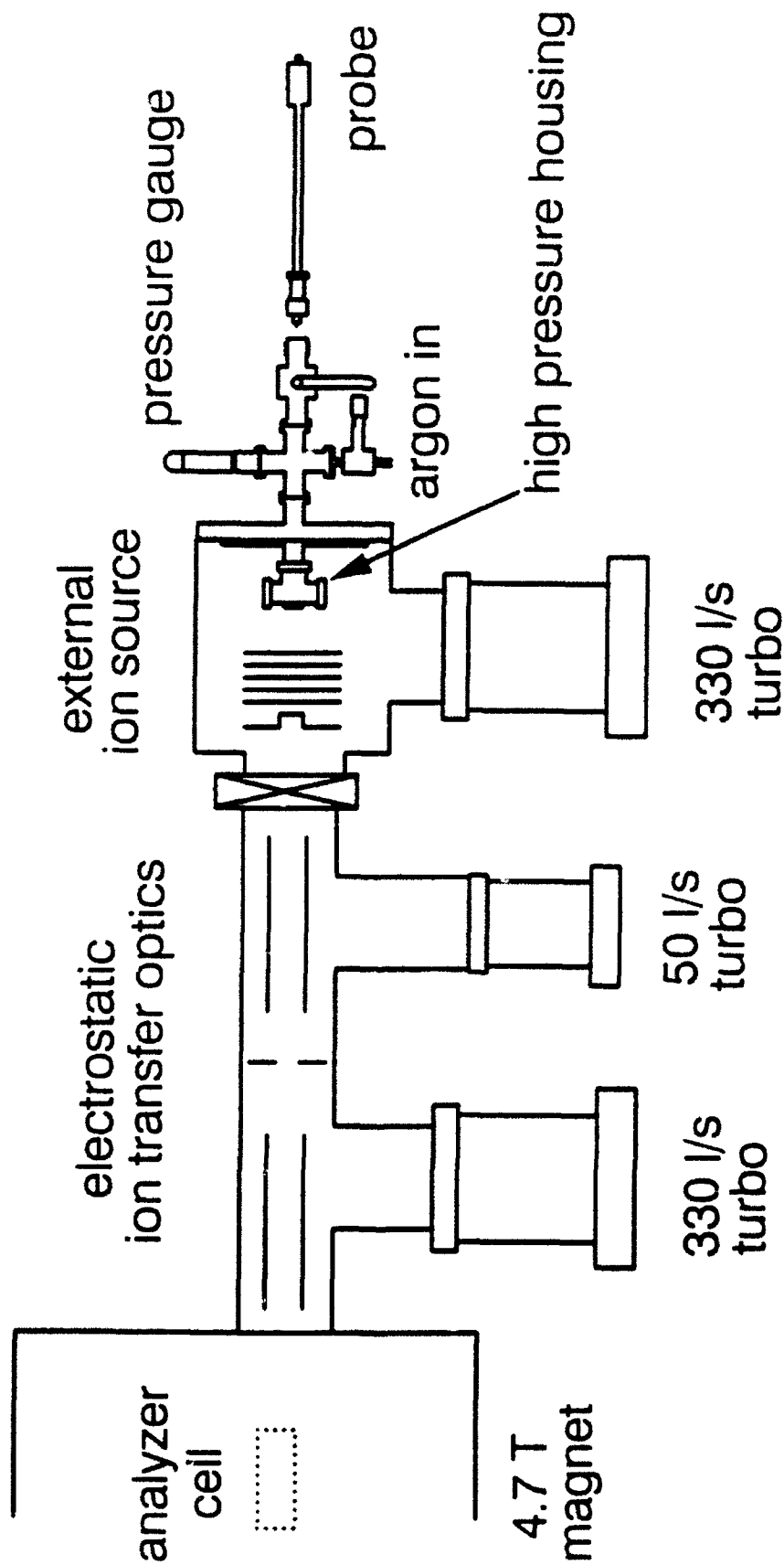


Fig. 2

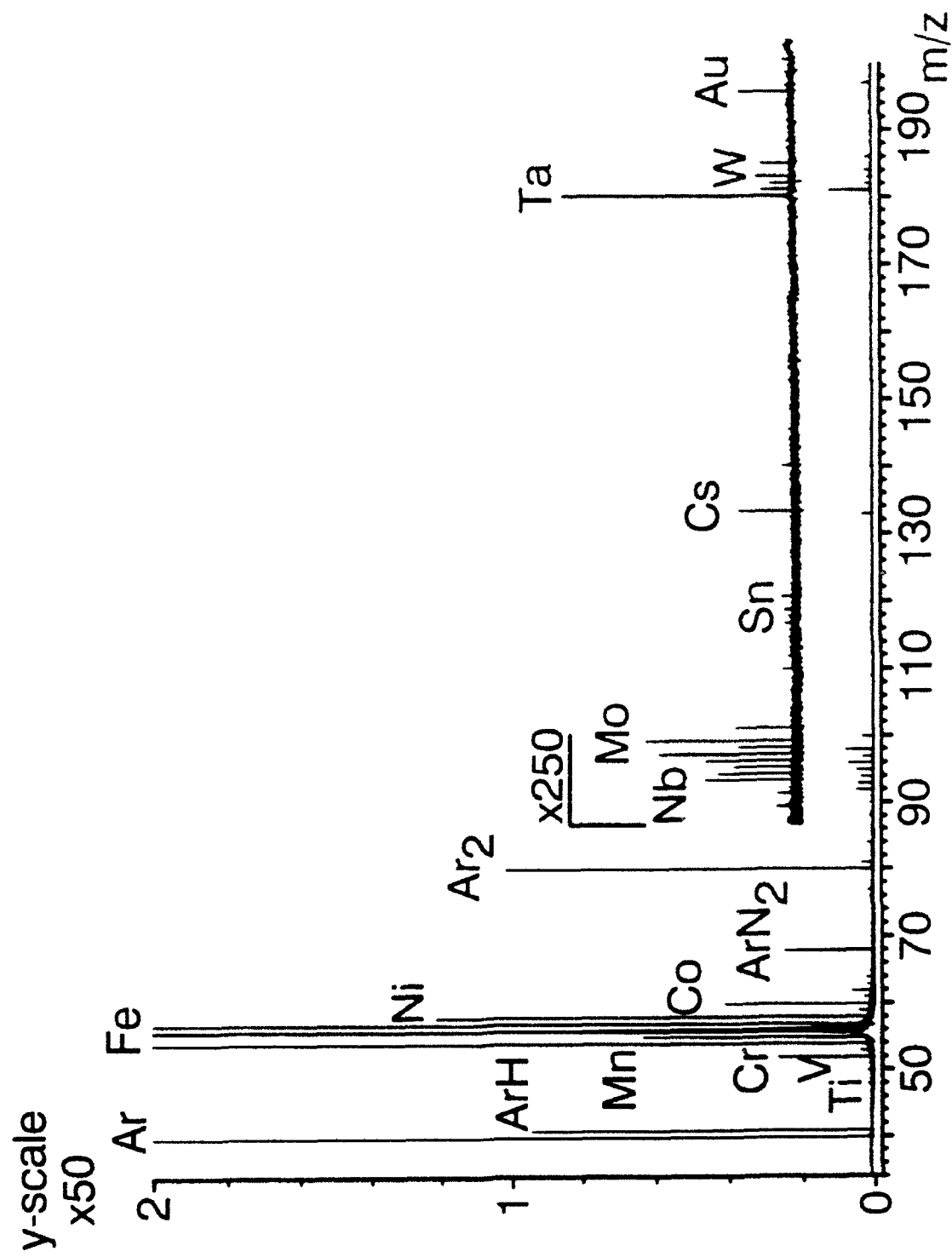


Fig. 3a

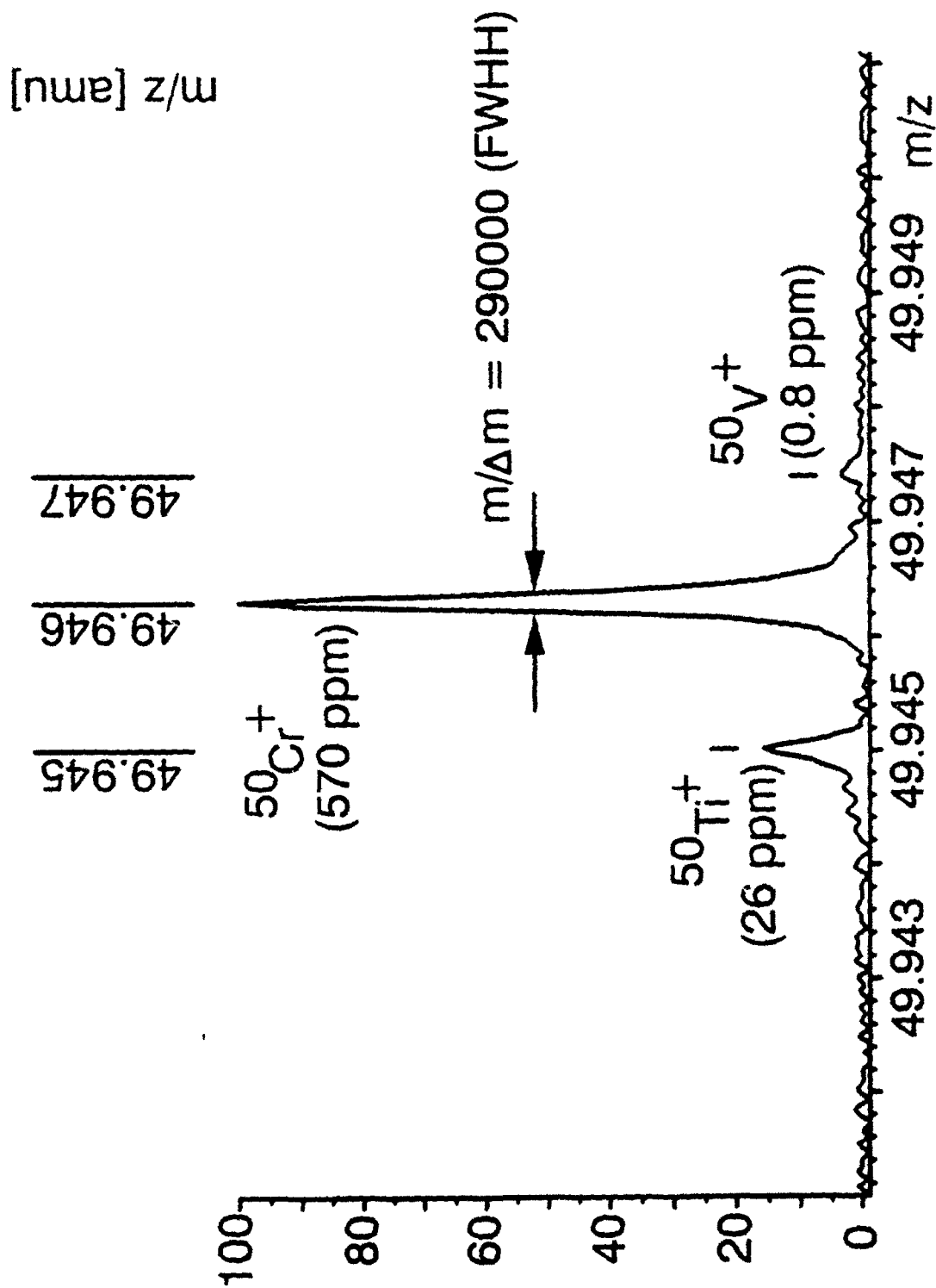


Fig. 3 b

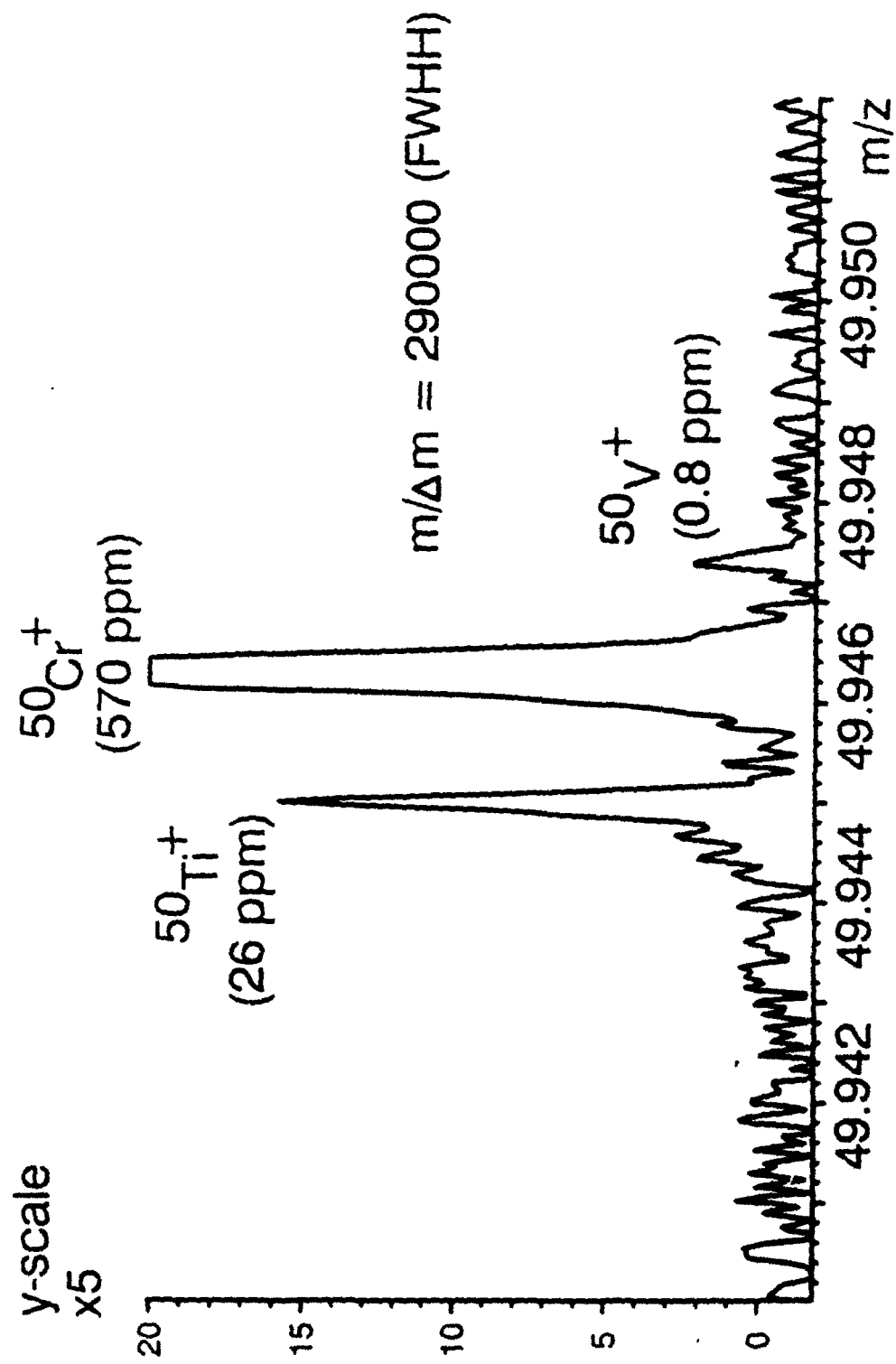


Fig. 4

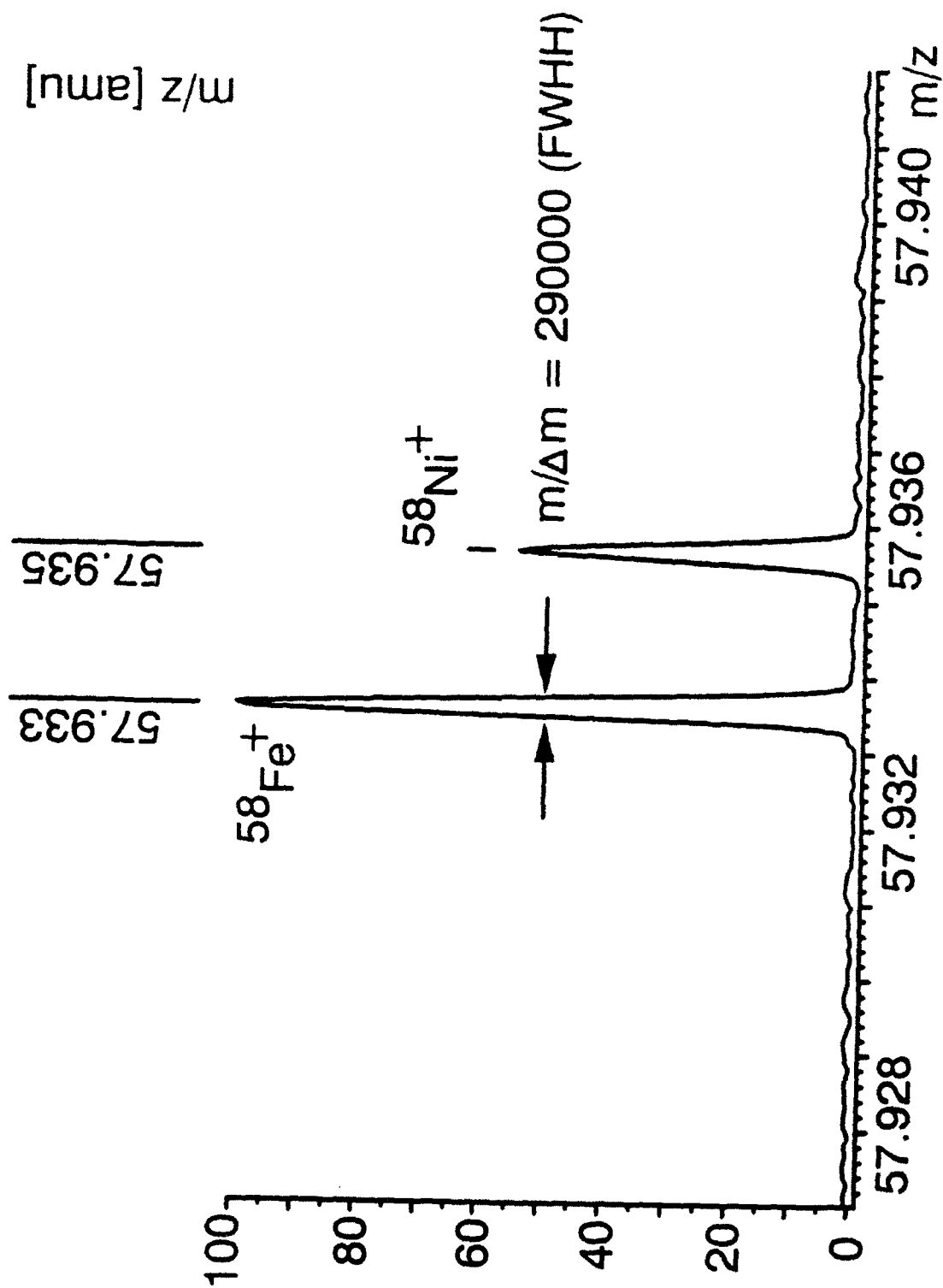


Fig. 5

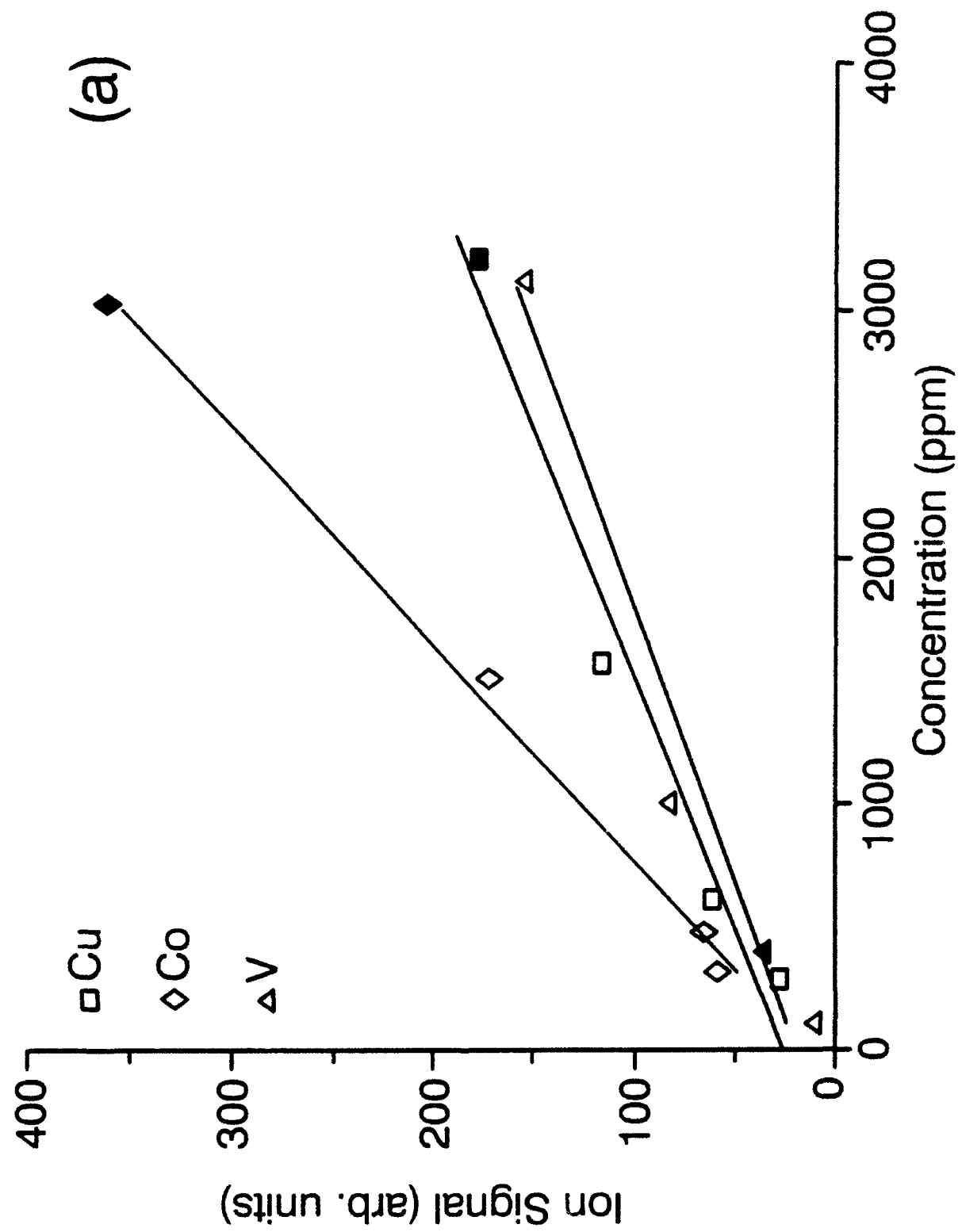


Fig. 5

