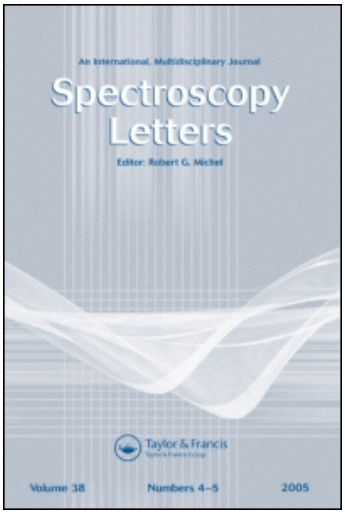

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Trace Analysis Using Position-Sensitive Detection in Magnetic Sector Mass Spectrometry

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TRACE ANALYSIS USING POSITION-SENSITIVE DETECTION IN MAGNETIC SECTOR MASS SPECTROMETRY

Key Words: Mass Spectroscopy; Position-Sensitive Ion Detection; Trace Analysis

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ABSTRACT

A position-sensitive ion detection system for trace analysis with magnetic sector mass spectrometers is described in detail, with particular application to high temperature mass spectrometry. The detection system consists of two stacked microchannel plates (Chevron assembly) backed by a resistive anode encoder and associated electronics. The range of masses simultaneously detectable is m to $1.2m$. For electron impact ionization of silver at an electron energy of 10.5 eV, the sensitivity is 1.6×10^{-7} Pa, and the mass resolution is 260 at mass 80 (valley 10% of the peak height definition). Additional applications for the detection system are discussed.

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INTRODUCTION

Magnetic sector mass spectrometers have been used for the analysis and measurement of small impurities for a variety of sample phases. Electronic measurements using sensitive electrometers, combined with magnetic field scanning has made this technique quite versatile and sensitive. These characteristics combined with ease of use have made the mass spectro*meter*, as opposed to the mass spectro*graph*, the instrument of choice for trace analysis. (see references 1-7). The particular application with which we are concerned is the determination of thermodynamic properties of unstable species using Knudsen cell high temperature mass spectrometry; this technique is quite versatile, and in some cases is the only available method for determining the thermodynamic properties of materials and gases at high temperatures. Well-known compilations of the thermodynamic properties of inorganic compounds, such as the JANAF Tables[8], consist in large part due to data obtained by high temperature mass spectrometry. The data has applications in numerous fields of study including materials research[9], the chemistry of inorganic vapors[10], and spacecraft interactions[11].

Improvements made to high temperature mass spectrometers since they were first introduced in the early 1950's include computer control of experimental parameters such as digital to analog sweeping of the magnetic field and electron energy, and data acquisition in the pulse-counting mode[12]. Another important innovation for single focusing magnetic instruments is the simultaneous detection of a mass spectrum (position-sensitive detection), described by Tuithof, Boerboom, and Meuzelaar[13], which was considered by them to have applications

in the detection of minute samples and short time scale ion events, and for the improvement of the alignment or focusing of ion optics. The use of a position-sensitive detector in combination with a magnetic-sector mass spectrometer combines aspects of mass spectro*graphy* (ie; simultaneous observation of large mass ranges) with those of mass spectro*metry* (ie, sensitivity due to electron multipliers). A distinct advantage of position-sensitive detection for magnetic sector mass spectrometry is that the mass of interest is constantly monitored, in contrast to scanning techniques, resulting in shorter data acquisition times. This is particularly useful in high temperature mass spectrometry, where signal levels are frequently be below 10 counts s^{-1}, and where it is often desirable to use small sample quantities because of high cost, limited material availability, or hazardous properties. Moreover, positive identification of elements and molecules is simplified because the isotopic ratios and the fragmentation patterns are visible in every mass spectrum, as are the detector noise levels. Finally, unexpected products or contaminants that might otherwise go unnoticed in conventional detection techniques, in which one mass at a time is focused onto the detector, may be observed in a simultaneously recorded mass spectrum.

The detection system described by Tuithof, Boerboom, and Meuzelaar[13] was a combination of a channeltron electron multiplier array with phosphor screen and a vidicon-multichannel analyzer combination. This arrangement resulted in a minimum detectable ion current of 3×10^{-16} A or ≈1500 ions s^{-1}. In high temperature mass spectrometry such a count rate is considered to be quite large. Since the investigation by Tuithof, Boerboom, and Meuzelaarin,[13] faster and less expensive electronics have become available. In this paper a simple and fast modification of a magnetic sector mass spectrometer which allows position-

sensitive detection in the pulse counting mode with count rates below 1 count s^{-1} is described.

EXPERIMENTAL

High Temperature Mass Spectrometer

The magnetic sector high temperature mass spectrometer (Nuclide model 12-60) illustrated in Figure 1 has been described in detail elsewhere [14,15] and will only be described briefly here. The apparatus is evacuated using 4 and 8 inch diameter cryopumps (CTI Cryogenics) and one 4 inch ion pump (Varian). A Knudsen cell containing the sample and optionally equipped with a gas inlet tube is radiatively heated. The temperature of the cell is determined by either thermocouples or by optical pyrometry. The neutral molecular beam effusing from the Knudsen cell orifice enters an electron impact ion source through a moveable shutter. The ion beam is accelerated by a 4500 V potential into a 60°, 12 inch radius magnetic mass filter where the ions are dispersed according to their mass-to-charge ratios. The final exit slit of the magnetic analyzer was removed, and as a result a selected range of ions is detected with a position-sensitive system which is described below. The electron energy and the magnetic induction are controlled by an AT-compatible computer.

Position-Sensitive Detection

A schematic diagram of the position-sensitive detector and associated electronics is shown in Figure 2. The arrangement is based on similar systems previously described in the literature [16,17]. The detector itself (Galileo Electro-Optics Corp.) consists of two stacked microchannel plates (Chevron assembly)

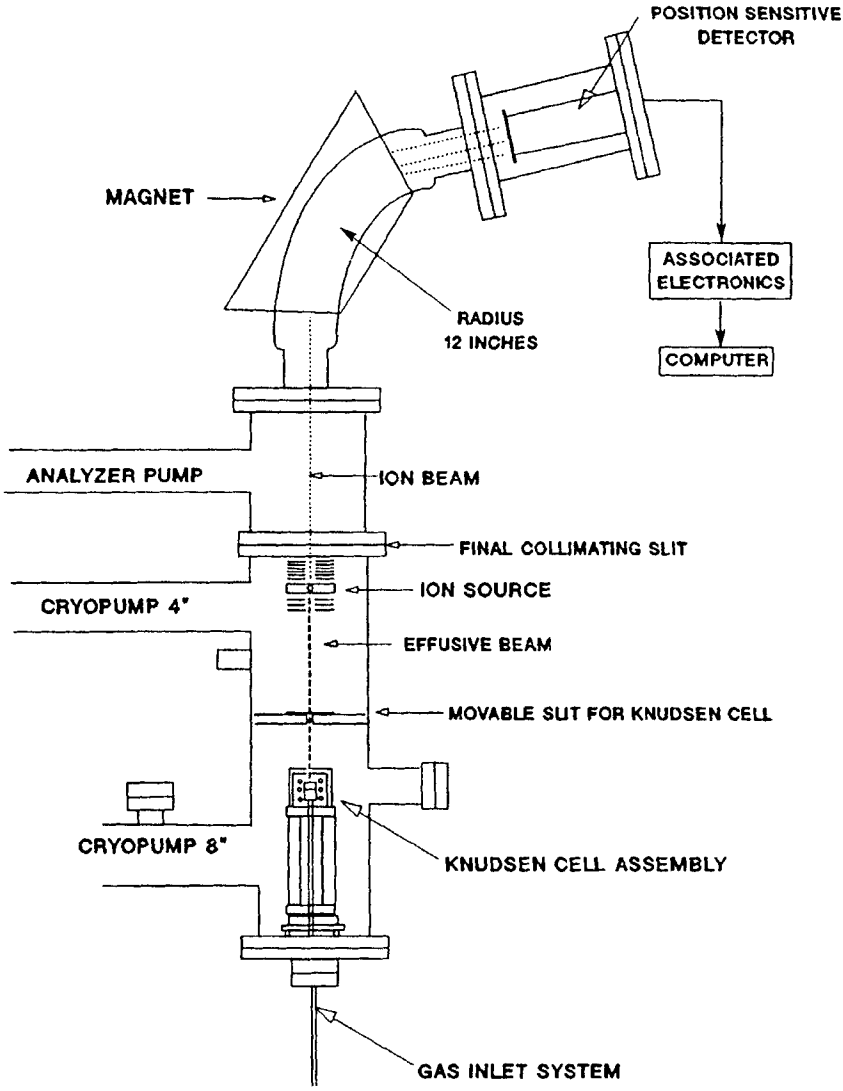

Figure 1. Mass Spectrometer with Position Sensitive Detection System

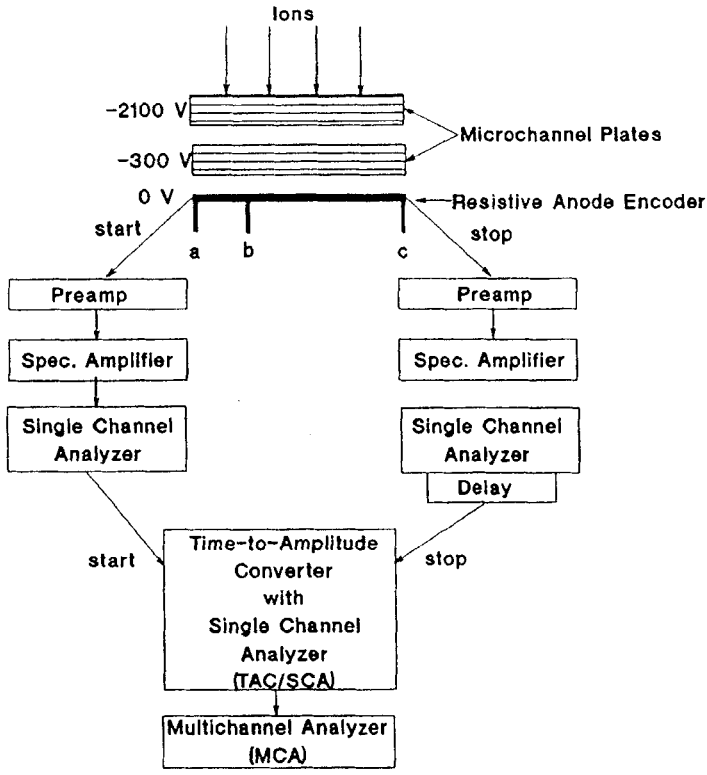

Figure 2. Position Sensitive Detector Electronics

backed by a resistive anode encoder. The usable area of the detector is 50 mm x 8 mm and is placed in the plane where the exit slit is normally located, with the longest dimension oriented parallel to the axis of dispersion, whereas the slit would have its shortest dimension perpendicular to the plane of dispersion as shown in Figure 2. The face of the upper microchannel plate is biased at -2100V, the lower plate at 300V. With 1800 V across the Chevron assembly, a secondary electron gain of 10^8 is achieved. The electrons emitted from the second plate are

accelerated toward the resistive anode encoder (RAE) by a 300 V potential drop. An electron pulse striking the RAE results in a signal which can be monitored at either end of the RAE. The RC characteristics of the signal depend on the distance between where the electron pulse strikes and the end of the RAE, where the signal is monitored. Therefore, referring to Figure 2, a pulse originating at point b will result in signals of different pulse widths arriving at points a and c. The width difference is related to the position where the ion originally strikes the upper microchannel plate, and therefore to the mass-to-charge ratio of the ion.

The pulses from each end of the RAE are processed in parallel. They are first amplified and shaped by a preamplifier and spectroscopy amplifier. The time constant of the spectroscopy amplifier is adjusted to match that of the RAE, thus optimizing the resolution of the detection system. Constant fraction timing single channel analyzers (CF TSCA) provide accurate timing of the rise time of the spectroscopy amplifier output. The difference in pulse widths is thus converted to a difference in the time of the CF TSCA TTL output pulses. The two TTL pulses are used as the "start" and "stop" signals of a time-to-amplitude converter/single channel analyzer (TAC/SCA). The stop signal is arbitrarily delayed to obtain a time range that is conveniently measurable. The TAC/SCA generates an output pulse that has a pulse height proportional to the time difference between the start and stop signals, and thus to the mass-to-charge ratio of the ion precursor. The TAC/SCA output pulses are the input of a microcomputer-based multichannel analyzer implementing a pulse height analysis mode.

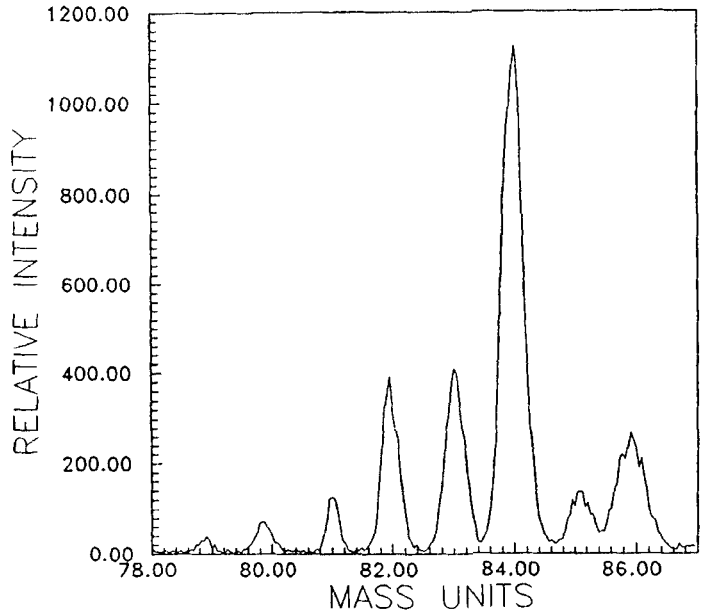

Figure 3. Mass Spectrum of Krypton Isotopes

RESULTS AND DISCUSSION

An example of a mass spectrum is shown in Figure 3. The range of the detected masses in given by $(m_2/m_1) = 1.2$, where m_1 is the first mass registered by the detector and m_2 is the last mass registered by the detector; for example, the mass range 15.5 to 19 or 72 to 87 can be simultaneously detected. The resolution for a single focusing magnetic sector, at a given ion accelerating voltage, is primarily determined by the sizes of the entrance and exit slits of the magnetic mass filter. When the position-sensitive detector is in use, however, the exit slit is removed allowing a broad mass range of ions to impinge on the surface of the

detector. The resolution is influenced by the size of the entrance slit, the accelerating voltage at the first plate of the detector, pulse shaping, and broadening of the electron cloud between the plates due to the radial velocity component of the electrons ("blooming"). The magnetic field entrance slit size, first microchannel plate voltage, and pulse shaping are empirically adjusted to maximize resolution within the tolerances of the equipment. The blooming is minimized as much as possible by the electron accelerating potential between the two microchannel plates and between the second plate and the RAE. The mass resolution ($m/\Delta m$ with valley equal to 10% of the peak height) of the position-sensitive detection described is 260 at mass 80. This resolution is more than adequate for most mass spectrometry experiments where single mass resolution enabling isotope identification of masses below 200 amu is of interest. The peaks at the edges of the spectrum in Figure 3 are broadened. This is a result of the inhomogeneous electric fields created by the potential between the detector cathode (-2100 v) and the detection chamber walls, which are at ground potential. This broadening does not affect the intensities of each mass because they are not obtained from the peak height but by integration of the peak area. Nevertheless, this broadening could be eliminated by installing a grid parallel to the face of the detector to homogenize the electric field.

The partial pressures of the neutral species effusing from the Knudsen cell are determined from ion current measurements by calibration of the instrument with a substance of known vapor pressure,[18] in this case silver (99.99% purity). The van't Hoff plot of ln(I*T) vs. 1/T, where I is the number of ions counted (normalized to one minute) and T is the temperature in Kelvin, is

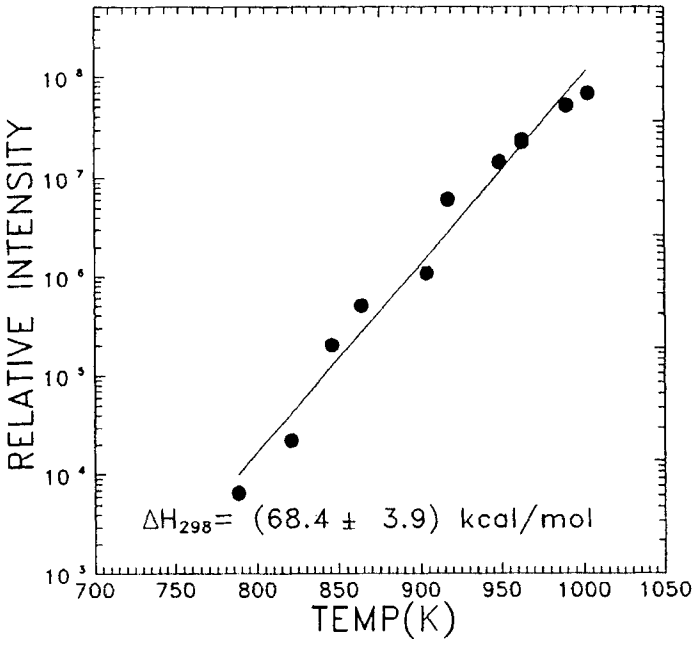

Figure 4. van't Hoff Plot for Silver

shown in Figure 4. The slope of the line is $\Delta_{sub}H/R$ (the heat of sublimation over the ideal gas constant) for silver at the midpoint of the temperature range of the measurements. The determined standard heat of sublimation for silver at 298 K, $\Delta_{sub}H^0$ is 286 ± 16 kJ/mol and agrees very well with the literature value of 284 kJ/mol.[19] The sensitivity of the instrument with the position-sensitive detector was demonstrated by the lowest temperature at which silver ion is identified during a 10 minute exposure. This temperature is 822 K for silver at an ionizing electron energy of 10.5 eV (3 eV above the ionization potential) and corresponds to 1.6 x 10^{-7} Pa. This is a factor of 40 times more sensitive than the previously used pulsed counting data acquisition method in which the voltage across a

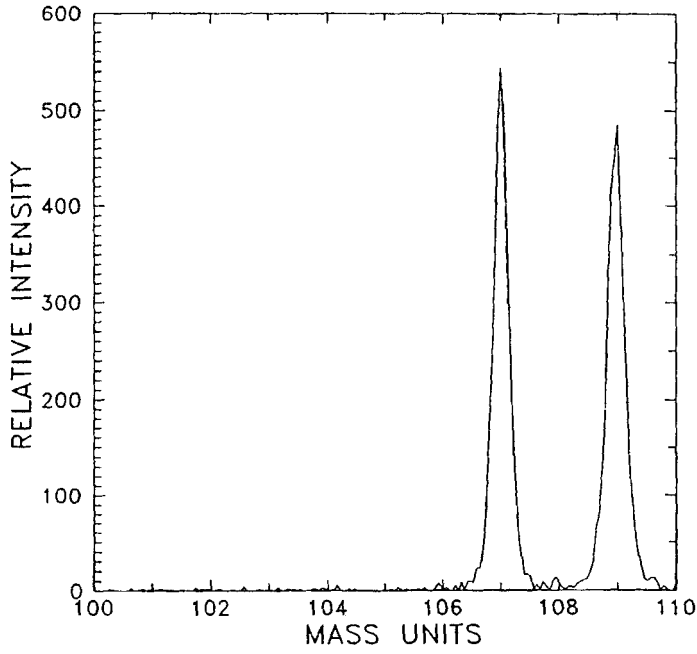

Figure 5. Mass Spectrum of Silver

resistor is read after amplification of the current by an electron multiplier. The sensitivity of the Nuclide model 12-60 using analog acquisition is specified as 7 x 10^{-6} Pa for silver at an ionizing electron energy of 70 eV. The spectrum of silver acquired by the position-sensitive detection system at 822 K is shown in Figure 5. The total count rate for the entire spectrum was 1 count s^{-1} and the total acquisition time was 10 minutes. The signal-to-noise ratio is about 3:1 and the calculated isotope ratios are within 10% of the literature values. Lower signal levels could be readily determined with longer acquisition times.

The position-sensitive detector can also be configured to acquire data for a single mass such as when an ionization efficiency curve is being recorded. A

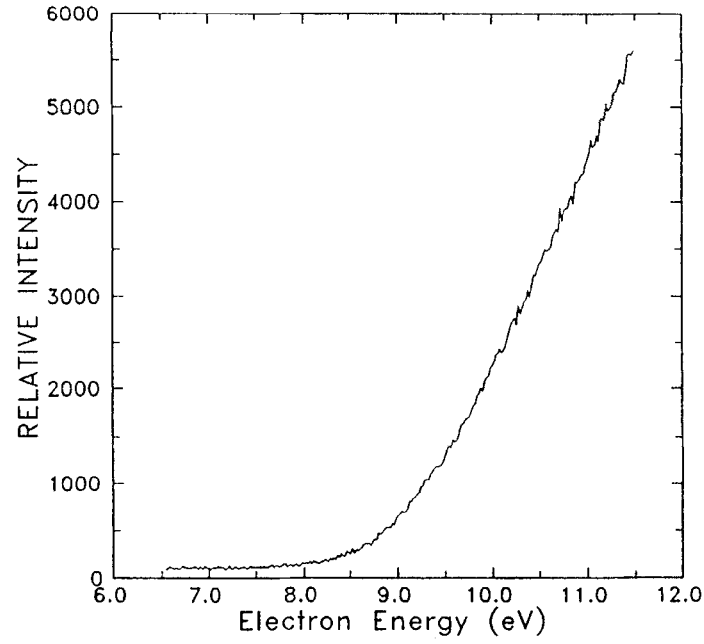

Figure 6a. Copper Ionization Potential

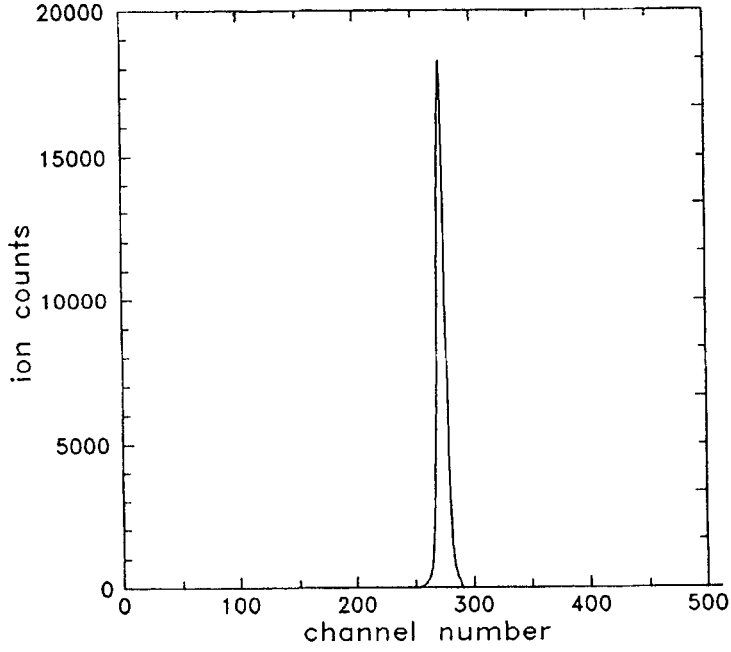

Figure 6b. Mass Spectrum of Single Ion (Copper)

time interval corresponding to a particular mass can be selected or rejected by use of the SCA of the TAC. Ionization efficiency curves of a particular species are obtained by computer-controlled repetitive scanning of the electron energy while monitoring the time window corresponding to a particular mass. An example of such a curve is shown in Figure 6.

ADDITIONAL APPLICATIONS FOR THE DETECTION SYSTEM

While our laboratory uses the instrument almost exclusively for high temperature mass spectroscopy, the ion detection system could be adapted for other applications, such as geological and analytical studies. For example, because a mass range is continuously displayed, the molecular ion peak (M) as well as the M+1 and M+2 peaks would also be displayed. This set of peaks is very useful in the determination of the molecular formula of the substance being studied. An example of this is p-Chlorobenzophenone where the M+1 (19.28%) and M+2 (33.99%) peaks are very predominate. For most samples these peaks will not be as intense as this but the M+1 peak should always be evident [20]

Although molecular ion identification is important, many times it will not appear or is very weak and therefore fragmentation patterns of organic compounds in the mass range 15-400 provide the information about the parent ion and the presence or absence of various functional groups. Systematic studies of fragmentation patterns have shown that straight chain paraffins will have a series of peaks separated by 14 mass units. Quite generally, the most stable hydrocarbon fragments contain three or four carbon atoms and the corresponding peaks are thus the largest. Cleavage of the C-C bond next to an oxygen is also

common and primary alcohols always have a strong peak at 31 due to the ion $CH_2=OH^+$.

This type of detection system could be used in the petroleum industry where quantitative data as to the types of compounds is often more important than analysis for individual components. For example, it has been found that paraffinic hydrocarbons give unusually strong peaks at masses 43, 57, 71, 85, and 99. Cycloparafins and monoolefins, on the other hand, exhibit characteristically intense peaks at masses 41, 55, 69, 83, and 97. Another group of peaks that is attributable to cycloolefins, diolefins, and acetylenes (67, 68, 81, 82, 95 and 96). Finally, alkylbenzenes are found to fragment to masses 77, 78, 79, 91, 92, 105, 106, 119, 120, 133, and 134. A mathematical combination of the peak heights of a set provides an analytical parameter for assessing the concentration of each type of hydrocarbon. The sensitivity of the detector system permits identification of very minute signal levels which would be a great benefit for sample identification.[21]

This type of detection system could also be used for geological samples providing information necessary to determine the age of the sample[22] by measurement of the isotope ratio of osmium. This method is based on the decay of the radioactive ^{187}Re isotope into the more stable ^{187}Os isotope at a known rate. A simultaneous detector for trace elemental analysis by laser plasma mass spectrometer has been described for use in the natural and technical sciences.[23] However, data was collected by a photoplate (without any signal amplification) making data analysis a cumbersome task. The same information can be obtained with greater sensitivity, much easier data collection, and faster analysis by using

the detection scheme described in this paper. The detection system could also be combined with either laser vaporization or arc/spark sources for solid sampling in the steel industry. Since Cr, Fe, Ni, Cu, and Zn could be displayed simultaneously, elemental analysis would be accelerated. Indeed, a study where an inorganic sample undergoes laser vaporization is underway.

SUMMARY AND CONCLUSION

A position-sensitive ion detection system with pulse counting for utilization in magnetic sector mass spectrometers has been described. The detector has increased the sensitivity of the magnetic sector instrument of this laboratory by a factor of 40. Other advantages gained using this ion detection system include ease of species identification by isotope ratios or fragmentation patterns, and commercial availability of all the necessary parts. The detection system can be used in any application where a magnetic sector mass analyzer is used.

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