sults from this procedure are compared with the results from our instrumental analysis and the NBS certified value in Table III, and, as can be seen, are in agreement with the latter values.

Careful examination of the γ-ray spectrum and half-life determination of the γ-ray peak (at 68.8 keV) in the residue indicates that the chief interference in the case of the Standard Reference Materials was ^{153}Sm, produced by ^{152}Sm(n,γ). Equal quantities of samarium and mercury, upon activation would yield a ratio of activities of Sm/Hg = 32:1, on the basis of cross section, natural abundance of the isotopes, decay scheme, and half-life. The abundance of samarium in the Earth's crust is almost an order of magnitude greater (*20*) than that of mercury, and an environmental sample free of mercury pollution would give an activity ratio of Sm/Hg = 300:1.

Figure 3 shows the 68-keV region of the γ-ray spectrum of a prepared mercury standard and of SRM 1630, as counted with an intrinsic-germanium detector, before and after separation of mercury. Even though the resolution of the detector is 400 eV (FWHM at 68 keV) the 68-keV x ray can be seen only as a small shoulder on the large peak due to the γ ray of ^{153}Sm. The higher-energy γ ray (77.6 keV) from a transition in ^{197}Au is also seen in the standard, but is subject to interference from the 79-keV γ rays of ^{169}Gd and ^{197}Pt.

CONCLUSIONS

We have shown that significant losses of mercury can occur during sample treatment and analysis, and we conclude that a method which can eliminate as many steps in trace-element determination as possible, will lead to the most accurate determination of mercury concentration in the sample. Neutron activation is such a method, affording good sensitivity, but the γ spectrum (particularly the x-ray region) must be carefully scrutinized for interfering activities. Therefore, preliminary examination (using a high-resolution detector) of the γ-ray spectrum of a sample must show the absence of interferences, otherwise radiochemical separation is required. In addition, we have provided evidence which supports the hypothesis that mercuric ion is reduced to mercury metal during sample pretreatments such as lyophilization and digestion. Although Nernst-equation calculations indicate the possibility of spontaneous reduction for the reaction conditions imposed, the fact that an equal amount of mercury is lost (as Hg^0) from nonvolatile oxidizing media, which theoretically maintain mercury as Hg(II), shows that a simple mechanism for reduction cannot be proposed at this time.

LITERATURE CITED

(1) J. Wood, F. Kennedy, and C. Rosen, *Nature (London)*, **220**, 173 (1968).
(2) C. Feldman, *Anal. Chem.*, **46**, 99 (1974).
(3) H. Rook and J. Moody, "Stabilization and Determination of Nanogram Quantities of Mercury in Water", Proceedings of the Second International Conference on Nuclear Methods in Environmental Research, University of Missouri, Columbia, Mo., 1975; and H. Rook, T. Gills, and P. LaFleur, *Anal. Chem.*, **44**, 1114 (1972).
(4) W. W. Scott, "Standard Methods of Chemical Analysis", D. Van Nostrand and Co., New York, 1925, Vol. 2.
(5) W. Hatch and W. Ott, *Anal. Chem.*, **40**, 2085 (1968).
(6) T. Rains and O. Menis, *J. Assoc. Off. Anal. Chem.*, **55**, 1339 (1972).
(7) R. Ginell, Department of Chemistry, Brooklyn College, private communication, 1974.
(8) F. D. and C. T. Snell, "Colorimetric Determination of Elements", D. Van Nostrand and Co., New York, 1936.
(9) K. K. Pillay et al., *Anal. Chem.*, **43**, 1419 (1971).
(10) P. D. La Fleur, *Anal. Chem.*, **45**, 1534 (1973).
(11] M. Friedman, E. Miller, and J. Tanner, *Anal. Chem.*, **46**, 236 (1974).
(12) D. MacKay, *Environ. Sci. Technol.*, **7**, 611 (1973).
(13) S. Harrison, P. LaFleur, and W. Zoller, *Anal. Chem.*, **47**, 1685 (1975).
(14) H. L. Finston and E. T. Williams, "Nuclear and Radiochemical Techniques in Chemical Analysis", *U.S. At. Energy Comm. Tech. Rep.* **NYO-3417-6**, June 1968.
(15) R. A. Horne, "Marine Chemistry", Wiley Interscience, New York, 1969.
(16) R. C. Weast, "Handbook of Chemistry and Physics", The Chemical Rubber Co., Cleveland, Ohio, 1974.
(17) C. Feldman, *Anal. Chem.*, **46**, 1606 (1974).
(18) J. Thompson and W. Linnett, *Trans. Faraday Soc.*, **32**, 682 (1936).
(19) R. Filby et al., "Role of NAA in the Study of Heavy Metal Pollution of a Lake River System", Second International Conference on Nuclear Methods in Environmental Research, Columbia, Mo., 1974.
(20) A. F. Trotmen, "Comprehensive Inorganic Chemistry", Pergamon Press, New York, 1973, Vol. 3.

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Atmospheric Pressure Ionization Mass Spectrometry: Corona Discharge Ion Source for Use in Liquid Chromatograph–Mass Spectrometer–Computer Analytical System

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A corona source for a liquid chromatograph–mass spectrometer–computer analytical system is described. The performance was compared with that of the ^{63}Ni source previously employed with direct injection of samples. Both ion sources gave the same positive ions with solvents and test compounds. The corona source had a larger dynamic response range. A separation of several polynuclear hydrocarbons was demonstrated; API detection was compared with UV detection. With isooctane as the solvent, the hydrocarbons formed MH^+ ions through solvent-mediated ion molecule reactions. Selective ion detection was used to monitor the elution of each hydrocarbon.

The technique of atmospheric pressure ionization (API) mass spectrometry, using a ^{63}Ni ionization source, has been described (*1, 2*). A second ionization method, using a corona discharge, was later employed in a liquid chromatograph–mass spectrometer–computer (LC-MS-COM) analytical system (*3, 4*). The primary purpose of the work described here was to compare the properties of the ^{63}Ni and corona ionization sources, and to define the circumstances governing limiting sensitivity of detection. In the positive ion mode, both ^{63}Ni and corona sources give essentially identical reactant ion spectra and lower limits of detection. The corona source, however, has approximately one hun-

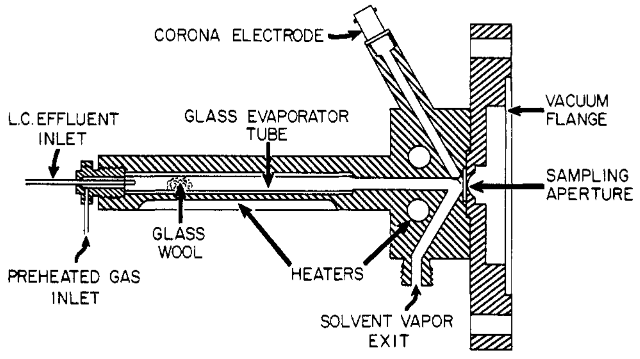

Figure 1. Schematic diagram of corona source

The voltage varied from 500 to 2000 V, depending upon the carrier gas and solvents

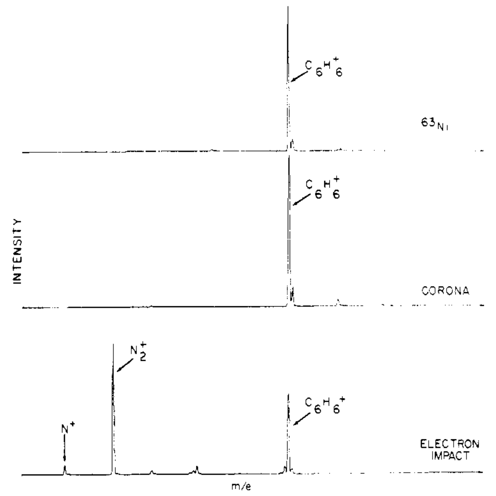

Figure 2. Ion profile observed for benzene in nitrogen at 200 °C with an API ^{63}Ni source, an API corona source, and a conventional electron impact source

dred times the reactant ion intensity of the ^{63}Ni source. This results in a greatly increased dynamic response range which is desirable for an LC-MS-COM system. The separation and detection of several polynuclear hydrocarbons with an LC-MS-COM system was accomplished with isooctane as the eluting solvent, and with detection as MH^+.

EXPERIMENTAL

Corona Source. A diagram of the LC-MS-COM vaporizer and corona source assembly is shown in Figure 1. The LC effluent enters the vaporizer through a stainless steel fitting ($\frac{1}{16}$-inch tube to $\frac{1}{4}$-inch pipe) which was modified to permit the admixture of preheated carrier gas (nitrogen or helium). The hot carrier gas aids the vaporization of the effluent stream, and it also stabilizes the corona discharge (the stabilizing effect is evident from the lowered discharge potential observed for gas/solvent mixtures). Direct syringe injections of samples in organic solvents can be made by replacing the LC effluent line with a silicone rubber cap; this mode of injection was used to obtain reference spectra. The solvent and solute in LC operation, and in direct sample injection, are vaporized in a glass evaporator tube which is normally maintained at 275 °C by a cartridge heater. The mixture of vaporized solvent, solute, and carrier gas then enters the source region; the source housing and vacuum flange are heated by two cartridge heaters, and are normally maintained at 250 °C. The corona electrode consists of a BNC connector, maintained below 200 °C, and a glass insulator sealed at the source end to a platinum point electrode. The point is sharpened to about 10-micron radius and is positioned approximately 2–3 mm in front of the sampling aperture (25-micron diameter). The aperture membrane is sealed to the vacuum flange with a gold O-ring and a small flange. This permits the entire vaporizer–source assembly to be removed for cleaning or modification without disturbing the vacuum system. The temperature of the vaporizer and source chamber is monitored with iron-constantan thermocouples. The temperatures were controlled with Thermo-Electric Model 400 proportional temperature controls. The mass spectrometer was a modified Finnigan Model 1015; this was described previously (*1, 2*).

Source Characteristics. A Fluke Model 404B high voltage power supply was used as the corona power supply. A 25-megohm current-limiting resistor was used in series with the supply. In normal operation, the supply potential was set at +2 kV for positive ions and −2 kV for negative ions. The actual voltage required depended upon the gas/solvent mixture and the temperature; it ranged from several hundred volts for helium alone to 5000 volts for solvent vapors alone.

The corona current under normal conditions was about 10^{-6} ampere. This is 10^3 to 10^4 times the current supplied by the ^{63}Ni source used previously. The current entering the mass spectrometer, measured on the first lens element, ranged from 10^{-11} to 10^{-10} ampere. The exact value depended upon the corona current and the distance from the corona point to the aperture. These ion currents imply that the ion densities in the region of the sampling aperture were two orders of magnitude higher for the corona source than for the ^{63}Ni source described previously. The resulting increased reactant ion densities do not appreciably increase the sensitivity of detection, but lead to a greatly increased dynamic range.

Computer Program. The computer program described previously was found to be inadequate for use with a corona source, because of a limiting count rate of 20000 pulses per second (*1*). The original program used a hardware clock to measure the dwell time per mass channel, and a software program to count each event on an interrupt basis. Each interrupt required approximately 50 μsec. for servicing. The current program was rewritten to use a high-speed 12-bit counter. The dwell time per mass channel is measured with a software program clock. At the end of each time interval (minimum 0.1 msec.), the accumulated pulse count is added to the current data buffer. The 12-bit counter has a maximum rate of 10^7 pulses per second; this is 500 times greater than that of the previous software interrupt counter.

The interface circuits of the SSR counter (described earlier) were modified to make use of an available prescaler to give output rates equal to the input rate divided by 1, 4, 40, or 400. Using a prescale factor of 4 gave an input pulse rate system capability of 4 × 10^7 pulses per second; this is the limit of the preamplifier-discriminator. Thus, the computer count rate capabilities were brought into line with the overall SSR rate meter capabilities.

Reference Compounds, Reactant Gases, and Solvents. The reference chemicals, reactant gases, and solvents were used as obtained. Benzo[*a*]pyrene (Practical grade), 1,2-benzanthracene (crystalline, approx. 95%) and anthracene (grade 1, approx. 98%) were obtained from Sigma Chemical Co. Isooctane, hexane, and benzene were Spectroanalyzed Grade from Fisher Scientific Co. The hexane was a mixture of isomers with some methyl cyclopentane.

Operation. The general operating procedures for an LC-MS-COM system and a direct injection MS-COM system have been described (*1–4*). Electron impact spectra of the solvents used in this work were taken using the internal calibration source at 20 eV. At all other times, this EI source was inoperative. The ^{63}Ni spectra were obtained by incorporating a ^{63}Ni foil cylinder into the corona source chamber (in the region immediately around the aperture). To ensure identical conditions for comparison purposes, the corona spectra were taken immediately after the ^{63}Ni spectra, with the ^{63}Ni source still in place. Thus, the corona spectra contain a small contribution (less than 1%) due to the ^{63}Ni source. Since the positive ion corona and ^{63}Ni spectra are essentially identical this contribution is not significant.

RESULTS AND DISCUSSION

Ions from Benzene, Isooctane, and Hexane in Nitrogen Carrier Gas When ^{63}Ni and/or a Corona Discharge Are Used as a Source of Electrons.

Benzene. The ions formed from benzene in nitrogen carrier gas, with a ^{63}Ni foil as the primary source of electrons, were described in a previous paper (*1*). Figure 2 shows the electron impact, corona, and ^{63}Ni mass spectra of benzene (approximately 1%) in nitrogen. In these studies, the electron impact spectra were employed for calibration as well as comparison purposes. The corona and ^{63}Ni positive ion mass spectra are very similar. The ion current is carried mainly

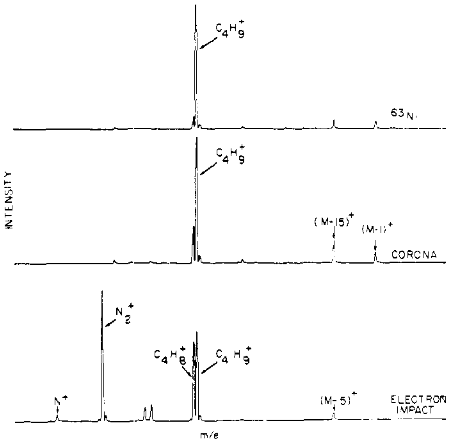

Figure 3. Ion profile observed for isooctane in nitrogen at 200 °C with an API ^{63}Ni source, an API corona source, and a conventional electron impact source

by $C_6H_6^+$ ions. A low concentration of $C_{12}H_{12}^+$ ions, not shown in the Figure, was also present in both instances. The ionization reaction probably involves charge transfer from N_4^+, as indicated earlier (*1*), but direct ionization may also occur. The concentration of $C_{12}H_{12}^+$ ions is dependent upon the temperature and upon the benzene concentration. Ions derived from water are not present. This is in part due to the fact that benzene has a lower ionization potential than water, and also to the fact that benzene is a stronger gas phase base than water. If water is added to the gas stream containing benzene, $[C_6H_7]^+$ ions are formed.

Isooctane. Figure 3 shows the electron impact, corona, and ^{63}Ni mass spectra of isooctane (approximately 1%) in nitrogen. In both corona and Ni^{63} spectra, $C_4H_9^+$ is the major ion product. In addition, low concentrations of $(M - H)^+$, $(M - CH_3)^+$ and $C_4H_8^+$ are also present in both mass spectra. The formation of these ions is believed to occur in the following way.

The $C_4H_8^+$, $C_4H_9^+$, and $(M - CH_3)^+$ ions are probably formed by charge transfer from N_4^+ to isooctane, accompanied by fragmentation. This may also occur by direct ionization. The $(M - H)^+$ ions are probably produced by hydride transfer from isooctane (M) to the $C_4H_9^+$ ion:

$$C_4H_9^+ + M \rightarrow C_4H_{10} + (M - H)^+ \qquad (1)$$

The relative rates for this reaction have been measured by Ausloos and Lias for a large number of alkanes (*5*).

The structure of the $C_4H_9^+$ ion arising from isooctane is probably predominately t-$C_4H_9^+$. This ion can be used as the reactant ion for sample ionization in the same way that the t-$C_4H_9^+$ ion from isobutane is used. When isooctane is employed as a solvent in an LC-MS-COM system the ionization of the sample is similar to that observed when isobutane is the reactant gas.

Hexane. Figure 4 shows the electron impact, corona, and ^{63}Ni mass spectra of commercial hexane (approximately 1%) in nitrogen. The corona and ^{63}Ni spectra are essentially identical. The $C_4H_8^+$ and $C_4H_9^+$ ions are probably formed by charge transfer from N_4^+ followed by fragmentation. The major ion, (M − 1), is formed by hydride abstraction by $C_4H_9^+$. The less abundant ions (M − 2), (M − 3) and (M − 4) are probably formed by similar reactions from other isomers, and by H_2 abstraction by $C_4H_8^+$ (*5*):

$$C_4H_8^+ + RH_2 \rightarrow R^+ + C_4H_{10} \qquad (2)$$

The ionization of reference samples, using hexane as a reactant gas, occurs in essentially the same fashion as when isooctane is used.

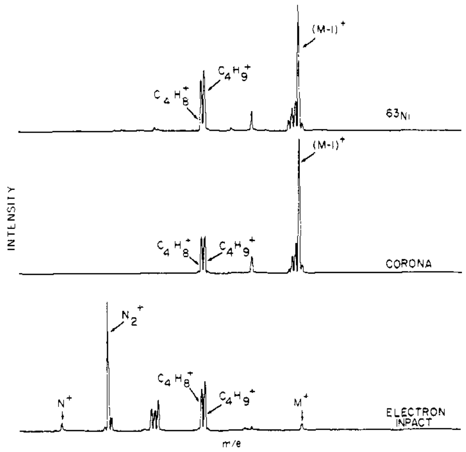

Figure 4. Ion profile observed for commercial hexane in nitrogen at 200 °C with an API ^{63}Ni source, an API corona source, and a conventional electron impact source

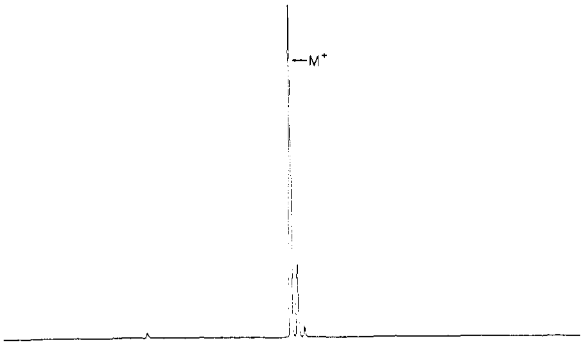

Figure 5. Ions observed for anthracene at 200 °C with an API corona source

The sample was injected in benzene solution; the carrier gas was nitrogen

Ionization of Polynuclear Aromatic Hydrocarbons. Aromatic hydrocarbons are bases in the gas phase; under appropriate conditions, proton transfer will occur to form MH^+. Ions that will serve as proton donors include t-$C_4H_9^+$, $(H_2O)_nH^+$, and $(CH_3OH)_nH^+$. It is generally convenient to employ the t-$C_4H_9^+$ ion as the proton donor, since these ions may be generated through use of a nitrogen/isobutane carrier gas mixture, or by use of the common commercial alkane solvents hexane and isooctane. This type of ionization is illustrated in a later section.

The ionization potentials of polynuclear aromatic hydrocarbons have not been determined with great exactness, but they are below that of benzene. A convenient way of generating M^+ ions is by charge transfer from benzene, using a nitrogen/benzene carrier gas mixture, or through the use of nitrogen alone. Figure 5 shows the ionization of anthracene in the presence of benzene with nitrogen carrier gas; the product is M^+.

It would be possible to generate a mixture of M^+ and MH^+ ions through use of appropriate mixtures of reagent ions. It is unlikely that this would be useful in quantitative analysis, since a single ionic species, M^+ or MH^+, would be more desirable as a reaction product. Where a confirmation of basic properties is desired, the use of appropriate proton donors provides an effective means of characterizing gas phase bases.

Benzene will form $C_{12}H_{12}^+$ ions when the concentration of benzene in the source is relatively high. Ions of this type, MM^+, have not been observed in work with anthracene, but no attempt has been made to use high concentrations of this hydrocarbon. In most gas or liquid phase analytical studies of polynuclear aromatic compounds, the concentra-

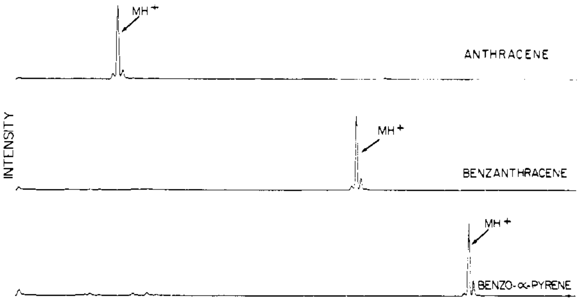

Figure 6. Ion profiles observed during elution of anthracene, benzanthracene, and benzo[*a*]pyrene

The solvent was isooctane; the ions correspond to MH^+. The LC-MS(API)-COM system was operated with a corona source

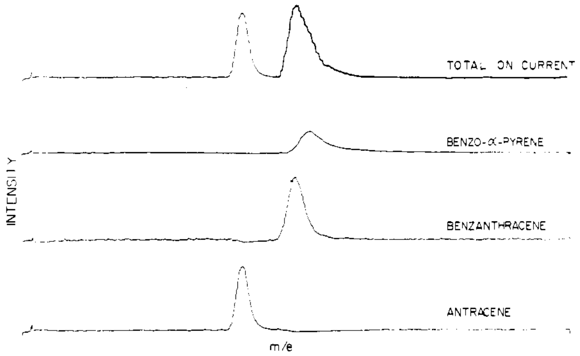

Figure 7. Comparison of total ion current chart with selective ion detection charts for separation of the hydrocarbons with the LC-MS(API)-COM system

The solvent was isooctane; each hydrocarbon was detected as MH^+

tions of the substances under study would be low and dimer ions would not be expected as reaction products.

Detection of Polynuclear Aromatic Hydrocarbons with Isooctane as a Solvent. It is possible to carry out LC separations of many organic compounds with isooctane as a solvent, and to detect the passage of the sample through the source by monitoring the total ion current. The total ion current is measured by rapidly scanning from a mass above the reactant ions to one amu above the highest mass of interest. The resultant signal is then integrated in the same manner as is usually done for chemical ionization spectra. Elution and separation can also be monitored by use of a UV detector. Ion profiles, taken during peak elution for three polynuclear aromatic hydrocarbons with isooctane as the solvent, are shown in Figure 6. Each compound was ionized by proton transfer from $C_4H_9^+$ to give MH^+ ions.

One of the difficulties encountered when UV or other relatively nonspecific detection methods are used is that peak overlap results in peak shapes that are difficult to quantify. When mass spectrometric techniques are employed, specific detection methods can be used to avoid this difficulty. An example is shown in Figure 7; the MH^+ ion response for anthracene, benzanthracene, benzo[*a*]pyrene and the total ion current traces taken during elution in isooctane are indicated. The total ion current chart shows that benzanthracene and benzo[*a*]pyrene are not separated under these conditions. The selective ion monitoring charts, however, for all three compounds show a separation. In this case, both peak area and retention times can be measured for the two compounds which are not resolved by nonspecific detection.

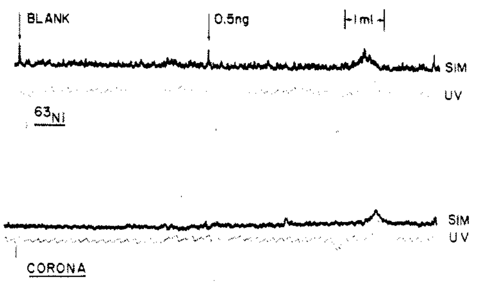

Figure 8. Comparison of records obtained with an API ^{63}Ni source, an API corona source, and the conventional Waters ultraviolet detector for the separation of anthracene with the LC-MS(API)-COM system

A 30-cm Corasil II column was employed. The limiting sensitivity of detection is about 500 pg; with gas phase injection, samples of 150 femtograms can be detected (*2*)

Lower Limits of Detection. The ion lifetimes and lower limits of detection expected for a field free high pressure ion source have been discussed previously (*2*). Under atmospheric pressure conditions, the steady state ratio of sample ion density to sample neutral molecule density is:

$$\frac{n_s}{N_s} = \frac{k_2 n}{k_1 n + k_2 N_s} \tag{3}$$

where n_s is the sample ion concentration, n is the total ion concentration, N_s is the sample molecule concentration in the source, and k_1 and k_2 are the recombination and sample ion production rate constants, respectively. If $k_2 N_s$ is much less than $k_1 n$, this reduces to

$$\frac{n_s}{N_s} = \frac{k_2}{k_1} \tag{4}$$

which is the ionization efficiency of the source. For typical values of k_2 and k_1, this efficiency is about 0.1% (*2*).

The source ionization efficiency, which determines the lower limit of detection, does not depend upon the total ion density in the source. It depends only upon the production and loss rate constants.

In a corona source, an appreciable electric field is present, and this serves to separate positive and negative charges. Thus, ion–ion and ion–electron recombination is not the main route of ion loss, as is the case for a field free high pressure source. In this instance, the major route of ion loss is to the source walls. The ions drift, under the influence of space charge and the corona field, to the walls and are neutralized. Because of the space charge and the geometry of the source, a direct calculation of ion lifetimes is not possible. However, it seemed likely that the ionization efficiency with a corona source would be slightly better than that found with a ^{63}Ni source. This was found to be true. Figure 8 shows a single ion detection chart for anthracene in isooctane solvent as the sample elutes from a liquid chromatograph, for both corona and ^{63}Ni sources. The ultraviolet detection chart is included for comparison. In this figure, the full scale count rate range for the corona source is three times that for the ^{63}Ni source. The lower limit of detection observed with the corona source is several times better than that found with the ^{63}Ni source.

The sensitivity of detection achieved with both the corona and ^{63}Ni sources in an LC-MS-COM system are comparable to that of a standard UV detector, for a highly absorbing compound. A sensitivity of detection of 0.5 ng may not seem impressive, compared to the previously demonstrated (*2*) gas phase sensitivity of detection of 0.15 pg. However, the 0.5 ng sample was eluted in approximately 0.5 g of solvent. This represents a solute to solvent mole fraction of 6×10^{-10}. This should be compared with the 1.5×10^{-13} g of solute in 2×10^{-3} g of solvent used previously, which gives, for 2,6-dimethyl-γ-pyrone in benzene, a mole fraction of 2×10^{-11} (2). The lower sensitivity of detection found with the LC-MS-COM system is due primarily to traces of contaminants in the solvent which leads to an increased noise level. As shown in Figure 8, however, the detection limit is still below one part per billion for both the corona and ^{63}Ni sources. This compares favorably with the sensitivity observed for a UV detector when a strongly absorbing compound is used.

LC-MS-COM Analytical Systems. A number of attempts have been made to design LC-MS-COM analytical systems. The most elementary approach is that of designing a mechanical carrier/vaporizer interface which will accept or sample the LC stream, remove the solvents, and convey the solute to the ionizing region of the mass spectrometer. This is essentially a qualitative approach, but stable isotope labeled compounds could be used as internal standards to achieve quantification. The major problem is that of transferring the solute from the end of the column (normally at atmospheric pressure) to the source. The mechanical design of Scott et al. (*6*) is an example of a way in which this can be done. The problem was approached in a different way by Arpino, Dawkins, and McLafferty (*7*). The LC effluent stream was introduced directly, after vaporization, into a CI source. The solute was ionized by solvent-mediated ion molecule reactions. This solution, although satisfactory in a theoretical sense, leads to considerable practical difficulties because of the introduction of relatively large amounts of solvent vapor into the ion source region. This approach differs from that of Scott et al. in that CI spectra were obtained, rather than EI spectra.

The use of API techniques provides a novel solution to the design of LC-MS-COM systems. The entire effluent stream may be vaporized and directed through the source. Since a pressure change is not required, the mechanical and physical problems of transferring the solute from the LC column to the source are not great. The ionization is solvent-mediated, but there is much choice in the way in which ionization can be effected (*3, 4*). The chief problem at this time is that of achieving a useful balance between retaining the advantages of LC separation methods and accepting the requirement for vaporization of the solute. Liquid phase separation methods have their greatest effectiveness when solutes contain polar functional groups; however, vaporization becomes difficult when too many polar groups are present. Nonpolar, volatile derivatives can be prepared (as in gas chromatography), but this usually increases the difficulty of finding appropriate LC separation conditions for complex mixtures. Additional studies will be required to determine the relative advantages of LC-MS-COM systems when compared with GC-MS-COM systems.

Future Studies. The identification and quantification of polynuclear aromatic hydrocarbons present in trace amounts in air, in smoke, and in water, is important in environmental studies. The use of an LC-MS(API)-COM system has advantages in some applications. Relatively large samples may be used because of the high capacity of LC columns, and ion-specific methods of identification and quantification may be used. In this instance, however, the sensitivity of detection for individual compounds may be too low for use except where initially large samples are processed. It is proposed to continue this study by comparing the results obtained here with those resulting from use of a GC-MS(API)-COM analytical system with nitrogen/isobutane or helium/isobutane carrier gas mixtures. The same ionic products, MH$^+$, should be formed, and subpicogram sensitivity of detection should be possible (*2*).

LITERATURE CITED

(1) E. C. Horning, M. G. Horning, D. I. Carroll, I. Dzidic, and R. N. Stillwell, *Anal. Chem.*, **45**, 936 (1973).
(2) D. I. Carroll, I. Dzidic, R. N. Stillwell, M. G. Horning, and E. C. Horning, *Anal. Chem.*, **46**, 706 (1974).
(3) E. C. Horning, D. I. Carroll, I. Dzidic, K. D. Haegele, M. G. Horning, and R. N. Stillwell, *J. Chromatogr.*, **99**, 13 (1974).
(4) E. C. Horning, D. I. Carroll, I. Dzidic, K. D. Haegele, M. G. Horning, and R. N. Stillwell, *J. Chromatogr. Sci.*, **12**, 725 (1974).
(5) P. Ausloos and S. G. Lias, "Ion-molecule Reactions", Vol. 2, J. L. Franklin, Ed., Plenum Press, New York, 1972.
(6) R. P. W. Scott, C. G. Scott, M. Munroe, and J. Hess, *J. Chromatogr.*, **99**, 395 (1974).
(7) P. J. Arpino, B. G. Dawkins, and F. W. McLafferty, *J. Chromatogr. Sci.*, **12**, 574 (1974).

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Selected Ion Monitoring for Multicomponent Analyses by Computer Control of Accelerating Voltage and Magnetic Field

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Applications of the selected ion monitoring (SIM) technique for multicomponent analysis with gas chromatograph–mass spectrometer (GC–MS) systems utilizing magnetic sector mass spectrometers have been severely limited by constraints in the mass range when obtained by means of accelerating voltage changes. An electronic interface has been developed that allows computer control of the magnetic field. When used in conjunction with computer control of the accelerating voltage, several compounds can be monitored during a single gas–liquid chromatographic run. This paper presents details of the circuit design, describes the programming concepts, and illustrates the utility of this device.

Selected ion monitoring (SIM) was first described in 1966 as a technique by which magnetic sector mass spectrometers could be used for the determination of stable isotopic abundance in peaks from a gas chromatographic inlet

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