

## Review

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### ELEMENT-SELECTIVE DETECTION FOR CHROMATOGRAPHY BY PLASMA EMISSION SPECTROMETRY

JON W. CARNAHAN, KEVIN J. MULLIGAN and JOSEPH A. CARUSO\*

*Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221 (U.S.A.)*

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#### SUMMARY

High-temperature argon and helium plasmas provide stable sources for emission spectroscopy. These plasmas have proven useful as a means of selective detection for column chromatography. This review is based on a survey of the literature from 1965, when the first communication on this topic appeared. The species for which liquid and gas chromatographic effluents are monitored include metal ions and elements not traditionally determined by atomic spectrometry such as C, H, N, P, O, S, and the halogens. Applications to a wide variety of samples are discussed.

The use of some feature of the chemical nature of the substances eluted as a label for monitoring and identifying chromatographic peaks is as old as the origin of the name "chromatography" would imply. However, it is only since the early 1960s that this aspect of separation science has been the object of intense scrutiny. Selective detection usually enhances the detection limit of the method, minimizes interferences from possible overlapping bands, and provides important qualitative information about the species of interest. A recent review [1] offers an excellent survey of this principle of detection.

Atomic spectroscopy has the potential of being one of the most selective, consistent, and versatile techniques of this kind because it exploits differences in the elemental composition of the analytes. While atomic absorption and fluorescence represent particularly convenient approaches [2–4], they are confined to the determination of a limited number of compounds and are not readily adaptable to multi-element tracking. The development of the plasma as a stable spectroscopic source capable of exciting intense emission from all of the elements of the periodic table with linearity over four or five orders of magnitude suggests that plasma emission spectrometry may well become the method of choice for element-selective chromatographic detection.

In 1965, McCormack et al. [5] introduced the effluent from a gas chromatograph into a microwave-induced plasma (m.i.p.) and monitored a variety of atomic line and diatomic band emissions to achieve selective detection. Over 50 publications have subsequently appeared. Applications of this

technique have involved the use of the inductively coupled plasma (i.c.p.), the direct current plasma (d.c.p.), and the m.i.p. for selective monitoring of effluents from gas or liquid chromatographic separations. Krull and Jordan [6] have recently published an overview of the interface between chromatography and plasma emission spectrometry.

## INSTRUMENTAL

While it is not the primary intent of this review to examine fully all the theoretical and operational aspects of the plasma, the discussion that follows may prove useful to the reader unfamiliar with the field. Excellent reviews of the inductively-coupled plasma [7–10], the microwave-induced plasma [11, 12, 12a], and the direct current plasma [13, 14] are available in the literature.

The plasma consists of a mass of predominantly ionized gas at a temperature of 4000–10000 K. This state can be maintained directly by an electrical discharge through the gas (d.c.p.) or indirectly via inductive heating of the gas by means of an electromagnetic field established using power generated at radio frequencies (i.c.p.) or microwave frequencies (m.i.p.). Analyte excitation results from electron impact and from collisions with metastable atoms of the plasma support gas (usually argon or helium) in accord with the Penning ionization scheme. The relative contributions of these two processes is uncertain at present.

A recent form of the d.c.p. is illustrated in Fig. 1. It consists of two graphite anodes and a thoriated tungsten cathode configured as an inverted "Y". The power supply is capable of providing about 15 A at 40–60 V d.c. Gas flow requirements (argon) are on the order of  $1.5 \text{ l min}^{-1}$  over each elec-

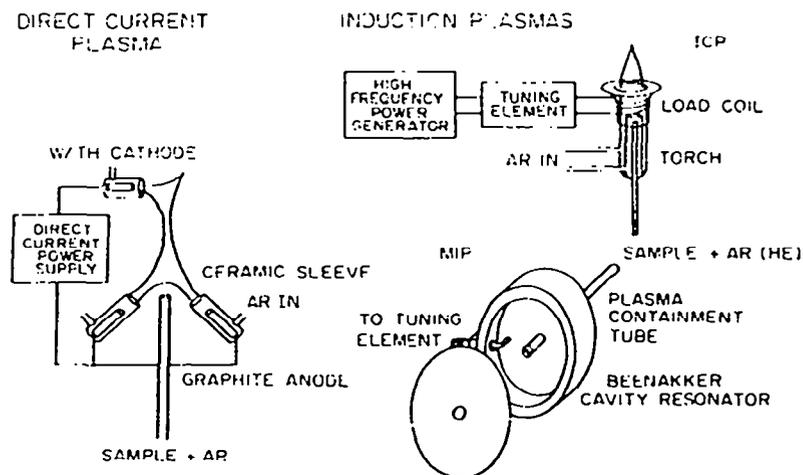


Fig. 1. Plasma sources for elemental emission spectroscopy.

trode with an additional 1 (with g.c.) to 6 (with l.c.)  $l\text{ min}^{-1}$  being necessary for sample introduction. The electrodes and electrode sleeves are subject to degradation, and may need to be replaced frequently.

Figure 1 also illustrates the design of induction plasmas. A high-frequency power generator supplies power to an induction device (an induction coil or a cavity resonator) which serves to maintain the plasma. To avoid interference with communication bands, high-frequency power generators in the United States that are commercially available for plasma work are constrained to specific frequencies such as 27.2, 912 and 2450 MHz. At the same time, these supplies are designed to provide power efficiently when the load impedance (the induction device plus the plasma) has a specific value, usually 50 ohms. This impedance is a function of frequency, the physical parameters of the induction device, and the composition of the plasma. As a result, tuning components such as stub tuners or variable capacitors are introduced in the transmission line to match the impedance of the load to that of the source. In Europe, "free running" generators are available which automatically compensate for a mismatch between the source and the load by altering the frequency of the output while maintaining the power level constant. In such cases, tuning components are unnecessary.

A block diagram of a plasma emission detector suitable for use with a gas chromatograph is presented in Fig. 2. Liquid chromatographic effluents may be routed directly into a nebulizer prior to the i.c.p. [15, 16] or the d.c.p. [17, 18]. Interfacing a gas chromatograph involves the removal of the nebulizer and the addition of supplementary plasma gas [19, 20]. These interfaces require simple fittings that are readily available, although care must be taken to minimize the dead volume. The m.i.p. is currently unsuited to normal liquid chromatography because it cannot tolerate sample introduction rates in excess of a few  $\text{mg s}^{-1}$ ; this is due to the low power levels of operation (usually less than 120 W). Only limited success has been realized by

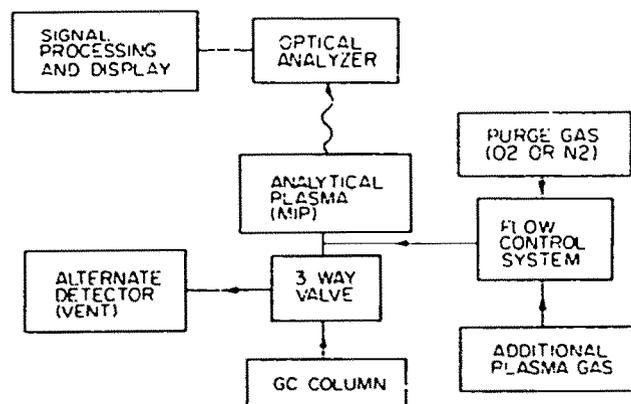


Fig. 2. Block diagram of the g.c./m.i.p. couple.

direct nebulization of aqueous aerosols [21–23]. However, the m.i.p. has enjoyed considerable use as a detector for gas chromatography (g.c.) and will be discussed below.

Emission from the plasma is focussed on the entrance slit of a suitable spectrometer. Since the plasma is a very rich and intense source, the quality of the results is significantly dependent on the quality of the spectrometer chosen.

Most publications have dealt with the use of the m.i.p. as a g.c. detector. Prior to 1976, the cavity resonators available would sustain an argon plasma at atmospheric pressure but helium plasmas could only be sustained at reduced pressure (1–10 Torr). Helium is a more desirable plasma support gas because it provides a simpler background spectrum yet produces a higher energy excitation medium. Not only is the helium plasma more robust than the argon plasma, it has improved the intensity and linearity of the emission produced by halogens and certain other elements. Two recent cavity designs [12, 23] permit a more efficient transfer of microwave power from the generator to the plasma, and will sustain the atmospheric helium plasma. A comparative study [24] has shown the  $TM_{010}$  cavity resonator of Beenakker [23, 25] to be superior to other designs. The application of this cavity to gas chromatography has only recently been illustrated [26–30]. Some improvements in design have been introduced by van Dalen et al. [31]. Because this cavity is relatively new, most g.c./m.i.p. to date has involved the use of other cavities.

#### METALS AND METALLOIDS

The i.c.p., m.i.p., and d.c.p. are well suited to the determination of metals. Detection limits, reproducibility, and linearity of response are generally comparable or superior to flame atomic absorption and emission. It is not surprising then, that plasma emission sources have shown great promise as chromatographic detectors for metals. Elemental hydrides, chelated metals, organometallics, and metal-containing proteins have all been separated by chromatography and quantified by plasma emission spectroscopy.

The feasibility of the separation and detection of metal chelates by g.c./m.i.p. has been investigated. Dagnall et al. [32] and Kawaguchi et al. [33] have shown the promise of this technique utilizing the acetylacetone and trifluoroacetylacetone (TFA) chelates of aluminum, beryllium, chromium, copper, iron, gallium, scandium, and vanadium. These authors used argon as the plasma support gas. Serravallo and Risby [34] compared the argon plasma to that of helium for chelates of chromium. Helium was found superior despite the low pressure requirement at the time of the work. Chromium yielded more intense and more numerous emission lines in the helium plasma. Application to real samples was made by Black and Sievers [35] who have determined 3 ppb chromium in blood as the 1,1,1-trifluoro-2,4-pentanedione complex. Also, copper and aluminum in zinc

were determined after extraction with TFA in chloroform from a neutralized aqua regia solution [36].

High-performance liquid chromatography (h.p.l.c.) has been used to separate copper complexed with nitriloacetate and ethylenediamine with detection by i.c.p. spectrometry [15]. Time-resolved minimum detectable concentrations were determined for twenty-four elements. Although the limits of detection were somewhat higher in the chromatographic mode than with continuous aspiration, only Pb, Na, and Mg were not within the same order of magnitude.

Copper, nickel, and cobalt diethyldithiocarbamates were separated by h.p.l.c. and monitored with a spectrometer in series with a d.c. argon plasma emission source [17, 18]. When a 5:15:80 mixture of acetonitrile:diethyl-ether:Skelly B (petroleum hydrocarbon mixture) was used, separation and quantification of the metal carbamates posed no major problems. However, when only the Skelly B hydrocarbon mixture was used as the solvent, the electrodes became coated with carbon black and the plasma was extinguished. A novel aerosol-nebulizer interface was applied to avoid this problem with a slight loss of sensitivity and reproducibility. The d.c. argon discharge plasma was also used to monitor the g.c. effluent of metal complexes of Ni, Pd, Cr, and Zn [20].

The m.i.p. spectroscopic detection of volatile elemental hydrides separated by gas chromatography [37, 38] has been investigated. Carbon dioxide and hydrochloric acid, products of the hydride generation procedure which are spectral interferents, were separated from the hydrides before elemental detection. In this way, Ge, As, Se, Sn, and Sb could be determined in nanogram amounts with a single element detection system. These eluents were also quantified simultaneously via a direct reading spectrograph after the chromatographic separation [38]. Although detection limits were somewhat higher, sub-microgram detection limits were retained. Hydrides of Ge, As, and Sb have been separated and determined utilizing a computer-controlled slew scanning monochromator [39]. A general review of hydride generation for atomic spectroscopy has appeared recently [40]. Detection limits of hydrides exceed those with solution nebulization and are comparable with m.i.p. and i.c.p. as seen in Table 1.

Several papers have appeared dealing with determination of environmentally important compounds by plasma emission spectroscopy. Work has been focussed on the methylmercury(II) species, tetraalkyllead (TAL) compounds, and methylcyclopentadienylmanganesetricarbonyl (MMT).

Mercury compounds have served as useful analytes for testing the microwave plasma. Because methylmercury compounds are simple and are relatively free of hydrocarbon emission in the ultraviolet region, the use of mercury emission (253.7 nm) makes detection by m.i.p. straightforward. Bache and Lisk [41] applied this system to methylmercury(II) chloride in fish. A linear response from 0.1 to at least 100 ng with a selectivity of 10000 to 1 compared to eicosane was obtained. Grossman et al. [42] have discussed the

TABLE 1

Comparison of detection limits (given in  $\mu\text{g ml}^{-1}$ ) for hydride-forming elements by atomic emission spectroscopy

	Inductively-coupled plasma/solution nebulization [9]	Inductively-coupled plasma/as hydrides [40]	Microwave-induced plasma/as hydrides [37]
Ge	0.15	—	0.00015
As	0.04	0.0008	0.00035
Se	0.03	0.0008	0.00125
Sn	0.3	—	0.002
Sb	0.2	0.001	0.0005
Te	0.08	0.001	—
Pb	0.008	—	—
Bi	0.05	0.0008	—

selectivity for dimethylmercury relative to many other compounds. Selectivities of  $10^3$  were typical of the m.i.p. Comparison of the m.i.p. to the electron capture detector (e.c.d.) for mercury gave results comparable to within 5% [43]. Another advantage of the m.i.p. is that its molar response is similar for all methylmercury species while the e.c.d. response varies considerably with the number of methyl groups. Talmi [44] and Talmi and Norvell [45] have described the rapid determination of organomercury compounds in aqueous samples, biological tissues, and insects, with detection limits in the picogram to sub-picogram range. Quimby et al. [27] have recently applied the  $\text{TM}_{010}$  resonance cavity to the detection of diphenylmercury with similar results.

Gasoline additives, MMT and TAL, have received considerable recent attention. Quimby et al. [27] determined microwave plasma emission detection limits of 0.25 and 0.49  $\text{pg s}^{-1}$  respectively, monitoring the metal emission lines. Five isomers of methyllead and ethyllead were determined in the atmosphere and in gasoline by this method [46]. Approximately 1% hydrogen was added to the plasma support gas to prevent the formation of lead deposits on the quartz plasma containment tube. Cyclopentadienylmanganesetricarbonyl (CMT) was used as an internal standard for the determination of MMT in gasoline by d.c.p. spectrometry [47]. Interferences were essentially absent as shown in Fig. 3A, B. The effluent was split for a detector response comparison with the flame ionization detector (f.i.d.). As is seen in Fig. 3C, plasma emission detection is far superior to the f.i.d. for the direct determination of MMT in gasoline.

Morita et al. [16] have demonstrated the use of an i.c.p. with a direct reading system as a multi-element detector for a protein molecular weight calibration kit and for vitamin  $\text{B}_{12}$ . The liquid chromatographic effluents were directed to the crossflow nebulizer of the i.c.p. Peak ratioing of the response for C, P, and Co in vitamin  $\text{B}_{12}$  ( $\text{C}_{63}\text{H}_{90}\text{CoN}_{14}\text{O}_{14}\text{P}$ ) yielded an

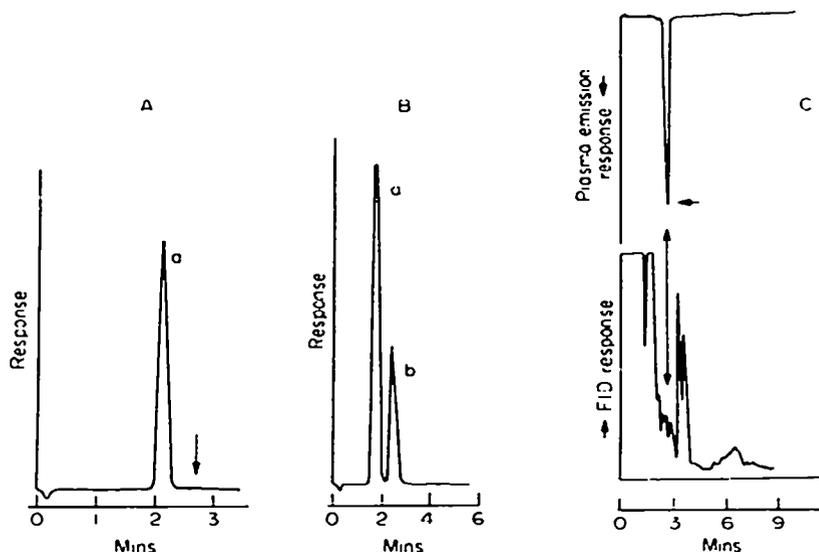


Fig. 3. Chromatograms using the d.c. argon plasma for detection with the 279.83-nm Mn line [47]. A, Leaded gasoline with 600 ng of methylcyclopentadienylmanganese tricarbonyl (a) added as internal reference. B, Cyclopentadienylmanganese tricarbonyl (a) (100 ng) and 50 ng of methylcyclopentadienylmanganese tricarbonyl (b) in 5  $\mu$ l of isooctane solution. C, Dual detector chromatogram of 5- $\mu$ l unleaded gasoline containing cyclopentadienylmanganese tricarbonyl [47]; effluent split 1:1 between f.i.d. and argon d.c.p. detectors. Reprinted with permission from ref. 47. Copyright, American Chemical Society.

atomic ratio of  $C_{64.2}P_{0.93}Co_1$ . Elemental ratios in excellent agreement with expected values were also obtained for cytochrome c. Unseparated peaks caused by ferritin and catalase can be resolved by monitoring phosphorus which is contained in the former compound.

## GASES

Radio-frequency and microwave excitation sources have found use in the determination of gases. Boos and Winefordner [48] used a radio-frequency (8 MHz) plasma to monitor gases from an exponential dilutor. Molecular emission bandheads were used to monitor CO, CO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>. Gas chromatographic separation was not utilized although its use was suggested.

Dagnall et al. [49, 50] separated atmospheric gases by g.c. using the m.i.p. as an emission source for detection. The atomic lines of carbon and sulfur could be used for CO, CO<sub>2</sub>, and SO<sub>2</sub> while N<sub>2</sub> and NO<sub>2</sub> were monitored via molecular emission bandheads. Oxygen could not be determined because it caused a negative background interference. McCormick et al. [5] noted that water could be monitored by utilizing the OH emission band.

## ORGANIC COMPOUNDS

Plasma emission spectroscopy shows great promise as a detector for organic compounds. The advantage lies in its ability to observe emission from most of the elements in these compounds. That several emission lines are generally available for each element aids in reducing interferences. By proper selection of lines, the emission of one element can usually be monitored while avoiding that of another.

This versatility of response mode is not available with other chromatographic detectors, except the mass spectrometer. While mass spectrometry is very sensitive, considerable experience is required for interpretation of the complex data produced. In its simplest form, plasma emission data analysis is straightforward. With computer control and the proper spectrometer, the data output can yield considerable information.

In many applications, an element characteristic of the compound of interest which is absent from the bulk sample is monitored. This is particularly advantageous with complex samples in which the analyte contains sulfur, silicon, antimony, arsenic, selenium, or a halogen. An excellent example of the single element concept is shown by Bostick and Talmi [51]. The g.c. effluent of a mixture of several *n*-alkanes and trimethylsilane derivatives was split between an m.i.p. and an f.i.d. The f.i.d. responded to all compounds in the sample. The m.i.p. detector responded only to the silanes. Moreover, the m.i.p. chromatogram showed a considerably smaller background from the solvent than did the f.i.d.

Feldman and Batistoni [52] have shown the advantages of monitoring more than one element using a helium glow-discharge detector. The chromatographed species included a mixture of hydrocarbons, silicon-containing compounds, and a compound containing arsenic and silicon. Results are shown in Fig. 4. Selectivity ratios of silicon (288.16 nm) and arsenic (228.81 nm) to carbon were 325:1 and 296:1, respectively.

Talmi and Bostick [53] have determined a series of arsenic acids by first converting the compounds to their corresponding arsines and using a g.c./m.i.p. system. The sensitivity ratio of equimolar amounts of monoethylarsine and dimethylarsine was 1.01:1.00, virtually independent of substituent groups. With instrumental precision at 2.1%, the major portion of the relative standard deviation of the technique was due to sample preparation. In a similar paper, arsenic and antimony were determined as the triphenyl compounds [54].

Talmi and Andern [55] used an argon g.c./m.i.p. to quantify selenium in environmental samples. Comparison was done with National Bureau of Standards certified standards and results from neutron activation. Excellent agreement was obtained as shown in Table 2. Relative standard deviations ranged from 5% for orchard leaves to 0.3% for fly ash.

With the increased emphasis in analytical chemistry on the determination of insecticides, fungicides, herbicides, etc., plasma spectroscopy promises to

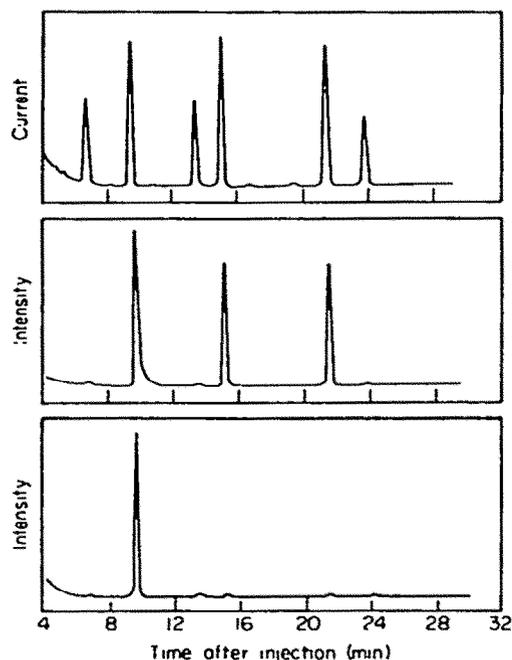


Fig. 4. Gas chromatograms of a silylated mixture of aliphatic acids, phenylarsonic acid, and hydrocarbons [52]. Top curve: flame ionization detector. Center and bottom curves: glow discharge detector with monochromator set for Si (288.1 nm) and As (228.8 nm) respectively. Reprinted with permission from ref. 52. Copyright, American Chemical Society.

TABLE 2

Determination of selenium in environmentally based samples [55]

Sample	Conc. of Se found (ppm)	Reported Se conc. (ppm)
Bovine Liver (NBS 1577)	$0.98 \pm 0.03$	$1.1 \pm 0.1^a$
Orchard Leaves (NBS 1571)	$0.083 \pm 0.004$	$0.08 \pm 0.01^a$
Coal (NBS 1632)	$2.86 \pm 0.13$	$2.9 \pm 0.3^a$
Fly Ash (NBS 1633)	$9.35 \pm 0.03$	$9.4 \pm 0.5^a$
Human hair	0.97	$0.95^b$
Air	$0.088 \pm 0.002$	$0.090^b$

<sup>a</sup>National Bureau of Standards certified value. <sup>b</sup>Value obtained by neutron activation.

play an important role. The first application of g.c./m.i.p. to complex samples [56] appeared simultaneously with the initial g.c./m.i.p. paper by McCormick et al. [5]. The work dealt with organophosphorus insecticide residues. Work has continued and pesticide constituents including H, C,

Se, N, P, O, S, Cl, Br, I, and F have been monitored by g.c. plasma spectroscopy.

Bache and Lisk [56] used an argon m.i.p. in work with 18 phosphorus-containing insecticides at the 253.6-nm phosphorus atomic line. Detection limits comparable to the electron affinity detector were obtained. Samples varied from grapes to lettuce to bees to whole chicken with excellent results. The system was modified for low pressure and was optimized for baseline-to-analyte signal ratio to extend the detection limits even further [57]. Using helium as the plasma support gas, Bache and Lisk found that eight phosphorus lines could be easily detected [58]. The 253.6-nm line was the most intense in both the argon and helium plasmas. Application of the helium plasma to complex samples (onions, carrots, and chicken flesh) was demonstrated [58, 59]. Moye [60] utilized the advantages of both support gases and found that the maximum peak height for the 253.6-nm line of parathion was obtained when 85% helium and 15% argon were used as the plasma support gas.

No scavenger gases were used in the above-mentioned work to rid the quartz plasma containment tube of carbon deposits. It is worth noting that van Dalen et al. [61] found that nitrogen is superior to oxygen for this purpose. Phosphorus oxides react with the walls of the tube to cause erratic behavior. With the use of nitrogen, this is avoided and detector response is doubled.

Bache and Lisk [58] characterized four sulfur emission lines in the m.i.p. using dimethylsulfoxide. Although the technique was very sensitive ( $5 \times 10^{-11} \text{ g s}^{-1}$ ), the selectivity to phenanthrene was relatively poor (22:1) with the low-pressure helium plasma. This system was applied to synthetic samples of seven sulfur-containing pesticides and five sulfa drugs [59]. This subsequently was applied to disyston, ronnel, and thinet extracts of natural samples. Derivatives of carbamate pesticides have also been determined by using a sulfur emission line [62]. Dagnall et al. [63] listed two other sulfur emission lines and a C=S bandhead which they used to monitor sulfur via the m.i.p.; the bandhead gave the better response for some compounds. Detection limits were extended to subnanogram levels utilizing the 247.9-nm carbon line and the 257.6-nm sulfur bandhead [64]. It is interesting to note that insertion of a platinum coil into a 1/4-wave foreshortened cavity increased atomic emission five-fold at both of these lines while a 25% decrease in emission was noted at 257.6 nm with the Evenson 1/4-wave cavity. This was attributed to incomplete molecular fragmentation in the foreshortened cavity. Braun et al. [65] have shown linearity of response over four orders of magnitude for sulfur. An argon d.c.p. has recently shown excellent selectivity and linearity of response over three decades when interfaced for g.c. [66].

Recently, Brown and Fry [67] have monitored oxygen-containing compounds by g.c./i.c.p. in the near-infrared region. An extended torch was used to avoid entrainment of atmospheric gases. A detection limit of 650 ng was obtained.

The halogens provide an interesting comparison for the argon and helium plasmas as emission detectors. Since the helium provides higher excitation energies than those of most atoms, atomic or ionic lines are more easily excited than in the argon plasma. Also, more complete molecular fragmentation is provided by the helium plasma because of the higher energy metastable states of helium compared to those of argon. An excellent discussion of these states is given by Beenakker [26].

Iodine in methyl iodide was the first halogen to be monitored via the atomic emission line [5]. This was done with an argon g.c./m.i.p. Iodinated herbicides were subsequently determined in soils and grains [68].

The argon m.i.p. detector has been utilized to provide the atomic emission lines of bromine from appropriate halogenated compounds whereas chlorine lines could not be obtained [49]. The 85% He:15% Ar m.i.p. used by Moyer [60] to obtain excellent results for phosphorus did not produce detectable atomic emission lines for chlorine. Windsor and Denton [69] used the atomic lines of F, Cl, Br, and I to detect g.c. effluents by i.c.p. spectroscopy with argon as the support gas, but detection limits in all cases were poorer than those obtained with the helium m.i.p. Fry et al. [70, 71] later extended the detection limits of F, Cl and Br by more than 100 fold, by utilizing low energy near-infrared lines. A comparison of detection limits for a variety of helium and argon plasmas is presented in Table 3.

The initial detailed study of the halogens was done by Bache and Lisk [58] in 1967 using a helium m.i.p. The work lists five atomic emission lines for both chlorine and bromine and nine for iodine. Data for over twenty compounds were given with sensitivities for the most intense elemental lines.

Halogen-containing pesticides have been successfully determined with the helium m.i.p. detector [59, 62]. Quimby et al. [28] later determined trihalomethane in drinking water. Detection limits of less than 1 ppb and selectivities greater than  $10^2$  were obtained. Mulligan et al. [30] have also utilized g.c./m.i.p. to monitor polybrominated biphenyl and related compounds with comparable results.

The most advanced g.c./m.i.p. system to date was applied by Quimby et al. [29] for the determination of aqueous chlorination products of humic sub-

TABLE 3

Detection limits (as ng) for halogens by chromatography with plasma emission spectroscopy

Halogen	Argon i.c.p.	Argon m.i.p.	Helium m.i.p.	Helium d.c.p.
I	24 <sup>a</sup>	20 <sup>d</sup>	1 <sup>e</sup>	4.5 <sup>f</sup>
Br	50 <sup>b</sup>	160 <sup>d</sup>	0.4 <sup>e</sup>	45 <sup>f</sup>
Cl	50 <sup>b</sup>	40 <sup>d</sup>	1 <sup>e</sup>	45 <sup>f</sup>
F	1000 <sup>c</sup>	—	—	4.1 <sup>f</sup>

<sup>a</sup>Taken from ref. 19. <sup>b</sup>Taken from ref. 71. <sup>c</sup>Taken from ref. 70. <sup>d</sup>Taken from ref. 49. <sup>e</sup>Taken from ref. 28. <sup>f</sup>Taken from ref. 52.

stances. A capillary g.c. column was used to separate this complex sample which was eluted into a TM<sub>010</sub> microwave cavity. The detection limit of pentachlorophenol was estimated at 40 ppt (ng l<sup>-1</sup>).

Halogens have also been monitored via a helium d.c. discharge plasma emission detector [72]. Atomic lines were utilized for F, Cl, Br, and I with detection limits in the 10<sup>-13</sup> g s<sup>-1</sup> range. Selectivities are from 40:1 to 70:1 for F, Br, and Cl in the compounds studied. Poor selectivities are obtained for iodine. Braman and Dynako [72] stated that this problem is due to extraneous line and band interferences at the 608.2 and 546.4-nm analytical wavelengths used. Had another iodine line been used, this problem might have been reduced. Feldman and Batistoni [52] modified this detector cell to prevent deposits of decomposition products.

#### ELEMENTAL RATIOS

The use of elemental ratios along with chromatographic retention times has the potential of making analyte identity a more systematic task. If the analyst had the empirical formula associated with each peak, most of the time spent analyzing the chromatogram could be utilized elsewhere. This approach is well suited for the laboratory which deals with a variety of sample types.

Several workers have used two different detectors. McLean et al. [73] and Lowings [74] have split g.c. effluent for simultaneous use of the f.i.d. and m.i.p. detectors. Hydrogen was monitored spectroscopically while carbon was monitored with the f.i.d. detector. It was found that the H/C response factors were relatively independent of molecular structure for the compounds studied. Experimental H:C ratios were generally within 1% of the theoretical value. Two monochromators were used to determine the ratios of C to S, P, Cl, I, and Br by g.c./m.i.p. [75].

While the determination of two elements in a compound provides qualitative insight, the determination of additional elements increases identification capabilities even more. This concept has been utilized by Bonnekessel and Klier [76] and Windsor and Denton [69] using m.i.p. and i.c.p., respectively. Each method required a direct reading multichannel spectrometer. A simultaneous chromatogram of 22 compounds is shown in Fig. 5. A sampling of results obtained by this method is shown in Table 4. Results are normalized to one of the atoms in each compound. It is clear that molecular structure is not an important factor in the results and that the results match well with the theoretical values.

#### CONCLUSION

In the past, plasma spectroscopy has been shown to be a versatile and useful means of chromatographic detection. It is expected that the technique will attain greater use as a chromatographic detector in the future.



Fig. 5. Multielement chromatogram of n-paraffins and chlorine and nitrogen derivatives of benzene, toluene and phenol [76].

TABLE 4

Normalized experimental elemental ratios

Molecular formula	C	H	Cl	I	N
$C_6H_6I^a$	4.06	9.00	—	1.00	—
$C_6H_5I^a$	5.92	4.69	—	1.00	—
$C_6H_5Cl^a$	3.98	8.97	1.00	—	—
$C_{15}H_{32}^b$	15.00	34.80	0.03	—	—
$C_6H_4NO_2Cl^b$	6.00	4.10	1.03	—	0.94
$C_6H_3NO_2Cl_2^b$	6.00	3.02	2.02	—	0.93
$C_6H_3NO_2Cl_3^b$	6.00	2.02	2.99	—	1.09
$C_6HN_2O_4Cl_3^b$	6.00	1.23	3.00	—	1.92

<sup>a</sup>Taken from ref. 69. <sup>b</sup>Taken from ref. 76.

Useful applications now exist and many possibilities can be considered for further research. Future work may include development of the helium i.c.p. Nitrogen has already been used as a plasma support gas [77]. Relatively inexpensive hardware is required for the d.c.p. and further investigation is in order. Reduction of the sample volume in the plasma will undoubtedly improve the detection limit of the technique. Solution nebulization into the m.i.p. should be an important objective for researchers in the coming decade. This would greatly enhance the attractiveness of this detector for multipurpose use. A particularly important and exciting area of study will be to pursue further the determination of halogens as a monitor for pesticides and other high-molecular-weight organic compounds.

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