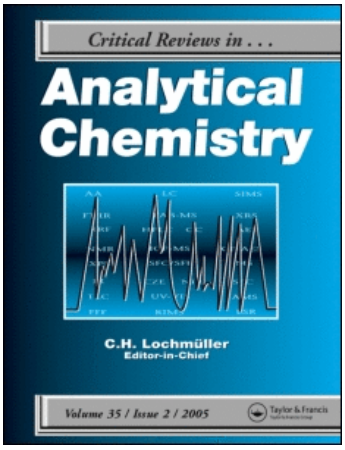

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E. R. Adlard; R. S. Juvet

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A REVIEW OF DETECTORS FOR GAS CHROMATOGRAPHY
PART II: SELECTIVE DETECTORS

Author: **E. R. Adlard**
Shell Research Ltd.
Thornton Research Centre
Chester, England

Referee: R. S. Juvet
Department of Chemistry
Arizona State University
Tempe, Arizona

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INTRODUCTION

Just as there is no completely universal detector, so there is no detector which is completely specific for one element or type of compound, and for this reason it is better to talk of "selective" rather than "specific" detectors. Again, as with the universal detectors, every selective detector has advantages and disadvantages which make it more suitable for some types of work than for others. Some selective detectors have a high specificity but a relatively low sensitivity; with others the reverse is true. A number of selective detectors depend on the performance of certain chemical operations on the sample before actual detection; e.g., nitrogen compounds may be reduced to ammonia and the amount of ammonia measured in some way, sulphur compounds may be oxidized to sulphur dioxide, and so on. These techniques usually involve a considerable dead volume

between the end of the column and the detector proper, and it is not possible to use detectors of this sort with high resolution open tubular (capillary) columns.

Selective detectors are often more susceptible to variations in operating parameters than are the two main universal detectors – the katharometer and the FID. They are usually inferior to an FID in their linearity of response and may require a considerable amount of calibration. In view of these disadvantages, it is reasonable to ask why there is such an interest in selective detectors and why nearly all new detectors developed in the last few years are selective. The answer lies largely in the achievements and failings of the high resolution open tubular column. The high resolution column has revealed the complexity of many types of sample, especially those of biological origin, but at the same time its small sample capacity makes isolation of specific components virtually impossible. When a gasoline is analyzed with a capillary column, it is not difficult to obtain 200 to 300 peaks representing compounds boiling between -42°C (propane) and 212°C (*n*-dodecane). Identification of these peaks is a relatively easy matter since it is known that all the compounds present in significant amounts (say greater than 0.01%) are hydrocarbons and many are available as pure reference materials. Large amounts of sample are generally (but not always) available so that other separation techniques such as fractional distillation, liquid chromatography, and selective GC methods may be used. With mixtures of biological origin, the reverse conditions apply: Only a small amount of sample may be available after considerable labor in extraction or isolation and it may be a mixture of many different types of organic compound with a wide boiling range. In addition to the wide boiling range, a large proportion of the sample may be high-boiling material, giving rise to problems of stationary phase "bleed," especially when using GC/MS. Finally, little information may be available as to what types of compounds may be present. An example of this sort of sample is the mixture of organic compounds present in water from various locations. Grob[1] has obtained chromatograms with several hundred peaks from such samples and has partially identified 135 of these peaks, mainly hydrocarbons, by GC/MS. Twenty-two of the compounds identified contain heteroatoms, the identification of which might have been aided or confirmed by suitable selective detectors.

The petroleum chemist may have a relatively easy task in the analysis of gasoline, but he is frequently presented with the problem of the identification and measurement of ppm quantities of heterocompounds such as mercaptans in a hydrocarbon matrix. Similarly, in the pesticide field the analyst has the problem of measuring minute quantities of pesticides in the presence of a vast excess of other organic matter. For problems of this sort, selective detectors are extremely attractive and well worth the extra care and effort required in their operation.

Many selective detectors exist and for some elements such as the halogens, nitrogen, phosphorus, and sulphur there is more than one detector available. A number of metallic elements may be measured by making strongly electron capturing derivatives or by using spectroscopic methods. Some detectors may be selective for several elements simultaneously; others may be selective for several elements sequentially. Although the performance of many of these detectors is good, there is still considerable scope for new detectors and the improvement of existing ones. It is unfortunate that with the exception of the electron capture detector and the mass spectrometer all selective detectors are element, not compound, selective.

To conclude this introduction it is worth considering whether it is better to use selective detectors with packed or with capillary columns by considering the separation of a hypothetical complex hydrocarbon mixture. Suppose this mixture has 100 hydrocarbon compounds present in equal amounts and 10 sulphur compounds spread throughout the boiling range of the sample, each at the 10 ppm level and separated from each other but not from the hydrocarbons. An inefficient packed column might separate such a mixture into 10 peaks, whereas an efficient capillary column would separate it into 100 peaks. If 1 mg of sample is used on the packed column and 10 μg on the capillary column, we can calculate the performance required from a selective detector in each case.

Packed columns – 10^{-3} g of the mixture has been separated into ten equal peaks, and therefore each peak contains 10^{-4} g of hydrocarbon. But the original mixture also contained ten sulphur compounds, each at a concentration of 10 ppm, and therefore each peak contains 10^{-8} g of a sulphur compound. Clearly the selective detector must have a selectivity of sulphur to hydrocarbon

of better than 10^4:1 since there is 10^4 times more hydrocarbon in each peak and a sensitivity for the sulphur compounds better than 10^{-8} g, i.e., 10 ng.

Capillary columns – 10^{-5} g of the mixture has been separated into 100 equal peaks, each containing 10^{-7} g of hydrocarbon, and each 10th peak will contain 10^{-10} g of sulphur compound. This will require a detector selectivity of better than 10^3:1 and a sensitivity better than 10^{-10} g, i.e., 0.1 ng.

It could be argued that these calculations are merely a long-winded way of stating the obvious, that the higher the selectivity the poorer the separation need be, to the point where a completely specific detector might require no chromatographic separation at all. It could also be argued that the figures used are quite arbitrary and if, for example, the capillary column could separate all the hydrocarbons from each other, it might equally be capable of separating all the sulphur compounds from the hydrocarbons as well as from each other. Both these arguments are valid, but the figures quoted are near enough to reality to conclude that a good detector should have a selectivity of at least 10^3:1 and a sensitivity of at least 10 ng/sec. It is also clear that there must often be a compromise between sample size and column resolution since ideally we require the sample capacity of the packed column combined with the resolution of a capillary column. Two types of column exist which go part of the way towards a compromise between the packed and the narrow bore capillary column. These are support coated open tubular (S.C.O.T.) columns and wide bore capillary columns of 0.75 mm in diameter or more. Adlard, Creaser, and Matthews[2] have shown the effectiveness of the latter type of column with sample sizes of up to 1 μl, and the carrier gas flow rates of such columns are high enough to allow them to be used with detectors of relatively large dead volume.

Finally, the author must admit to a certain degree of surprise, if not consternation, on discovering the number of papers published on selective detectors. As a consequence, the same principle of selectivity has had to be employed with respect to the original literature, and no attempt has been made to give a comprehensive list of references.

SELECTIVE DETECTORS

Optical Emission and Absorption Detectors

The first detector depending on the emission characteristics of a flame was described by Grant.[3] A photocell measured the light emission from a coal gas flame at the exit of a GC column, and it was found that aromatic compounds gave a much greater response than paraffins and naphthenes. Apart from the automatic titrimeter described by James and Martin,[4] this device was the first detector to exhibit selectivity. No further development along these lines was reported until 1963.[5a] Since then a number of optical spectroscopic detectors have been reported, and these may be classified according to the method of production of the excited species as follows:

1. Chemiluminescent band spectra produced in cool hydrogen flames, e.g., the Tracor sulphur and phosphorus detector.[6]
2. Line and band spectra produced in high temperature flames, e.g., the work of Juvet and Durbin on the detection of metallic elements such as chromium, titanium, arsenic, etc.[5b]
3. Line spectra produced by microwave excitation of the GC effluent, e.g., the detector described by McCormack, Tong, and Cook for the determination of nonmetallic elements in organic compounds.[7]
4. Line spectra produced as in (2) and then observed by atomic absorption spectroscopy, e.g., the determination of lead alkyls by Kolb et al.[8]

The first of these methods has been commercially available for a number of years and has become established to the point where most, if not all, of the major instrument manufacturers offer their own version. The reasons for the ready acceptance of this detector are described below. A microwave plasma detector is now also commercially available, but at a cost of about three times the price of a conventional GC apparatus it is unlikely to achieve the widespread popularity of the sulphur/phosphorus detector. The other two methods are not currently offered by any manufacturer as an adjunct to a GC apparatus, possibly because their value is mainly in the detection of metallic compounds, which represents a field of limited interest well catered for by existing instrumentation.

The Flame Photometric Detector (FPD)

The flame photometric detector of Brody and Chaney[5] for the determination of sulphur and phosphorus has now achieved acceptance as a device of considerable value in a wide variety of work. A diagram of Brody and Chaney's FPD published in 1966 is shown in Figure 1, and this design has proved so successful that it has been little modified since then.

The effluent from the column is mixed with oxygen/air and excess hydrogen and is burnt inside a shielded jet. When sulphur compounds emerge, a deep violet chemiluminescent cap appears on the top of the cup of the jet and is sensed by a photomultiplier after passing through a plain glass heat filter and a 394-nm interference filter. For phosphorus compounds the chemiluminescence is in the green part of the spectrum and a 526-nm filter is used.

There are now at least half a dozen different instrument manufacturers offering FPDs of their own design, and the properties of two of these – the Tracor and the United Analysts detectors – have been described in detail. There are considerable differences between the optimum gas flows reported for these detectors,[9,10] and it is plain that the best flow conditions vary greatly from one design to another. Mizany[9] claims that there is an optimum oxygen:hydrogen flow ratio for the Tracor FPD of 0.4 to 0.5, but the peak heights of a model compound quoted by him for oxygen: hydrogen ratios of 0.2 and 0.4 are 9.6 cm and 11.9 cm, respectively. Within these ratio limits, therefore, the oxygen:hydrogen ratio does not seem to be very critical. Smaller hydrocarbon signals are obtained with the Tracor FPD if only air is used with no additional oxygen, and the selectivity is improved. Figure 2 shows a chromatogram of a gasoline to which 3 ppm of dibutyl disulphide has been added obtained with an FPD using air and oxygen. Figure 3 shows a chromatogram of a C_6-C_8 olefin mixture containing an added 10 ppm of diethyl disulphide obtained with an FPD run with air and no extra oxygen. The sensitivity in the second chromatogram is about half that of the first (expressed on the basis of sulphur content), but the small hydrocarbon peaks demonstrate a considerable improvement in selectivity. Beroza and Bowmann[11] reported a sulphur (as parathion) to hydrocarbon (as aldrin) selectivity of 10^4:1: The author, working with simpler sulphur compoundst and hydrocarbons, has obtained selectivities better than 10^5:1: Rupprecht and Phillips[12] reported a selectivity, with a detector of their own design, of 10^6:1; and Perry and Carter[10] even reported complete specificity. However, these figures only apply if the sulphur compounds are completely separated by the chromatographic column from

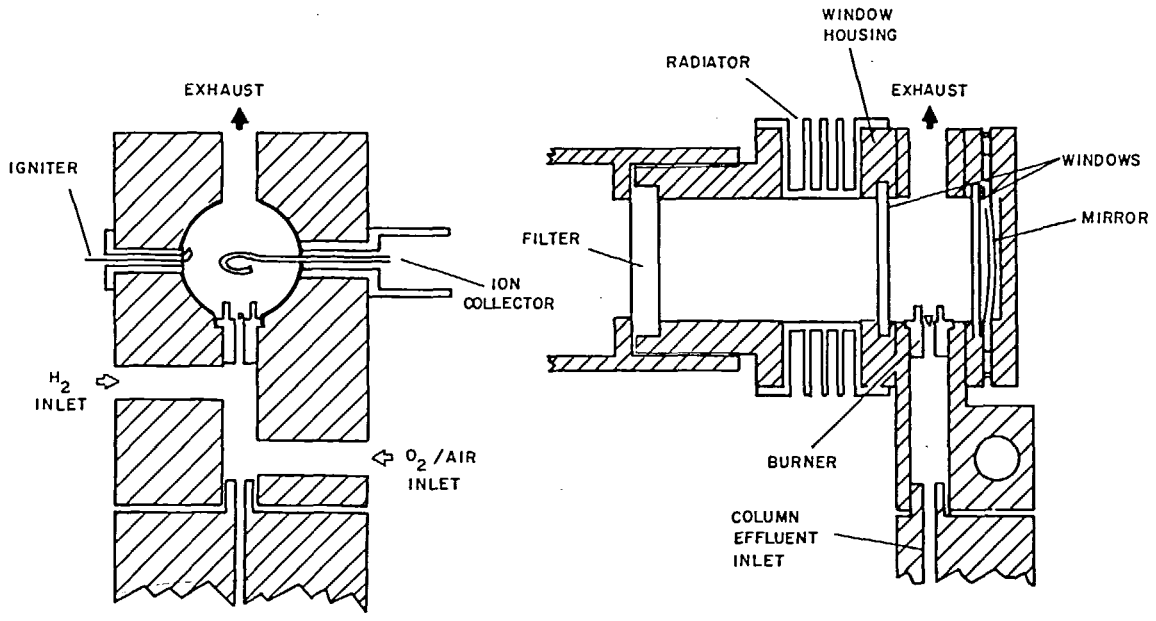

FIGURE 1. Cross-section views of the Tracor FPD. (Courtesy of Tracor Inc.)

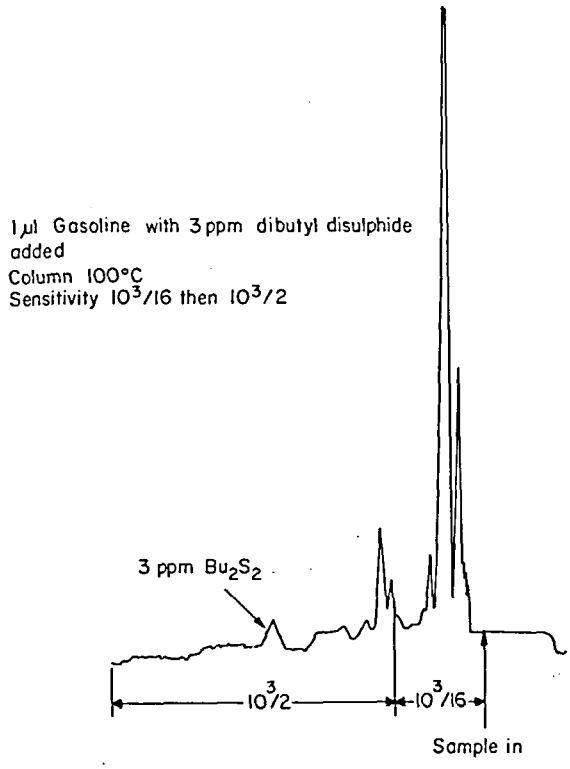

FIGURE 2. Response of Tracor FPD with air and oxygen.

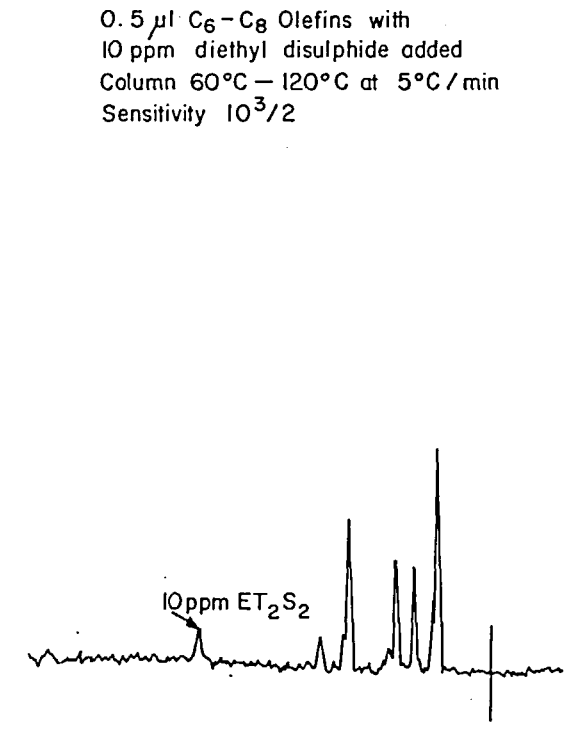

FIGURE 3. Response of Tracor FPD with air only.

other compounds. If this is not the case, quenching of the sulphur chemiluminescence can take place, resulting in a considerable decrease in response. Figure 4 shows the effect of different coemerging compounds on the FPD signal for 10 ppm of thiophen and 20 ppm of tert-butyl mercaptan. The addition of 1% of benzene reduces the thiophen signal to less than 20% of the original, and the addition of 1% of isobutanol reduces the mercaptan signal to little more than a tenth of the original signal. Rupprecht and Phillips overcame this quenching effect by combusting the sample in a primary flame to CO_2, water, and SO_2/SO_3 and then passing these gases to a secondary chemiluminescence flame since they found that CO_2 produced little quenching (Figure 5). This technique is only valid if the combustion products are mixed with the hydrogen, as they are in Rupprecht and Phillips detector, and not with the oxygen/air.

The original workers reported that the reponse for sulphur was proportional to the square of the concentration.[5] Figure 6 shows a calibration graph obtained by the author for dibutyl disulphide.

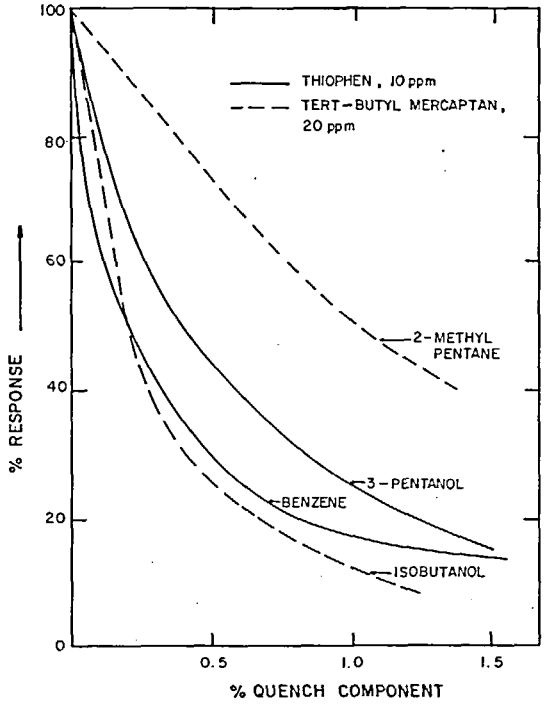

FIGURE 4. Sulphur emission quenching of the FPD due to co-eluted compounds. (From Perry, S. G. and Carter, F. W. G., *Gas Chromatography 1970*, Stock, R., Ed., The Institute of Petroleum, London, 1971. With permission.)

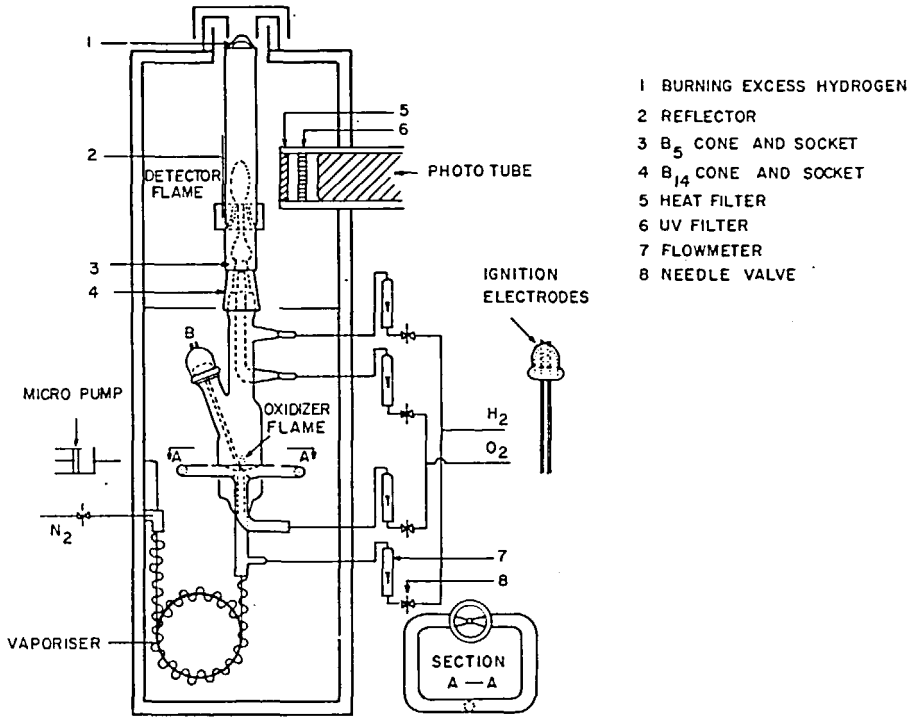

FIGURE 5. Double burner flame photometric detector. (From Rupprecht, W. E. and Phillips, T. R., *Anal. Chim. Acta*, 47, 439 (1969). With permission.)

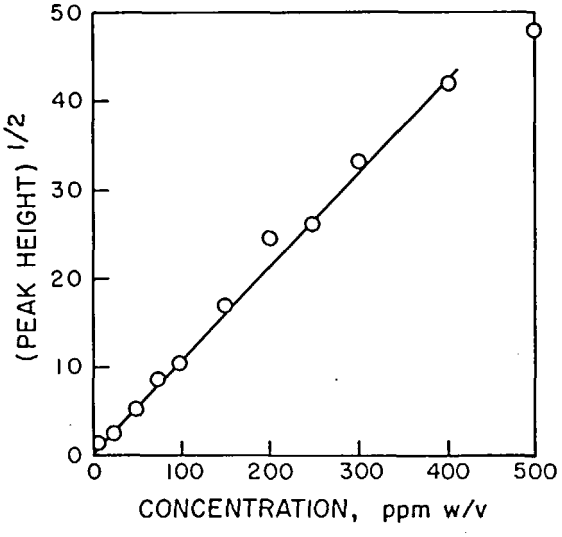

FIGURE 6. Calibration graph of dibutyl disulphide in gasoline for an FPD.

Unfortunately the work was not extended to higher concentrations, but the 500-ppm point probably shows the beginning of a departure from linearity. The departure from linearity at high concentrations has been attributed to the loss of emitted energy by self-absorption in the flame.[13]

Because of the exponential nature of the response, Crider and Slater[14] suggested that a given amount of sulphur would produce a bigger signal if it were measured as an addition to a constant background signal produced by feeding a low concentration of SO_2 into the flame continuously. In this way they were able to effect a five-to-tenfold increase in response, but obviously the linear range must be decreased if self-absorption does take place. Several papers have reported that the response depends on the environment of the sulphur atom(s) in the molecule, especially if oxygen is present.[9,15,16] For simple sulphur compounds, others have obtained a response independent of the type of compound.[12]

The fundamental investigations of operating parameters of the FPD in the sulphur mode do not seem to have been carried out to the same extent with the detector in the phosphorus mode. Much of the reported work in the phosphorus mode has been done by Bowmann and Beroza[11,15] on the analysis of phosphorus-containing pesticides. These authors obtained a phosphorus selectivity of 10^5:1 and a lower limit of detection of 0.1 ng; Brody and Chaney[5] found a linear response for phosphorus over a range of concentration of 10^4.

The quenching effects of coemerging compounds observed with the detector in the sulphur mode have not been noted for the phosphorus mode, but it has been reported[5,15] that sulphur compounds give an appreciable response when a 526-nm filter is used so that although the phosphorus:hydrocarbon selectivity is better than 10^5:1, the phosphorus:sulphur selectivity may be as low as 20:1.

The Tracor FPD is a symmetrically constructed device and can be used quite easily with two filters and two photomultipliers for the simultaneous determination of sulphur and phosphorus, and indeed it is not difficult to imagine a cross-headed combustion chamber on which four channels could be used simultaneously. In addition to the two FPD channels, an FID channel is provided by means of a ring collector situated above the flame cup. At first sight this would seem to be an attractive idea, but a study of the best conditions for the production of chemiluminescence makes it clear that these probably coincide with the worst conditions for the production of ions in the flame. The poor collecting geometry of the ring electrode and the low potential applied to it (22½ V) also contribute to the poor sensitivity of this device. In the author's opinion it is better to split the effluent from the GC column and take half to a conventional FID and half to the FPD. In view of the possible ambiguities of response possible with the FPD – signals from nonsulphur or nonphosphorus compounds, suppression of chemiluminescence by coemerging compounds, nonlinearity, and cross-interference from sulphur and phosphorus – it is highly desirable to use the FPD in conjunction with a universal detector such as the FID. One final drawback of the Tracor FPD is that the flame is extinguished by large solvent peaks and has to be reignited after the elution of the solvent. Two ways have been described for dealing with this difficulty: the use of a solvent vent valve[17] or reversal of the hydrogen and the air/oxygen lines on the detector.[18] Under optimum gas flow conditions, the sensitivity and linearity for both sulphur and phosphorus in this reverse gas flow mode was at least as good as in the normal mode and the selectivity was unaffected.

In spite of all the drawbacks of the FPD described above, it is one of the best of the selective detectors with a high sensitivity, a high selectivity, a relative insensitivity to variations in operating parameters, and a very small dead volume. The possibility of ambiguous response must always be borne in mind, however.

In conclusion, attention must be drawn to the recent work of Krost, Hodgeson, and Stevens[19] in which they report on the FPD determination of nitrogen compounds. The equipment is essentially the same as the Tracor detector, but a 690-nm filter and a red sensitive photomultiplier are used to observe chemiluminescence from the HNO species. The work was specifically aimed at the determination of NO and NO_2 in air, but two other nitrogen compounds, methylamine and ammonia, also gave a high response. Surprisingly, elemental nitrogen gave no response since the flame temperature is so low that oxides of nitrogen are not formed from the element itself. The sensitivity of the method appears to be high and the selectivity better than 10^3:1 except for sulphur dioxide, which gave a signal half that of an equivalent concentration of NO.

The Tracor FPD has also been used to detect boron compounds eluted from a GC column,[20] but chemiluminescence is not involved and the technique used is more akin to those discussed in the following section.

Flame Emission and Absorption Detectors

The flame photometric detectors described above make use of small low-energy hydrogen-rich flames to obtain chemiluminescent band spectra of molecular species. Juvet and Durbin[5a,5b] used the large oxy-hydrogen flame of a flame emission spectrometer to obtain line and band spectra of metals eluted as volatile organometallic compounds or as volatile chlorides. The light emitted by the flame was measured at selected wavelengths by means of a Beckman monochrometer and a photomultiplier. Table 1 shows the compounds examined, the wavelengths used, and the limits of detection. With the exception of rhodium and chromium, the band widths are large enough for interference filters to be used in place of a monochrometer, thereby increasing the sensitivity. Zado and Juvet[21] extended the work by the addition of a second, nonselective photomultiplier channel measuring the total emission from 355 to 625 nm in a manner somewhat analogous to that of the total ion monitor of a mass spectrometer. Very high selectivity was obtained with respect to one metal from another, but the ratio of the signals from the selective/nonselective channels was relatively small (Table 2). However, the

TABLE 1

Compounds Detected with a Flame Emission Spectrometer

Flow rates: carrier gas, 52 ml/min (S.T.P.);
O_2, 3.1 l/min; H_2, 5.7 l/min

Sample	Emission wavelength, nm	Half-intensity bandwidth, nm	Limit of detection, moles
$TiCl_4$	544.9 (band)	10.6	4×10^{-11}
$AsCl_3$	500.0 (band)	10.2	2×10^{-9}
$ZrCl_4$	564.0 (band)	8.7	2×10^{-8}
*$Rh(hfa)_3$	369.2 (doublet)	2.1	1×10^{-11}
*$Cr(hfa)_3$	425.4 (triplet)	3.7	1×10^{-10}
C_6H_6	431.5 (band)	6.5	1×10^{-7}
CO_2	431.5 (band)	6.5	7×10^{-7}

*hfa = hexafluoroacetylacetonate.

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TABLE 2

Compounds Detected with a Selective/Nonselective Flame Emission Spectrometer

Compound	Limits of detection (moles): Selective mode and wavelength[a]	Limits of detection (moles): Nonselective mode (total emission), (355–625 nm)	Emmissivity ratio = selective det. limit/ nonselective det. limit
MoF_6	3×10^{-10} (520 nm)	2×10^{-11}	15
WF_6	7×10^{-10} (520 nm)	6×10^{-11}	12
$SnCl_4$	7×10^{-9} (358 nm)	2×10^{-9}	4
*$Al(tfa)_3$	5×10^{-9} (486 nm)	2×10^{-10}	25
†$Cr(hfa)_3$	6×10^{-10} (427 nm)	2×10^{-10}	3
†$Rh(hfa)_3$	7×10^{-10} (369 nm)	3×10^{-10}	3
C_6H_6	1×10^{-6} (431 nm)	2×10^{-8}	50
CH_3COCH_3	2×10^{-6} (431 nm)	3×10^{-8}	66

[a]Half-intensity band width, 6 nm.
* tfa = tetrafluoroacetylacetonate.
† hfa = hexafluoroacetylacetonate.

Reprinted with permission from Zado, F. M. and Juvet, R. S., *Anal. Chem.*, 38, 569 (1966). Copyright by the American Chemical Society.

authors pointed out that an increase in sensitivity of 10^2 would not be difficult to obtain, and since sensitivity and selectivity are often inversely related, an improvement in selectivity could, perhaps, be obtained at the expense of sensitivity.

In a more recent investigation of this type of detector, Aue et al.[22-24] have shown that even a "small" flame little bigger than that used in the normal FID is capable of giving emission spectra at acceptable sensitivity levels for a variety of metallic elements. There seems little doubt from the work which has been published that most, if not all, the metals capable of being chromatographed could be detected by emission spectrometry. Kolb et al.[8] and, more recently, Coker[25] have demonstrated that lead alkyls eluted from a GC column

can be detected with an atomic absorption spectrometer, and Gonzalez and Ross used GC/AAS to measure trace quantities of mercury compounds in fish.[26] It is probable that the generalization made about the detection of metals by emission spectrometry can be applied equally to their detection by absorption spectrometry.

In the work described above, it was mainly the metallic elements which were detected, but the halogens can also be detected by monitoring a specific wavelength characteristic of a metal halide produced by the reaction of the column effluent with a suitable metal; e.g., the flame can be made to impinge on a copper wire to produce a green color in the presence of chloro compounds, an instrumental version of the classical Beilstein test.[27,28] It was pointed out by Gilbert[29] that a burner containing indium emitted the much more specific band spectrum of InCl with a maximum at 359.9 nm. Gutsche and Herrmann[30-32] extended Gilbert's work to obtain characteristic emission spectra at 359.9, 372.7, and 409.9 nm, respectively, for chloro, bromo, and iodo compounds emerging from a GC column. There is little overlap between the emission spectra of the indium halides so that by this choice of wavelengths a considerable degree of individual halogen selectivity can be obtained. Fluorine compounds do not produce an InF spectrum but can be observed by mixing the column effluent with calcium metal vapor and passing the mixture into an oxy-acetylene flame to measure a CaF_2 band at 529 nm.[33,34] The burner used in Gutsche and Herrmann's work was a large stacked flame type, but Bowman, Beroza, and Nickless[35] have described a much smaller indium sensitized burner which gave a halogenated organic compound:nonhalogenated compound response ratio of about 10^4:1. Since they used only one interference filter with a transmission at 360 nm, they were unable to obtain individual halogen selectivity, and it is apparent from the account of their work that the burner requires a considerable amount of routine maintenance, e.g., daily replacement of the indium-coated gauze. However, in view of the considerable success achieved by both groups of workers, it is surprising that no instrument manufacturer has (to the author's knowledge) followed up this elegant technique and produced a commercial version of the detector.

Another optical emission detector for halogens has been described in which the increase in sodium emission from a sodium-sulphate-coated wire in the presence of halogens is measured with a 589-nm interference filter and photomultiplier.[36] This device is interesting in that it would seem to be the optical analogue of the flame thermionic detector (*vide infra*).

The chief spectrometric competitor to the flame emission devices described above is the microwave plasma detector, which operates on essentially the same principle except for the method of obtaining the emitting species. In view of the simplicity and cheapness of flame sources, the author can again only wonder at the lack of interest on the instrument manufacturers' part.

Microwave Plasma Detector (MPD)

The use of a microwave plasma to excite emission from a GC effluent was first described by McCormack, Tong, and Cook in 1965.[7] These workers used argon carrier gas, and the discharge was operated at atmospheric pressure. The apparatus was developed by Bache and Lisk in the course of applying the detector to the analysis of a variety of pesticides and herbicides.[37,38] The main improvement made by Bache and Lisk was the replacement of the atmospheric pressure argon plasma by a helium plasma operated at 5- to 10-mm pressure.[39,40] Moye[41] reported that a mixture of 85% helium and 15% argon gave the best signal-to-noise ratio with the discharge operating at 25-mm pressure. This observation has not been followed up in subsequent work since helium on its own gives excellent sensitivity and avoids the complications associated with the use of a gas mixture. A helium plasma has a higher excitation energy than has argon or argon/helium and consequently produces atomic line spectra rather than band spectra. This in turn permits a high resolution monochrometer to be employed with advantage, giving a concomitant increase in selectivity. The apparatus has been further developed by McLean, Stanton, and Penketh[42a,42b] by the addition of a small amount of oxygen or nitrogen to the plasma tube to remove carbon deposits from the inner wall of the tube. Figure 7 shows a block diagram of their apparatus. The use of ultra-pure helium, a completely leak-free system, and well-conditioned GC columns operated well within their temperature limits is essential for good performance, and in these respects the apparatus has much in common with GC/MS.

The design of McLean, Stanton, and Penketh is now commercially available as a multi-element (up

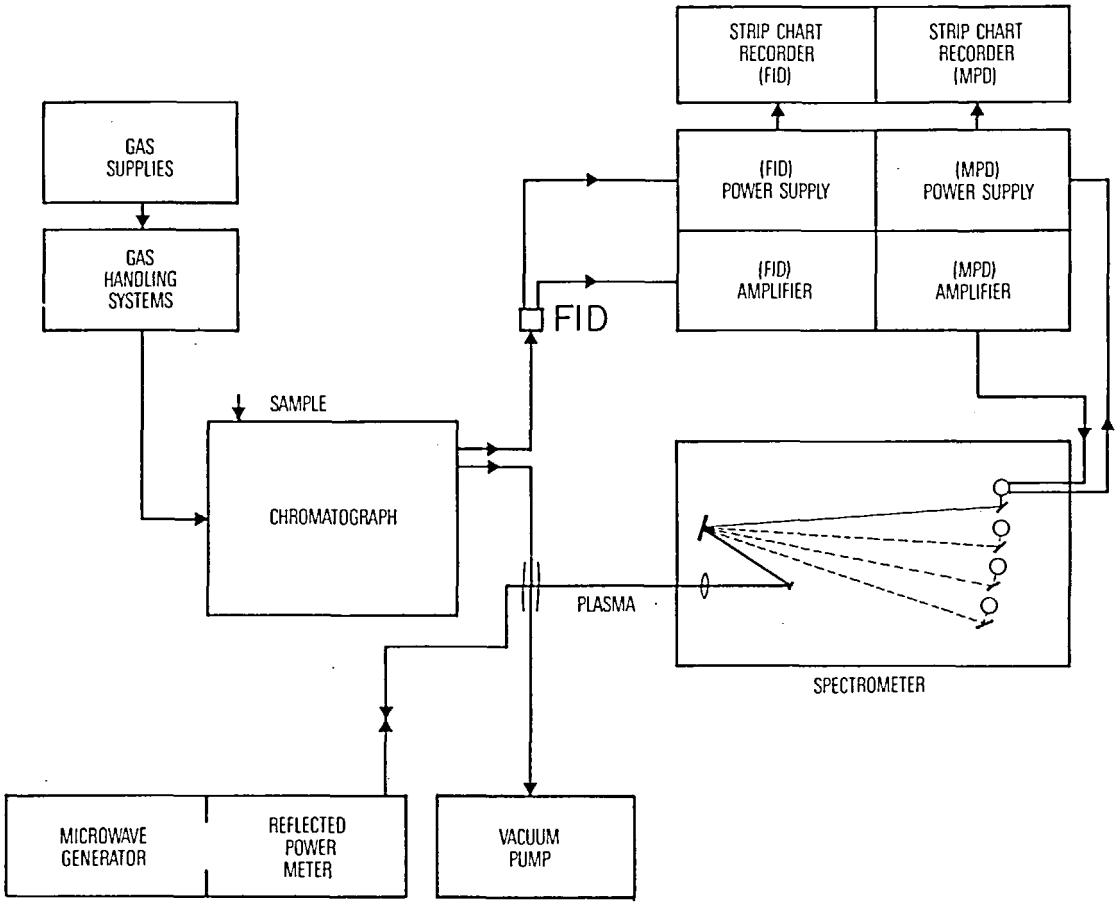

FIGURE 7. Block diagram of microwave plasma detector. (From McLean, W. R., Stanton, D. L., and Penketh, G. E., *Analyst*, 98, 432 (1973). With permission.)

to 15) detector.[43] To avoid the inconvenience of a number of pen recorders, the output may be obtained in an integral form, and the background from the carbon continuum is compensated for electrically. It is claimed that the selectivities quoted in Table 3 are improved tenfold by these modifications, giving selectivities better than 10^3:1 for most elements with detection limits of about 0.1 ng/sec. The relatively poor detection limits of oxygen and nitrogen are due to the high background signals for these elements.

In addition to its attractive properties as a selective detector, McLean, Stanton, and Penketh showed that the detector is capable of giving empirical formulas after calibration with a known compound (Table 4).

Although the papers cited above deal exclusively with nonmetallic elements, Bache and Lisk[44] have used the MPD to detect mercury compounds, and, more recently, Japanese workers have used it (with argon carrier gas at atmospheric pressure) to detect the acetylacetonates of aluminum, beryllium, chronium, copper, iron, and vanadium.[45]

The MPD is an extremely attractive device, approaching the direct coupled mass spectrometer in the amount of information it can yield. It is, however, expensive (about $22,000 for a six-element detector, excluding the GC), and on the score of information per unit cost a quadrupole mass spectrometer is almost certainly better value. In spite of the cost it is probable that this detector will achieve much more widespread use in the future, especially if the performance can be further improved, for example, by replacing the quartz plasma tube by tubes of more refractory oxides, thus permitting plasmas of higher energy.

The Flame Thermionic Detector (FTD)

The addition of a heated sodium compound to

TABLE 3

Detection Limits, Spectral Background Levels, and Selectivity for the MPD of McLean, Stanton, and Penketh[42]

Element	Detection limit*/ng s^{-1}	Total background as element/ng s^{-1}	Selectivity ratio versus *n*-heptane*
C	0.08	0.81	–
H	0.03	0.22	–
D	0.09	0.17	880
F	0.06	0.091	2,300
Cl	0.06 (0.06)	0.46	510 (44)
Br	0.091 (0.02)	0.72	1,300 (38)
I	0.05 (0.05)	0.56	400 (38)
S	0.09 (0.05)	1.1	390 (22)
P	– (0.009)	–	– (1,000)
N	2.9	113.0	–
O	3.0	98.0	–

*Figures in parentheses are values obtained by Bache and Lisk[40] for detection limits and selectivity ratio versus phenanthrene.

From McLean, W. R., Stanton, D. L., and Penketh, G. E., *Analyst*, 98, 432 (1973). With permission.

TABLE 4
Hydrogen to Carbon Atomic Ratios Found in Hydrocarbons Using an MPD

	H to C ratio found	Theoretical H to C ratio
Cyclopentane	1.990	2.000
Cyclohexane	2.020	2.000
Cyclo-octane	2.023	2.000
Methylcyclohexane	2.015	2.000
Dimethylcyclohexane	2.012	2.000
Trimethylcyclohexane	2.019	2.000
Isopropylcyclohexane	2.008	2.000
Cyclohexene	1.652	1.667
Pent-1-ene	1.997	2.000
Hex-1-ene	2.052	2.000
Hept-3-ene	2.047	2.000
Oct-1-ene	2.027	2.000
Dec-1-ene	2.041	2.000
n-Hexane	2.347	2.333
n-Heptane	2.335	2.286
n-Octane	2.300	2.250
n-Nonane	2.266	2.222
n-Decane	2.249	2.200
n-Undecane	2.251	2.182
Benzene	0.982	1.000
Toluene	1.142	1.143
Ethylbenzene (reference standard)	5/4	5/4
o-Xylene	1.253	1.250

From McLean, W. R., Stanton, D. L., and Penketh, G. E., *Analyst*, 98, 432 (1973). With permission.

the flame of an FID to obtain an enhanced response for compounds containing phosphorus or halogens was first described by Karmen and Giuffrida in 1964,[46] although devices almost certainly operating by similar mechanisms were reported by Cremer, Kraus, and Bechtold in 1961[47] and by Goulden, Goodwin, and Davies in 1963.[48] The detector of Karmen and Giuffrida gave a considerable signal for compounds not containing halogens or phosphorus so that the selectivity was poor, and Karmen therefore developed a double, "stacked" flame detector in which the upper flame responded only to halogens and phosphorus in the combustion products from the first flame; this permitted selectivities of better than 10^5:1 to be achieved.[49,50] Another version of a stacked FTD was published by Abel, Lanneau, and Stevens[51] in which the support carrying a sodium salt was heated electrically rather than by the lower flame as in Karmen's design. Later work demonstrated that a selective response could also be obtained for nitrogen compounds, especially if caesium or rubidium salts were used.[52,53]

By the late 1960s several of the major GC manufacturers offered flame thermionic detectors in which the alkali metal salt was either a pellet positioned above the flame or formed the tip of the flame jet itself. In spite of its commercial availability, the detector seems to have received extensive use only in the pesticide field, and there are numerous papers on the determination of herbicides and pesticides containing phosphorus or halogens, e.g., References 54 to 59, and a few on the determination of nitrogen-containing drugs, e.g., Reference 60. The main reason for this limited acceptance is probably the extreme susceptibility of the FTD to small variations in the operating parameters,[61,62] especially those affecting the temperature of the alkali metal salt, such as the hydrogen, air, and carrier gas flow rates, the distance between the flame and the alkali salt pellet, and the temperature of the body of the detector. One manufacturer specifies a hydrogen flow rate of 40 ± 0.07 ml/min and another specifies 16 ± 0.01 ml/min. These requirements would seem to the author to be extremely difficult to achieve.

A new design of FTD has been described recently by Kolb and Bischoff[63] in which the alkali metal source is an electrically heated rubidium glass bead. The detector is operated with a very small (1 to 3 ml/min) hydrogen flow rate to detect both nitrogen and phosphorus compounds or with a normal hydrogen flow rate for an FID (≈ 30 ml/min) in which case only phosphorus compounds are measured. The limits of detection for nitrogen and phosphorus are claimed to be 1.2×10^{-13} and 0.5×10^{-13} g/sec, respectively, which brings this detector within the sensitivity range of the electron capture detector. The linearity in both modes is 10^5, and the nitrogen:hydrocarbon, phosphorus:hydrocarbon selectivities are 5×10^3:1 and 10^5:1. The life of the rubidium glass bead is more than 6 months of continuous operation. From the results presented by Kolb and Bischoff, it would seem that this detector offers a considerably higher order of stability than previous designs.

There are many papers on the mechanism or mechanisms of the FTD, and since these have been extensively reviewed by Brazhnikov, Gur'ev, Sakodynsky[64] and by Sevčik,[65] there seems little point in repetition. According to the latter author, the signal obtained from the detector represents the sum of several processes such as ionization of the alkali metal, electron capture, and the formation of short-lived radicals in the flame.

The main advantage of the FTD for the detection of phosphorus and nitrogen compounds is that, like the FID and FPD, it has a high sensitivity and a low dead volume, making it very suitable for use with open tubular columns. (It must be pointed out, however, that most, if not all, the work done with this detector has been carried out with packed columns.) The main disadvantage to date has been the general instability of the detector and its extreme susceptibility to small changes in operating conditions. It is probable that it will receive wider use if the latest designs prove better in these respects.

Coulometric and Conductometric Detectors

These devices have been linked together since they possess a common feature which is probably the greatest disadvantage of both. With these detectors it is necessary to oxidize or reduce the organic compounds emerging from the GC column to simple inorganic gases such as SO_2, H_2S, HCl, and NH_3.

The Dohrmann microcoulometer is made to the design of Coulson and Cavanagh;[66] although there are other so-called microcoulometers on the market, the Dohrmann equipment has a monopoly

as far as GC is concerned. The microcoulometer cell has four electrodes – two for generating, one for sensing, and one as a reference electrode. A bias is applied so that under equilibrium conditions a small concentration of a chemically active ion is present in the electrolyte in the cell, e.g., Ag^+, H^+, and I_3^-. When a reactive species enters the cell, the ion concentration falls and this fall is sensed by the measuring and reference electrodes. The resulting signal is fed via an amplifier to the generating electrodes, which pass a current through the electrolyte until the original equilibrium ion concentration is restored. Three types of cell are available, the "silver" cell, the "iodine" cell, and the "hydrogen" cell, called after the reactive ion species generated in each case. The silver cell can be used at the exit of GC column to measure H_2S and mercaptans,[67] but other sulphur compounds and halogen compounds have to be reduced with hydrogen over a suitable catalyst to H_2S or a halogen acid. With the iodine cell, sulphur compounds are oxidized to SO_2/SO_3 with oxygen in a combustion tube heated to 750°C before entering the cell. The hydrogen cell can measure lower amines directly, but other nitrogen compounds have to be reduced to NH_3 before detection with a reduction furnace similar to that used with the silver cell.

The microcoulometer gives an absolute response, has a sensitivity in the nanogram range, and has a very high selectivity ($\approx 10^6$:1). However, the oxidation/reduction furnaces have large dead volumes and their quantitative efficiency is often variable. It has been found possible to operate the conductometric detector with a smaller volume reduction furnace and 0.75 mm bore capillary columns, but this approach is unlikely to be successful with the microcoulometer since the cell and its associated electronics have a relatively long response time of about 20 sec. The microcoulometer is, therefore, best suited for use with packed columns and relatively simple mixtures, e.g., Reference 67, although more complex mixtures have been analyzed.[68] Furthermore, considerable experience is needed to achieve good and consistent results with the microcoulometer. Because of these drawbacks and the availability of other detectors, it is unlikely that the current design of microcoulometer will continue to be used as a GC detector. It might survive, however, if a smaller volume cell such as that described by Sevčik[69] is used in conjunction with small oxidation/reduction furnaces.

In the Coulson conductometric detector (CCD),[70] the column effluent is oxidized or reduced as with the microcoulometer, but the resulting inorganic gases are passed into a circulating water system and the electrical conductivity of the water is monitored by means of a simple D.C. Wheatstone bridge. After being measured, the inorganic compounds are removed by passing the circulating water through a column of mixed acid/base ion exchange resins. In this way a differential record is obtained instead of an integral one which would otherwise be produced. Figures 8, 9, and 10 show various aspects of the construction of the CCD. Selectivity can be improved by the use of suitable chemical absorbers at the exit of the oxidation/reduction furnace. For example, when using a reduction furnace to change nitrogen compounds to ammonia, an absorber of strontium hydroxide has been found effective in removing the reduction products of sulphur, chlorine, and phosphorus compounds. Although sulphur and chlorine compounds are claimed to be detectable by oxidation,[70] the author has found the apparatus virtually unusable in the oxidative mode owing to the large response produced by CO_2; others have also reported large signals for CO_2 in the oxidative mode.[71] Lawrence studied the effect of hydrogen and water flow rates on the response of the conductometric detector,[72] and Dolan and Hall reported the effect of cell voltage on sensitivity.[73] With a cell of their own design, Jones and Nickless showed that dilute electrolytes in place of water could give selectivity without recourse to gas scrubbers.[74] Adlard and Matthews obtained a nitrogen:hydrocarbon selectivity of about 10^6:1 and were able to detect readily 0.5 ng of nitrogen in nitrobenzene.[61] Figure 11 shows a calibration graph for various nitrogen compounds indicating that, as expected, different types of nitrogen compounds give an equivalent response if the reduction stage is quantitative. The linear range shown is only slightly more than 10^2 but is probably considerably better than this.

Recently Hall[71] has described a completely new design of conductivity detector with a sensitivity better than 0.1 ng for sulphur, chlorine, and nitrogen, a linear range of 10^5, and a selectivity of 10^6:1. The cell is of a compact concentric design, and ethanol is used as the electrolyte in conjunction with an A.C. bridge.

In spite of its good performance and relatively low cost, the conductivity detector has not been

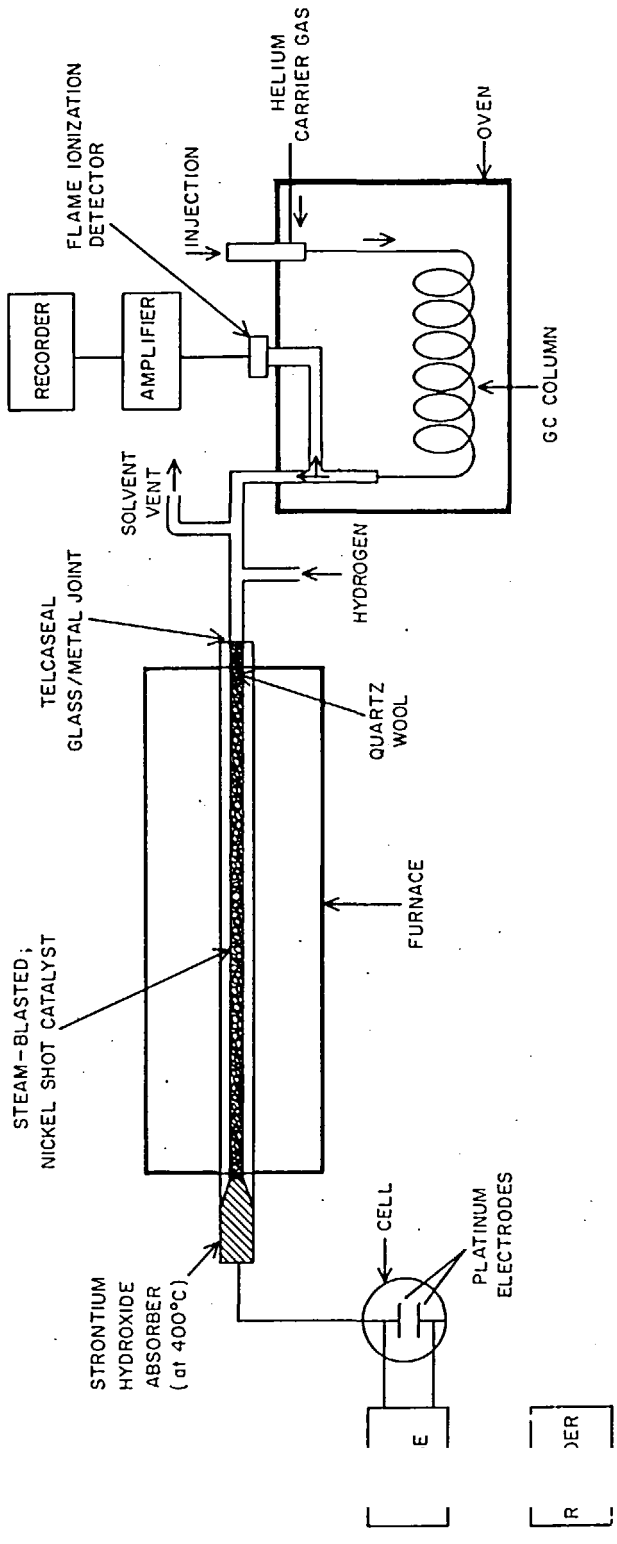

FIG. 8. Diagram of a complete system for the Coulson conductometric detector. (From Adlard, E. R. and Matthews, P. H. D., *Recent Analytical Developments in the Petroleum Industry*, Hodges, D. R., Ed., Applied Science Publishers, 1974. With permission.)

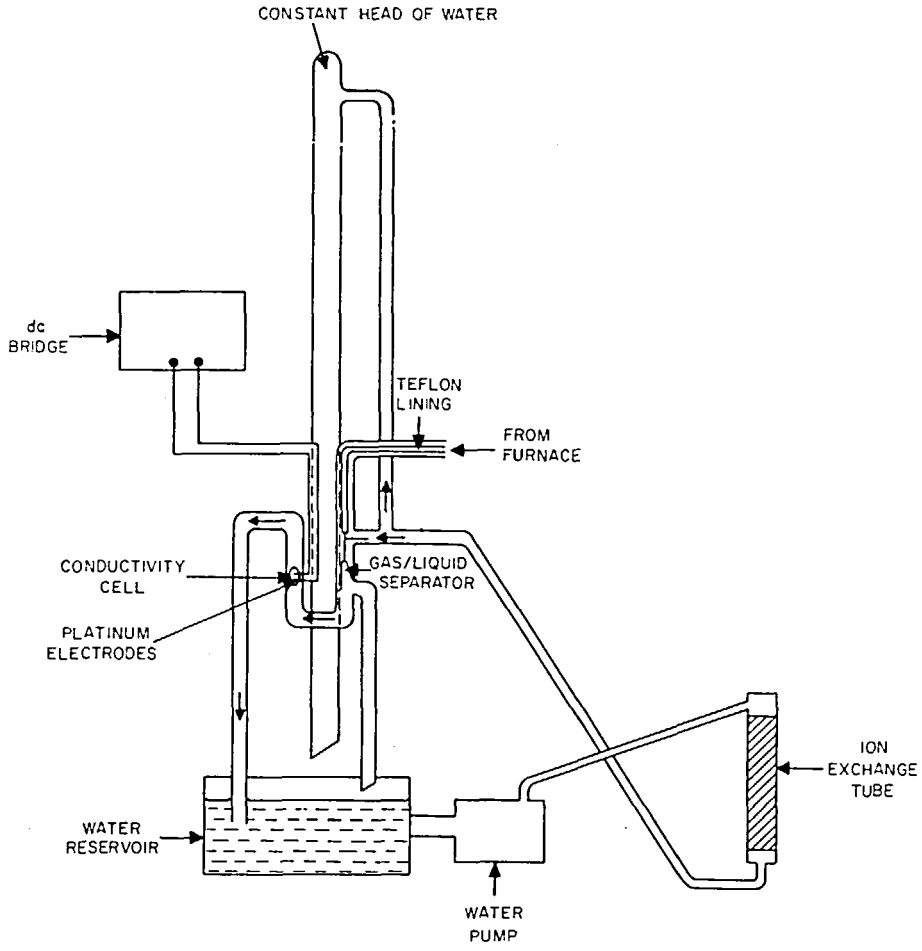

FIGURE 9. Schematic diagram of the Coulson conductometric detector. (From Adlard, E. R. and Matthews, P. H. D., *Recent Analytical Developments in the Petroleum Industry*, Hodges, D. R., Ed., Applied Science Publishers, 1974. With permission.)

used a great deal and then mainly for the analysis of herbicides,[72] pesticides,[73-75] and nitrosamines.[62,76] It has also been used to measure small amounts of nitrogen-containing additives in synthetic aviation turbine oils.[61] However, it is probable that the range of samples analyzed will increase considerably in the next few years, and it will be interesting to see whether the conductivity or flame thermionic detector becomes the more popular and more generally accepted, especially for the determination of nitrogen compounds.

The Electron Capture Detector (ECD)

The development of the ECD presents an interesting and perhaps unique example of continuous development over a period of more than 20 years. In 1951 D. J. Pompeo and J. W. Otvos constructed a β-ray ionization cross-section detector at Shell Development Company's laboratory in Emeryville (Calif.) for monitoring changes in the composition of liquid plant streams. The detector was later adapted for GC by Boer[77] at the Koninklijke Shell Laboratory in Amsterdam and by Deal et al.[78] at Emeryville. This detector possessed little advantage over thermal conductivity cells and had the considerable disadvantage of a ^{90}Sr radioactive source. It is now of historic interest only, but from it Lovelock developed the β-ray "argon" detector in 1958.[79] The construction is almost identical to that of the cross-section detector, the two significant differences being the use of argon and operation with up to 1,000 V across the cell electrodes. Under these conditions, the following ionization mechanisms can take place:

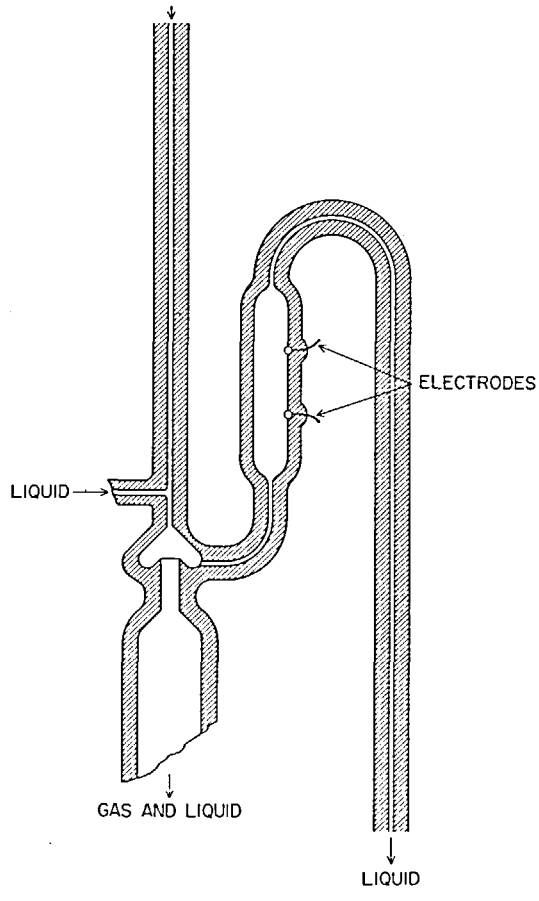

FIGURE 10. Construction of conductivity detector cell. (From Coulson, D. M., *J. Gas Chromatogr.*, 3, 134 (1965). With permission of the publisher.)

$$Ar + \text{"radiation"} \longrightarrow Ar^+ + e^- \quad (1)$$

$$Ar + \text{"radiation"} \longrightarrow Ar^* \quad (2)$$

The radiation in Equation 2 may be the primary electrons produced by the radioactive source or the secondary electrons emitted when some of the argon atoms are ionized by the mechanism of Equation 1. Ar* is a metastable, excited atom of argon which is not ionized but which possesses enough energy (11.7 eV) to ionize most organic molecules:

$$M + Ar^* \longrightarrow M^+ + e^- + Ar \quad (3)$$

The mechanisms of Equations 2 and 3 are both efficient processes; each primary electron from the radioactive source can give up to 10^4 organic ions.[80]

After the β-ray argon detector had been in use for some time, it was found that an anomalous response was sometimes obtained, especially with highly halogenated compounds such as carbon tetrachloride. Lovelock[81] pointed out that several competing ionization processes could take place and that the anomalous results with halogenated compounds were due to their ability to capture electrons to form large negatively charged molecular ions. These large slow-moving negative ions lose their charge much more quickly than do free electrons so that when molecules with a high electron affinity enter the detector the standing current is considerably reduced.

There are two general designs of ECD: the plane parallel cell and the concentric cell.[82] Examples are shown in Figures 12 and 13. There is a tendency towards the concentric design nowadays since it is easier to make a small, low dead volume cell in this form. The commonly used radioactive sources are tritium adsorbed on titanium or ^{63}Ni. Tritium has the advantage that a source with a high specific activity can be used, giving a large standing current and a high sensitivity, but it has the disadvantage that the energy of the electrons emitted from tritium is so low that the source is extremely susceptible to contamination. This is exacerbated by a maximum working temperature of 225°C. ^{63}Ni is a higher energy source (0.067 MeV max. compared with 0.018 MeV max. for tritium) and can be used up to 400°C. It is therefore much less susceptible to contamination than tritium but is only available at very much lower specific activities. A ^{63}Ni cell is therefore not as sensitive as a tritium cell at its best but is, in general, more reliable and consistent in its performance. Recently a scandium based tritium source has become available with a maximum working temperature of 325°C.[83] Argon with 5 to 10% V methane is the preferred carrier gas for the ECD since this mixture ensures that the free electrons in the cell are in thermal equilibrium. The electrodes are pulsed with pulses of (typically) 50-V amplitude and 0.5-μsec half-width at 100-μsec intervals. This mode of operation is more reliable than one employing a constant potential between the electrodes and is analogous to a fractional distillation column under total reflux for 99.5 sec followed by removal of liquid for 0.5 sec, ensuring the minimum departure from equilibrium conditions.

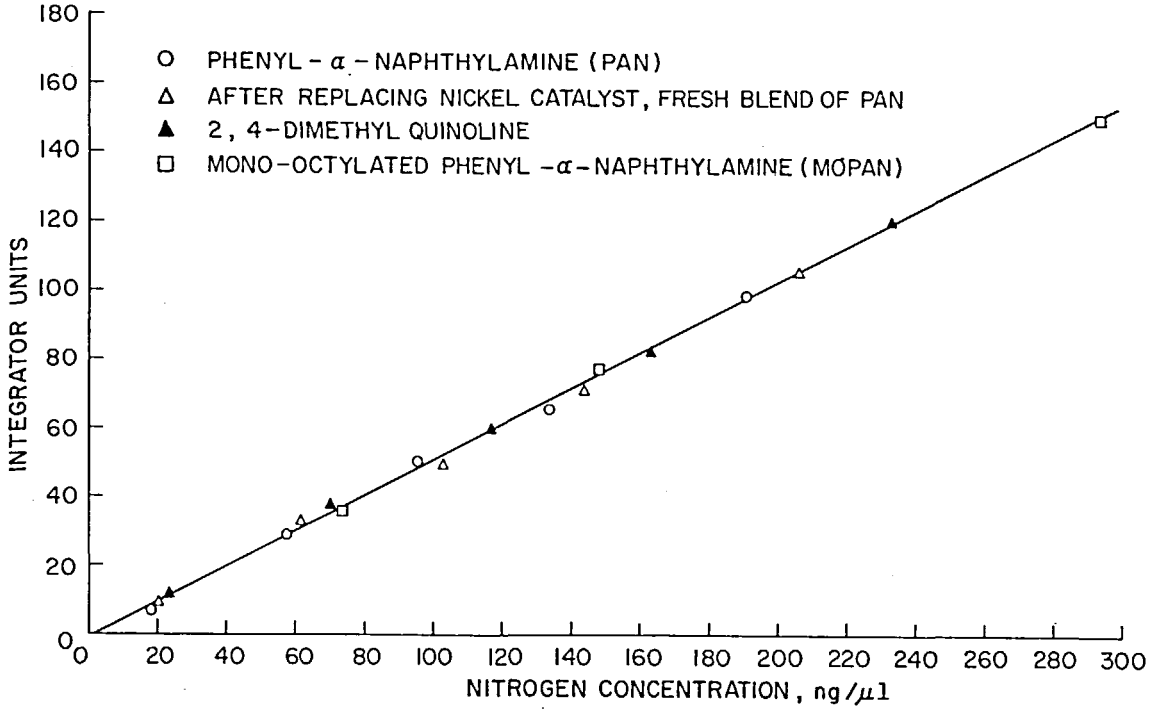

FIGURE 11. Response of Coulson conductometric detector for various nitrogen compounds. (From Adlard, E. R. and Matthews, P. H. D., *Recent Analytical Developments in the Petroleum Industry*, Hodges, D. R., Ed., Applied Science Publishers, 1974. With permission.)

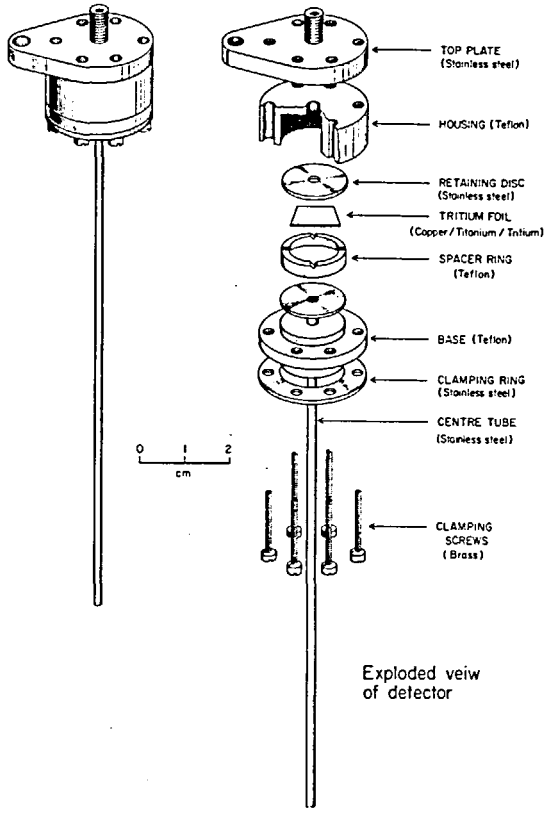

FIGURE 12. Plane parallel ECD.

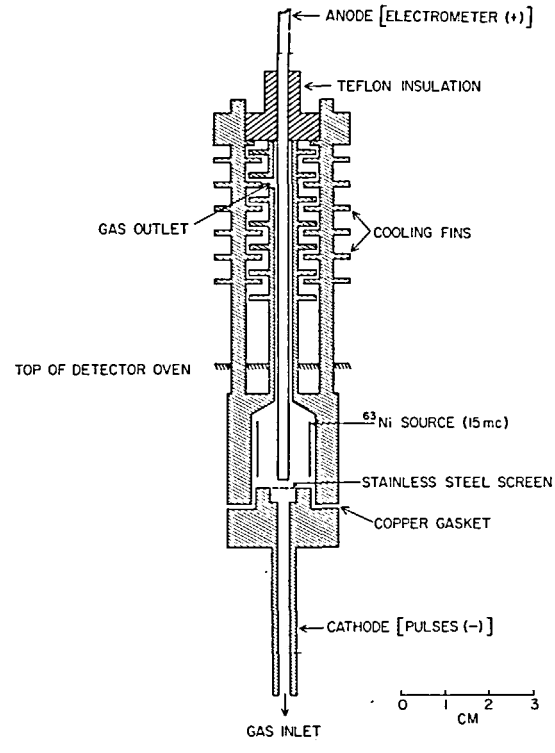

FIGURE 13. Concentric design ECD. (Reprinted with permission from Simmonds, P. G., Fenimore, D. C., Pettitt, B. C., Lovelock, J. E., and Zlatkis, A., *Anal. Chem.*, 39, 1428 (1967). Copyright by the American Chemical Society.)

The ECD is unique among GC detectors in that it measures a *decrease* in standing current. This means that the cell can become saturated if a high concentration of an electron capturing species is present and also that the response is related to the size of the standing current. Lovelock[81] suggested that the response of the detector followed a Beers Law relationship –

$$I = I_o e^{-kc} \quad (4)$$

where

- I_o is the standing current with no electron-capturing species present;
- I is the current when the concentration of electron-capturing species is c;
- k is a constant for the cell and a particular molecular species.

If c is small, then

$$I_o - I \triangleq kc \quad (5)$$

Equation 4 can be rewritten as

$$\log\left(1 - \frac{I_o - I}{I_o}\right) = kc \quad (6)$$

Later, however, Wentworth, Chen, and Lovelock[84] proposed the following relationship:

$$\frac{I_o - I}{I} = kc \quad (7)$$

Table 5 is a set of data obtained by the author for blends of $(CF_2\ Br)_2$ in *n*-heptane, and Figure 14 shows these data plotted in the forms given in Equations 5, 6, and 7. As expected, Equation 5 only gives a linear response over a concentration range of 10^2, corresponding to a reduction in standing current of about 20%. Equation 6 gives a linear response of 5×10^2 and a working range with suitable calibration of 10^3. Equation 7 gives a linear response for higher concentrations, but the results are nonlinear at low concentrations. A linear range of 10^4 has been claimed for this last method of interpretation, and an analogue device for calculating the results has been described.[85] However, the most recent development is the introduction of the variable frequency pulsed ECD.[86] In this mode of operation the cell current is kept constant as an electron-capturing species enters the cell by varying the frequency of the pulses applied to the electrodes, and the variation in frequency becomes the measure of the concentration of a compound in the detector. A linear response of better than 10^4 is claimed for this method of operating the ECD, which also has the advantage that the variable frequency output is ideally suited for electronic integration.

TABLE 5
Response of ECD to $(CF_2\ Br)_2$

Conc $\times 10^{-8}$ w/v	$I_o - I$ amps $\times 10^{-9}$	$\log\left(1 - \frac{I_o - I}{I_o}\right)$	$\frac{I_o - I}{I}$
5.2	0.09	0.005	0.011
10.4	0.18	0.010	0.022
26.1	0.45	0.025	0.058
52.2	0.86	0.048	0.117
78.3	1.31	0.076	0.190
104	1.72	0.103	0.265
157	2.26	0.145	0.381
209	2.94	0.194	0.559
261	3.57	0.259	0.771
313	4.17	0.317	1.035
418	4.83	0.407	1.433
522	5.40	0.489	1.929
783	6.21	0.661	3.121

Standing current 8.20×10^{-9} A.

Calibration of the ECD is essential, not only because of the limited linear response of the detector in its simpler forms of operation but also because of the enormous variations in electron affinity (and hence sensitivity) between different compounds. There seems to be no simple method for the accurate prediction of response, but a few general guidelines exist. The sensitivity for halogenated compounds increases in the order $F < Cl < Br < I$, and the addition of more than one halogen atom to a molecule causes a disproportionate increase in response which eventually levels out to a plateau for polysubstituted compounds. This is illustrated in a graphical form in Figure 15; although numbers have been put on the figure, it must be emphasized that they are at best only semiquantitative and are not intended to give accurate values. Tables 6 and 7[87] also give a guide to the sensitivity of various classes of compounds, although once more the figures are only intended as a rough guide and variations in sensitivity of 10^2 or more can be obtained for apparently minor variation in composition. For

TABLE 6

The Electron Absorption Coefficients of Various Compounds and of Classes of Compound for Thermal Electrons

Electron absorption coefficient[a]	Compounds and classes	Electrophores
0.01	Aliphatic saturated, ethenoid, ethinoid and diene hydrocarbons, benzene, and cyclopentadiene.	None
0.01–0.1	Aliphatic ethers and esters, and naphthalene.	None
0.1–1.0	Aliphatic alcohols, ketones, aldehydes, amines, nitriles, monofluoro and chloro compounds.	· OH · NH_2 · CO · · CN Halogens
1.0–10	Enols, oxalate esters, stilbene, azobenzene, acetophenone, dichloro, hexafluoro and monobromo compounds.	· CH:C · OH · CO · CO · Halogens
10–100	Anthracene, anhydrides, benzaldehyde, trichloro compounds, acyl chlorides.	CO · O · CO · Phenyl · CO · Halogens
100–1,000	Azulene, cyclooctatretrene, cinnamaldehyde, benzophenone, monoiodo, dibromo, tri, and tetrachloro compounds, mononitro compounds.	Halogens NO_2 Phenyl · CH:CH · CO ·
1,000–10^4	Quinones, 1,2-diketones, fumarate esters, pyruvate esters, diiodo, tribromo, polychloro, and polyfluoro compounds, dinitro compounds	· CO · CO · · CO · CH:CH · CO · Quinone structure Halogens NO_2

[a]Values are relative to the absorption coefficient of chlorobenzene, which is arbitrarily taken to be unity.

From Lovelock, J. E. and Gregory, N. L., *Gas Chromatography*, Brenner, N., Callen, J. E., and Weiss, M. D., Eds., Academic Press, New York, 1962. With permission.

example, on a relative basis, the sensitivity of the trifluoroacetate of testosterone is 0.012 and that of the chlorodifluoroacetate is 1.67.[88] Similarly one might expect the ECD to have a higher sensitivity for 1,2-dibromoethane than for 1,2-dichloroethane but not perhaps by a factor greater than 10^3 found experimentally. Another factor affecting the response of the detector to different compounds is its temperature since the mechanism whereby a · molecule captures an electron may be different at different temperatures.[84,87-93] For this reason the comparison of response between different compounds should be made at the same stated temperature. The subject of the relationship between molecular structure and response has been reviewed by Pellizzari.[94] It has been shown that under favorable experimental conditions compounds of high electron affinity may be completely ionized and the detector response is coulometric.[95] In spite of this, it is likely that calibration of the ECD will remain essential for analysis.

The applications of the ECD to analysis are so numerous that it would be pointless to give references to a few of them and impossible to try to give a comprehensive list. First and foremost the detector has been used in the pesticide field where many compounds such as dieldrin, aldrin,

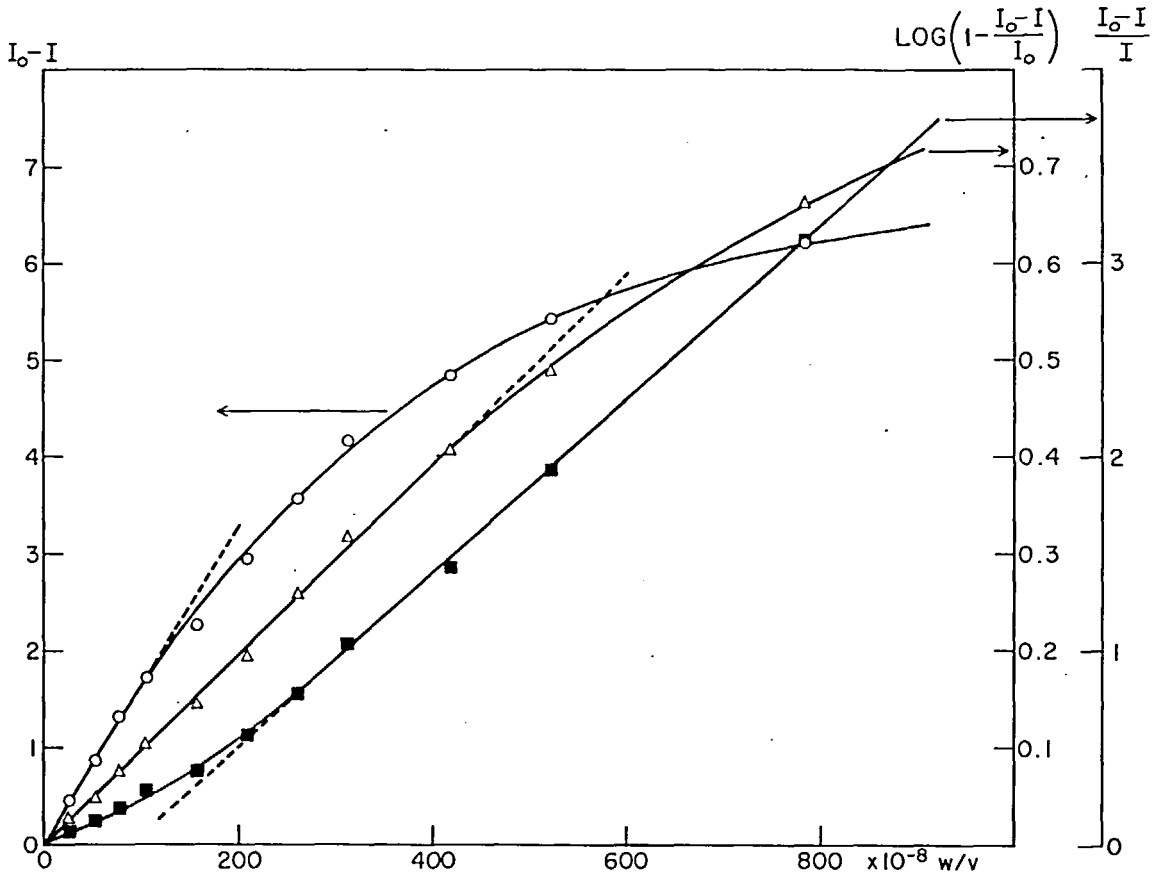

FIGURE 14. Response of an ECD to $(CF_2Br)_2$.

and DDT have high electron affinities. It has also been used extensively in the analysis of organometallic compounds either directly, e.g., the lead alkyls, or via halogen derivatives such as fluorinated β-diketones. It has been used in the analysis of steroids, phenols, acids, and many other types of organic molecules, generally as halogenated derivatives. The extreme sensitivity of the ECD to compounds such as sulphur hexafluoride ($\approx 10^{-14}$ g/s) means that they can sometimes be used in a manner analogous to radioactive tracer techniques for purposes such as following the course of pollution plumes from chimneys and locating the interface between liquids in a pipeline.

The main disadvantages of the ECD are its susceptibility to contamination, its relatively small linear range, and the unpredictability of its response. In order to minimize contamination from oxygen, all-metal piping should be used from the carrier gas cylinder to the apparatus and a trap containing molecular sieves should be used in the line to remove moisture. Wherever possible, all the pipework to and in the apparatus should be washed with an organic solvent and then baked. The unpredictability of response is a particular drawback when analyzing unknown mixtures since it is impossible to decide whether an unknown peak represents a small amount of a compound of high electron affinity or a large amount of a compound of low electron affinity.

With the advent of reliable element-selective detectors there seems to be a trend towards these for pesticide residue work, but the ECD is still used extensively and its unique properties are likely to render it indispensible for many years to come in a wide variety of applications.

CONCLUSION

In the discussion of selective detectors, it is apparent that a number of elements may be measured with several different detectors, and the

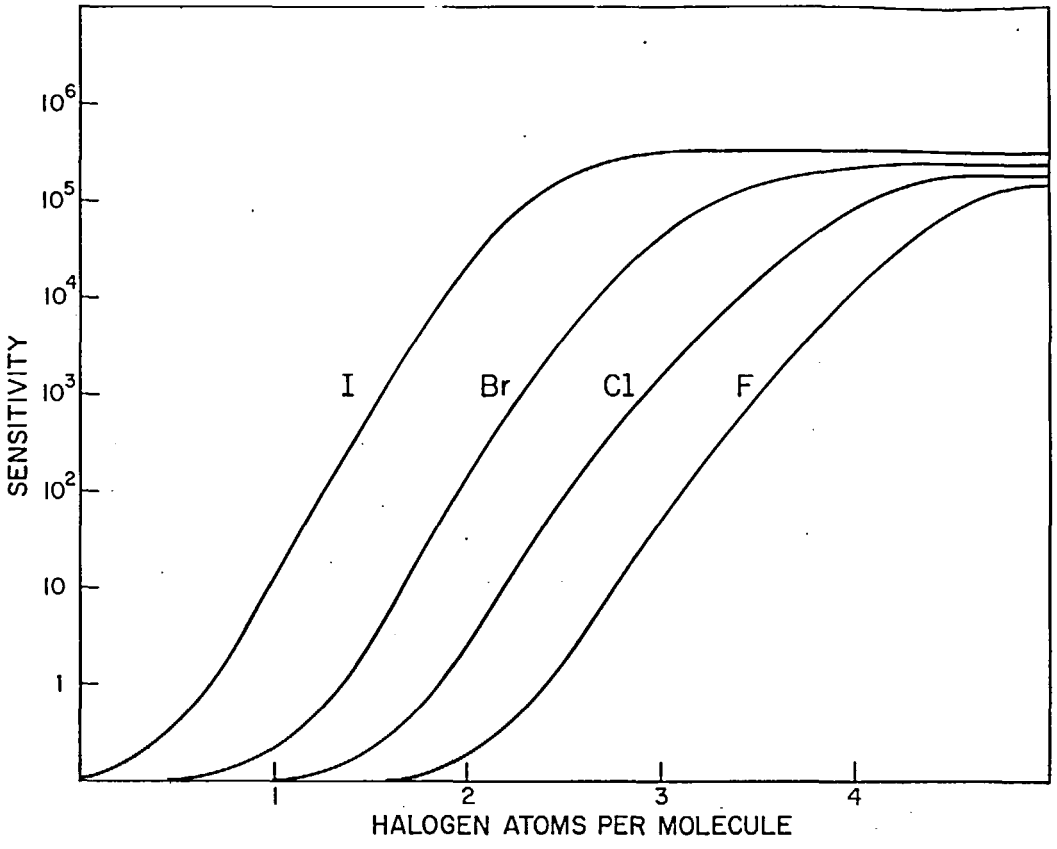

FIGURE 15. Electron affinity of halogenated compounds.

TABLE 7

The Effect of Position and of Multiple Substitution of Electrophores on Electron Absorption

Electrophore	Compound or class	Absorption coefficient
Cl	Vinylic	0.2
	Aromatic	1
	Aliphatic	0.3
	Allylic	55
	Benzylic	110
Cl_2	Benzene *o*	42
	Benzene *m*	30
	Benzene *p*	11
	· $CHCl_2$	1
Cl_3	Benzene 1,2,3	113
	Benzene 1,2,4	75
	Benzene 1,3,5	60
	· CCl_3	500
Cl_6	Hexachlorobenzene	1,100

From Lovelock, J. E. and Gregory, N. L., *Gas Chromatography*, Brenner, N., Callen, J. E., and Weiss, M. D., Eds., Academic Press, New York, 1962. With permission.

question must inevitably arise as to which detector should be used for a particular element. This is a question to which no direct answer is possible since so much depends on individual circumstances. In this article the author has tried to emphasize the advantages and disadvantages of each detector so that the reader may make his own assessment of his requirements. As indicated in the Introduction, one of the most important facts to be considered is the complexity of the sample to be analyzed. Is it a simple mixture of known compounds or a complex mixture of unknown compounds? Are the compounds of interest present in percentage amounts or at the ppm level? For halogenated compounds is there more than one halogen present? These are questions which the analyst should be able to answer before choosing a detector. But there are other questions concerned more with costing than with the scientific aspects which must be answered before a choice can be made: Is the analyst prepared to construct his own detector or is he limited to those available from the instrument manufacturers? If more than one element is to be measured have they to be determined simultaneously or will sequential methods suffice? All of these factors and many others besides must be considered before a choice is made, and under these circumstances the author feels that it is futile and even misleading to suggest that one detector is better than another.

It must also be reiterated that many other GC detectors exist which for various reasons have not been described. Of these omissions the most important is the mass spectrometer, but it was felt that this was a topic which warranted a complete article of its own.

Selective detectors have only now reached the stage where manufacturers take them seriously, and it can be expected that the next 2 to 3 years will see a consolidation and improvement of some existing detectors and the disappearance of others. There is still scope for the development of new detectors for those elements, in particular oxygen, which are currently catered for poorly.

Finally, it is to be hoped that the Retention Index system will become internationally standardized for a few reproducible stationary phases. Despite the remarks above about the mass spectrometer, the sensitivity of most selective detectors is already so high that often identification can only be made by means of retention data, and a reliable library of such data would be of inestimable value in analysis in general and with selective detectors in particular.

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