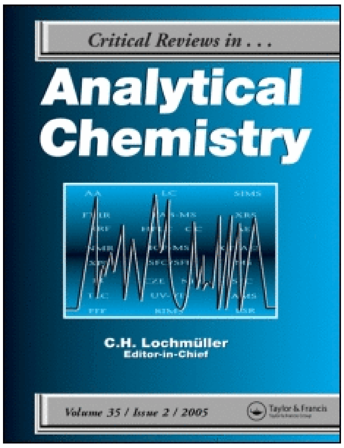

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E. R. Adlard; R. S. Juvet

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A REVIEW OF DETECTORS FOR GAS CHROMATOGRAPHY
PART I: UNIVERSAL 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

The writer of an article on gas chromatography detectors is faced with a dilemma which has no satisfactory solution. Practically every physical characteristic of gases and vapors has been used or suggested as the basis for a detector and the temptation is to write an article in which each of these methods is briefly discussed. The other extreme is a detailed discussion of the three or four detectors which have become universally accepted and offered by all the manufacturers of GC equipment. The third approach is to discuss the common detectors and a few of the less common ones which seem to the author to have promise or to have been unduly neglected. This middle course is the one which has been followed here, although it is recognized that it is a subjective approach and that a detector which appears important to the author may not do so to some of his readers and conversely a detector may have been omitted which some readers find indispensible in their work. Clearly, as in all analytical techniques, each detector has specific advantages and disadvantages, and it is the aim of this article to highlight these for the detectors discussed.

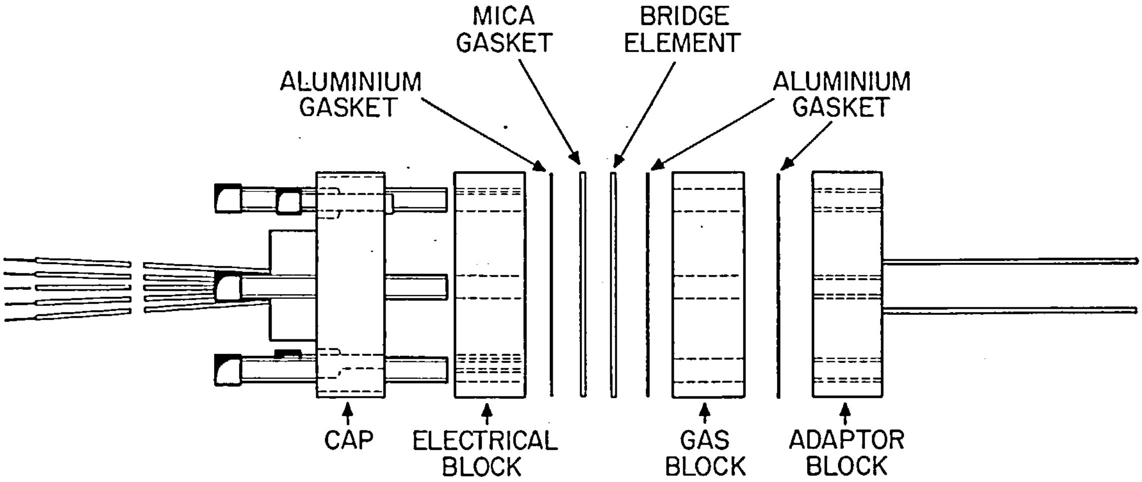

FIGURE 1. *Taylor Servomex microkatharometer. (Courtesy of Taylor Servomex Ltd.)*

Detectors may be classified in several different ways. In the early days of gas chromatography, detectors were often classified as integral or differential, but the former have now virtually disappeared. Classification can be based on other properties such as destructive/nondestructive, high sensitivity/low sensitivity, etc., but the most satisfactory method of classification in the present state of the art is to group detectors as universal or selective, although no existing detector is completely universal or completely specific.

UNIVERSAL DETECTORS

Katharometers

Commercial GC equipment has been available for 20 years, and for most of this time the imminent demise of the katharometer has been constantly predicted. In spite of this the katharometer remains the only detector in general use from the earliest days of the technique. Indeed, the katharometer pre-dates gas chromatography, as evidenced by Daynes' book on the analysis of gas mixtures published in 1933.[1] Katharometers were also used by Turner,[2] Claesson,[3] and Phillips[4] in their early work on gas-solid chromatography. The modern katharometer is far more sophisticated in construction and incomparably better in performance than the early models, and this continuous improvement in performance is one of the reasons for its survival.

The great advantage of the katharometer is its almost universal response, a property in which it is excelled by no other detector. Only gas mixtures containing hydrogen and/or helium present problems of detection, although these may be overcome by using a gas of low thermal conductivity such as argon or CO_2 for one analysis to measure the hydrogen/helium, followed by an analysis using helium to measure the compounds of low thermal conductivity.

In addition to its universal response, the katharometer is rugged and can be made small and compact; it requires only one gas supply and, if used at ambient temperature, requires only a small electrical power supply. This latter point is especially true if thermistors are used in place of metal filaments.* The katharometer is, therefore, ideally suited for portable equipment for the determination of mixtures of permanent gases and light hydrocarbons up to and including normal pentane. Wilhite has described a micro GC apparatus to analyze the atmosphere of Mars during the descent of a landing capsule.[5] The katharometer had an internal volume of 0.1 μl and a sensitivity of 5 ppm in a 1-μl gas sample. A microkatharometer with a dead volume of 2.6 μl made by Taylor Servomex Ltd. in the U. K. is shown in Figure 1. It consists of two chambers formed by slots cut in a pair of mica disks sandwiched between two short stainless steel cylinders; the sensing elements are made from 7.5-μm diameter platinum wire (Plate

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*Since thermistors are made from metallic oxides, hydrogen must not be used as the carrier gas with a thermistor katharometer. If hydrogen is used in such a detector, the characteristics of the thermistors are irreversibly altered and the Wheatstone bridge becomes totally unbalanced.

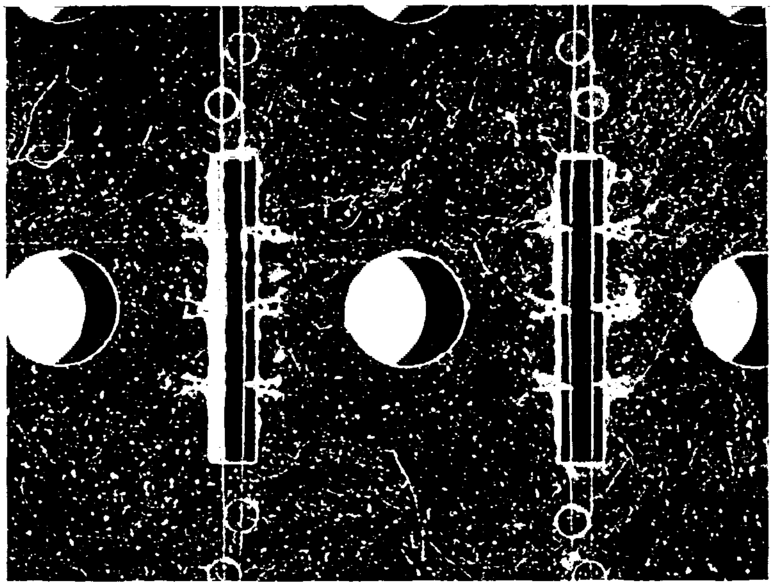

PLATE 1. Microkatharometer sensing elements (X 5).

1). When used with small bore packed columns or capillary columns, sensitivities approaching 200,000 mV - ml/mg can be obtained.[6]

The main disadvantage of the katharometer is its complex and unpredictable quantitative response. This is particularly true if low thermal conductivity carrier gases such as nitrogen are used, and gases of low thermal conductivity are not recommended unless there is some special reason for using them. If hydrogen or helium, gases with high thermal conductivity, are used the quantitative response is much more reliable and linear over a greater concentration range. With these two gases, the composition by weight of a mixture of similar compounds over a small range of molecular weights is approximately proportional to the areas under the peaks. Table 1, taken from the paper of Dietz,[7] shows the relative responses, with benzene as standard, for a number of hydrocarbons. From the table it can be seen, for example, that a mixture of C_6 paraffins, olefins, cycloparaffins, and benzene could be analyzed on an area basis to an accuracy of about 10% using the assumption of identical thermal conductivity response. The figures for the paraffins and olefins show a very common phenomenon: The properties of the lowest members of a homologous series often deviate considerably from the properties of the higher members. If greater accuracy is required or there is a considerable spread of molecular weights and a mixture of molecular types, it is essential to calibrate with blends of known composition, bracketing the expected values whenever possible. Calibration of a complex mixture is a lengthy and time-consuming affair, and this, of course, is assuming that all the compounds required for calibration are available in high purity. However, all GC detectors should be calibrated if the highest accuracy is required, so the katharometer is not unique in this respect.

The other disadvantage of the katharometer is that, despite the improvements described above, it is still considerably less sensitive than many other detectors and there seems little possibility of improving the sensitivity much further. It is possible that the use of an amplifier might improve the sensitivity by a factor of ten or more. Analytical Instruments Ltd. in the U. K. makes a microkatharometer/amplifier for use as a leak detector, but no commercial GC equipment seems to employ such a combination.

The Flame Ionization Detector

The flame ionization detector (FID) was first described almost simultaneously by McWilliam and Dewar[8] and Harley, Nel, and Pretorius[9] at a crucial moment in the development of gas chromatography when a high sensitivity, low dead volume detector was required for use with capillary columns. The ease of construction of the FID and its relative insensitivity to variations in operat-

TABLE 1

Weight Response Relative to Benzene for Hydrocarbons in a Katharometer

Compound	Relative weight response*
Methane	0.58
Ethane	0.76
Propane	0.87
Butane	0.87
Pentane	0.88
Hexane	0.90
Heptane	0.90
Octane	0.91
Nonane	0.92
Decane	0.91
Isobutane	0.91
Isopentane	0.91
Neopentane	0.94
2,2-Dimethylbutane	0.95
2,3-Diemthylbutane	0.95
2-Methylpentane	0.91
3-Methylpentane	0.94
2,2-Dimethylpentane	0.96
2,3-Dimethylpentane	0.95
2,4-Dimethylpentane	0.99
3,5-Dimethylpentane	0.96
2,2,3-Trimethylbutane	0.99
2-Methylhexane	0.94
3-Methylhexane	0.96
3-Ethylpentane	0.98
2,2,4-Trimethylpentane	0.99
Ethylene	0.76
Propylene	0.83
Isobutylene	0.87
Butene-1	0.90
trans-Butene-2	0.85
cis-Butene-2	0.82
3-Methylbutene-1	0.91
2-Methylbutene-1	0.91
Pentene-1	0.91
trans-Pentene-2	0.86
cis-Pentene-2	0.91
2-Methylpentene-2	0.96
2,2,4-Trimethylpentene-1	0.91
1-Methylcyclohexene	1.07
Cyclopentene	1.08
Cyclopentane	0.92
Methylcyclopentane	0.94
1,1-Dimethylcyclopentane	1.01
Ethylcyclopentane	1.00
Cyclohexane	0.95
Methylcyclohexane	1.05
1,1-Dimethylcyclohexane	1.02
1,4-Dimethylcyclohexane	0.99
Ethylcyclohexane	0.99
n-Propylcyclohexane	1.03
1,1,3-Trimethylcyclohexane	1.16
Benzene	1.00
Toluene	1.01
Ethylbenzene	1.05
m-Xylene	1.04
o-Xylene	1.08
p-Xylene	1.04
Isopropylbenzene	1.09
n-Propylbenzene	1.06
1,2,3-Trimethylbenzene	1.04
1,2,4-Trimethylbenzene	1.03
1,3,5-Trimethylbenzene	1.04
p-Ethyltoluene	1.03
Tetralin	1.17
trans-Decalin	1.18
cis-Decalin	1.17

*Peak areas multiplied by the appropriate response factors and then normalized give the weight percent of each compound.

After Dietz, W. A., *J. Gas Chromatogr.*, 5(2), 68 (1967). With permission of the publisher.

ing parameters ensured an instant success which later experience has consolidated. Furthermore, the electronic requirements of the detector were simple adaptations of existing amplifiers so that, initially, no great development work was required. It was found later that the range of linear response of the FID was considerably better than that of most commercial amplifiers, and this eventually led to a second generation of specially designed wide-range amplifiers which could be used with electronic integrators. The construction of a typical modern FID is shown in Figure 2.

There are a few elements and compounds which give little or no positive response with the FID; they are mainly the inorganic materials listed in Table 2.

Although these compounds do not give a positive response, they may affect the base current of the detector by altering the flow conditions in the flame. The effect of water on the response of

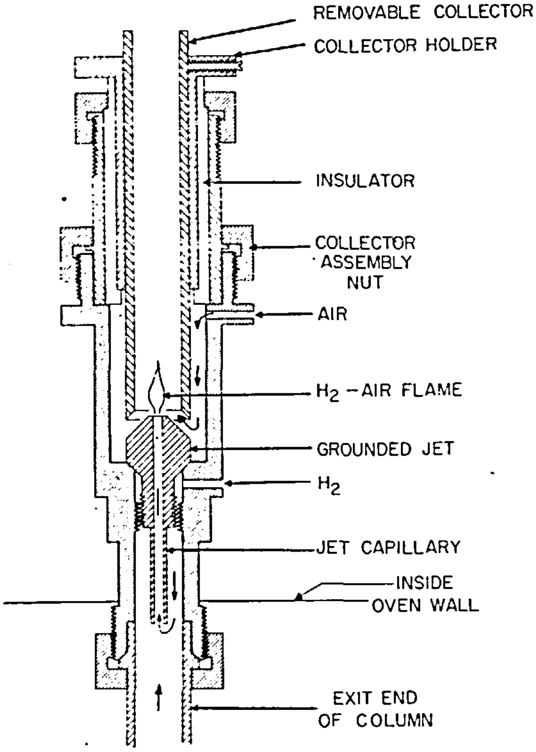

FIGURE 2. Hewlett-Packard flame ionization detector. (Courtesy of Hewlett-Packard Ltd.)

TABLE 2

Compounds to Which the FID Gives Little or no Response

Helium
Neon
Argon
Krypton
Xenon
Hydrogen
Oxygen
Nitrogen

Carbon monoxide
Carbon dioxide
Carbonyl sulphide
Carbon disulphide
Sulphur dioxide
Hydrogen sulphide
Ammonia
Nitrous oxide

Nitric oxide
Nitrogen dioxide
Silicon tetrafluoride
Silicon tetrachloride
Trichlorosilane
Water

From Condon, R. D., Scholly, P. R., and Averill, W., *Gas Chromatography 1960*, Scott, R. P. W., Ed., Butterworths, London, 1960. With permission.

the FID has been studied by Hill and Newell[11] and found to be relatively small. It will be noted that none of the compounds in Table 2 contains a C-H bond, but the presence of such a bond is not essential for the FID to give a positive response since carbon tetrachloride gives a normal signal. The mechanism or mechanisms by which the detector functions are still not resolved after more than a decade of study; an excellent summary of the various theories has been given by Blades.[12]

Whatever the mechanism of ion formation in the flame, operation under the correct conditions gives a signal for hydrocarbons for which the area under each peak is approximately proportional to the weight composition of the mixture. Condon, Scholly, and Averill[10] suggested that the accuracy of the relationship could be improved by correcting for the percentage of carbon in each compound. The C factor is given by $C = \frac{\text{Molecular weight}}{(\text{No. of carbon atoms}) \times 12}$. The real answer to more accurate results is, as always, calibration with pure compounds. McTaggart and Mortimer[13] have published the normalization factors for 35 hydrocarbons using normal heptane as a standard and have compared their results with others published in the literature (Table 3). It is clear from this table that the departure from unity for most of the factors obtained by McTaggart and Mortimer must be close to the experimental error with the exception of 1-*cis*-3-dimethylcyclopentane, 1-*trans*-2-dimethylcyclopentane, cyclohexene, 1-methyl-4-ethylbenzene, and 1,2,3,-trimethylbenzene. The results of Durrett, Simmons, and Dvoretzky quoted in Table 3 show a significant departure from unity only for benzene and toluene. The differences in the two sets of results are probably accounted for by differences in the construction of the detectors, but the deviation of benzene and toluene reported by Durrett, Simmons, and Dvoretzky is certainly common with many FIDs, and frequently in the analysis of complex hydrocarbon mixtures such as gasolines these two hydrocarbons are the only ones for which it is worth making a response correction.

Table 4 shows the response factors for some nonhydrocarbon compounds taken from the paper by Dietz.[7] These exhibit gross departures from unity, and although suggestions have been made for the calculation of response factors for various functional groups,[15,16] calibration is essential for all types of compounds, with the possible exception of hydrocarbons, where accurate results are desired. It can be seen from Table 4 that the response factor moves towards unity as the compound becomes more hydrocarbonlike, i.e., as the percentage of the hetero-atoms in the molecule decreases. At the same time isomeric compounds of the same type, e.g., propanol and isopropanol, can have different response factors. The very low response of formic acid is noteworthy since this compound also gives a low response with a katharometer.

TABLE 3

Normalization Factors for Various Hydrocarbons with an FID

Component	Ref. 13	Ref. 14
n-Hexane	1.00	0.97
n-Heptane	1.00	1.00
n-Octane	0.96	1.03
n-Nonane	0.94	1.02
3-Methylpentane	1.02	0.96
2,3-Dimethylpentane	0.97	1.01
3-Methylhexane	0.97	0.98
3-Ethylpentane	1.00	0.98
2,2-Dimethylhexane	0.97	0.99
2,2,4-Trimethylpentane	0.98	1.01
Cyclopentane	0.98	0.96
Methylcyclopentane	1.04	0.99
Cyclohexane	1.01	0.99
Methylcyclohexane	1.05	0.99
1,1-Dimethylcyclopentane	0.96	0.97
1-*cis*-2-Dimethylcyclopentane	1.05	1.00
1-*cis*-3-Dimethylcyclopentane	1.07	1.00
1-*trans*-2-Dimethylcyclopentane	1.10	0.99
Ethylcyclopentane	1.02	1.00
Hexene-1	1.04	–
2,2,4-Trimethylpentene-1	1.06	–
Cyclohexene	1.09	–
Benzene	0.97	0.89
Toluene	1.02	0.93
Ethylbenzene	1.01	0.97
m-Xylene	0.98	0.96
o-Xylene	0.97	0.98
p-Xylene	1.00	1.00
Isopropylbenzene	1.02	1.03
n-Propylbenzene	1.03	0.99
1-Methyl-3-ethylbenzene	1.03	0.99
1-Methyl-4-ethylbenzene	1.11	1.00
1,2,3-Trimethylbenzene	1.07	1.02
1,2,4-Trimethylbenzene	1.04	1.03
1,3,5-Trimethylbenzene	1.04	1.02

TABLE 4

Response Relative to *n*-Heptane for Various Nonhydrocarbons with an FID

Compound	Relative weight response*
Methanol	0.23
Ethanol	0.46
Propanol	0.60
Isopropanol	0.53
n-Butanol	0.66
Isobutanol	0.68
n-Octanol	0.85
Butyraldehyde	0.62
Octaldehyde	0.78
Formic acid	0.01
Acetic acid	0.24
Propionic acid	0.40
Butyric acid	0.48
Octanoic acid	0.65
Methyl acetate	0.20
Ethyl acetate	0.38
n-Butyl acetate	0.55
Isoamyl acetate	0.62
Ethyl-2-ethylhexanoate	0.72
Acetonitrile	0.39
Aniline	0.75
di-*n*-Butylamine	0.75
Acetone	0.49
Methyl ethyl ketone	0.61
Methyl isobutyl ketone	0.71
Ethyl pentyl ketone	0.80
Cyclohexanone	0.72

*Peak areas divided by the Relative Response Factor and normalized give weight percent.

From Dietz, W. A., *J. Gas Chromatogr.*, 5(2), 68 (1967). With permission of the publisher.

The FID is relatively insensitive to variations in operating conditions, but several authors have shown that there are optimum hydrogen and air flow rates for a given detector. Figure 3 from the paper of McTaggart and Mortimer[13] shows the effect of hydrogen and air flow rates on response, and Figure 4 from the same paper shows the variation of normalization factors with hydrogen flow rate. Optimum flow rates for commercial detectors are usually given by the manufacturers and should be adhered to as closely as possible. On the electrical side, the collector for the ions produced in the flame should more or less completely surround the flame, as shown in the detector in Figure 2, and the voltage between the electrodes should be sufficient to ensure that the saturation plateau on the current/voltage curve has been attained. An example of a detector where, for various reasons, none of these conditions is satisfied is the FID part of the Tracor flame photometric detector (vide infra) and the result is a considerable reduction in sensitivity.

To summarize, the FID is a near-perfect detector in many ways. It has a high sensitivity, a low dead volume, an insensitivity to variations in operating parameters, and a similar weight re-

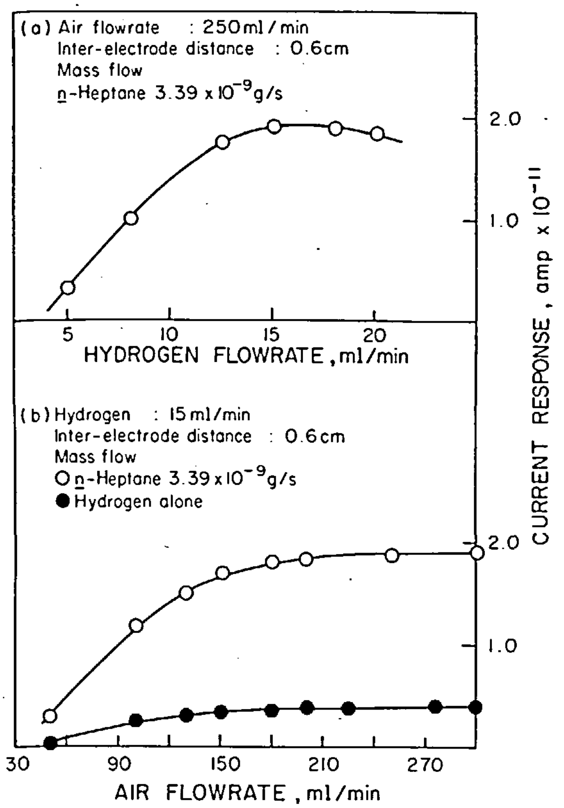

FIGURE 3. Effect of hydrogen and air flow rates on current response of FID. (From McTaggart, N. G. and Mortimer, J. V., *J. Inst. Petrol.*, 50, 255 (1964). With permission.)

sponse for all hydrocarbons above C_4. It does not suffer a fall-off in sensitivity as the body temperature is raised and is therefore better suited to deal with high boiling mixtures than, for example, the katharometer. The main disadvantage of the FID is the need for two controlled gas supplies (hydrogen and air) in addition to the carrier gas.

Other Universal Detectors

The two detectors described above have been so well proven over the years and satisfy such a high proportion of the market that any new universal detector would have to possess outstanding advantages to displace them. Only one new detector which has been developed in recent years – the piezoelectric crystal detector – seems to stand some chance against the FID and the katharometer. A brief account of this detector is given below. There are also several detectors which, although more or less universal in response, have particular properties which make them suitable for some specific applications. An account of two detectors in this category – the gas density balance and the reaction coulometer – is given below. It should also be pointed out that some detectors commonly used in a selective mode, e.g., the flame photometric detector of Zado and Juvet,[17] may be used in a nonselective mode for the detection of most organic and inorganic compounds.

The Piezoelectric Crystal Detector

In 1963 Bevan and Thorburn developed the "Brunel" detector, in which organic compounds emerging from GC column were absorbed on charcoal contained in a small aluminium foil bucket attached to an electrobalance.[18-23] Little use has so far been made of this detector since it is somewhat lacking in sensitivity and produces an integral record. However, the principle behind the detector is sound, and a detector has been described recently which depends on the mass of material eluted from the column altering the oscillation frequency of a piezoelectric crystal.[24] Unfortunately, the response is no longer directly proportional to weight as with the Brunel detector so that response factors, which vary considerably from compound to compound, have to be determined.

In the P/Z Chromatograph made by Laboratory Data Control of Riviera Beach, Florida (Figure 5), the effluent from the GC column passes over a piezoelectric crystal coated with stationary liquid and connected to an oscillator. The crystal and oscillator measuring unit is operated back to back with an identical reference unit. A compound emerging from the column is absorbed in and then desorbed from the liquid coating on the measuring crystal, causing a frequency change which is measured as a beat frequency between the measuring and reference circuits. Table 5, taken from the paper by Karasek and Tiernay,[25] shows the sort of accuracy that can be achieved, and Table 6 from the same paper shows the lower limit of detection for a number of compounds. Selective coatings on the measuring crystal can, in some cases, reduce the lower limit of detection tenfold, although the sensitivity is still about two orders of magnitude less than that of an FID.

With a sensitivity in the nanogram range, a speed of response of about 40 msec, and a small dead volume, the detector is attractive for use with open tubular columns. Only time can tell whether

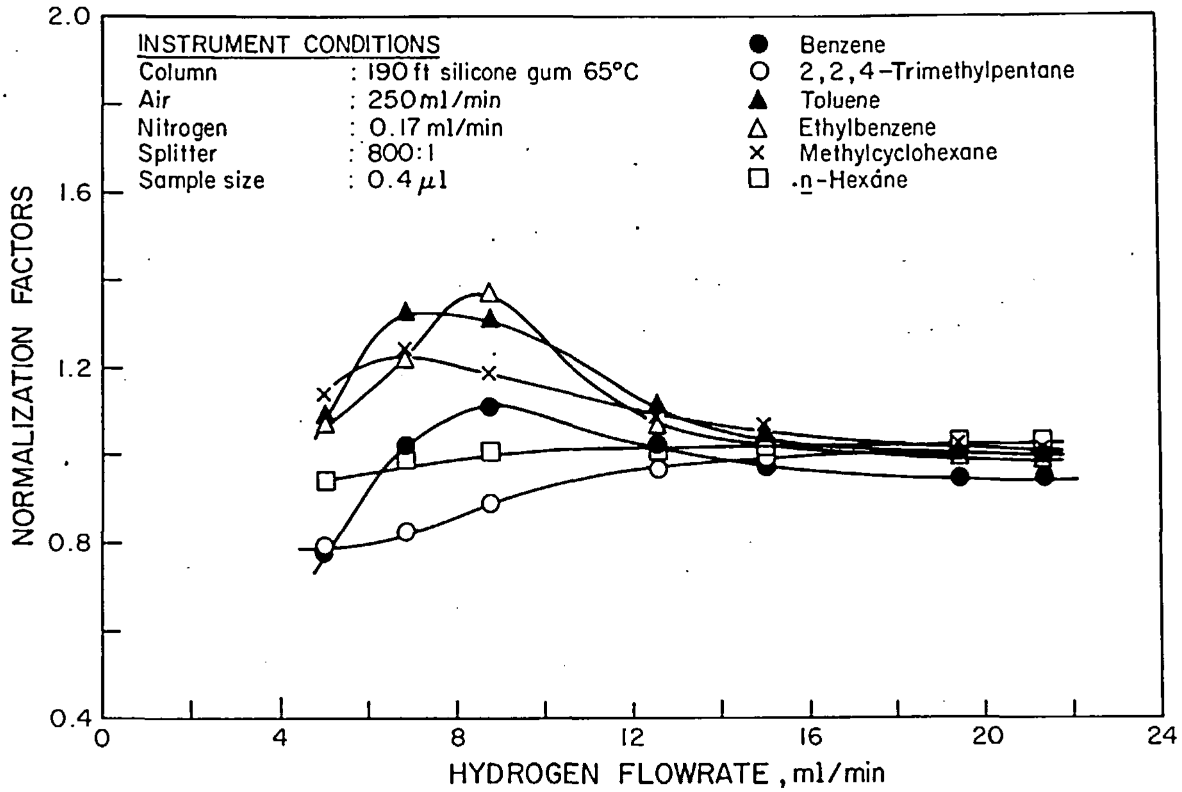

FIGURE 4. Variation of normalization factors with hydrogen flow rate for an FID. (From McTaggart, N. G. and Mortimer, J. V., *J. Inst. Petrol.*, 50, 255 (1964). With permission.)

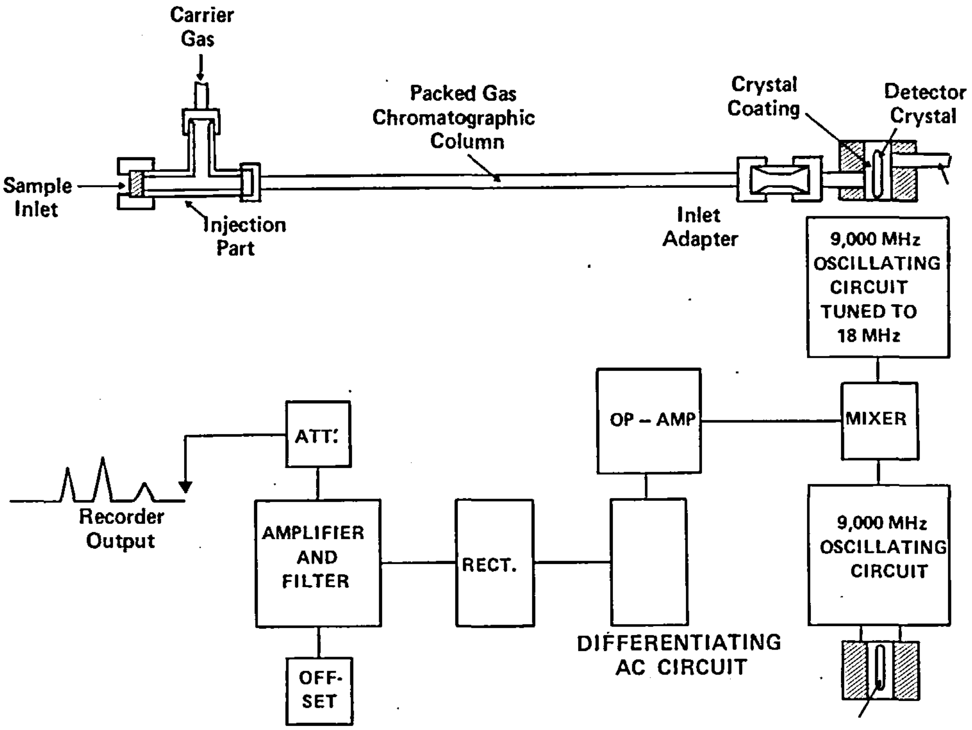

FIGURE 5. Schematic diagram of P/Z chromatograph. (Courtesy of the *Journal of Chromatography*.)

TABLE 5

Quantitative Analysis of an Alcohol and a Paraffin Mixture with the P/Z Detector

Compound		Relative response	Known wt%	Found wt%
Ethanol	Sample 1	1.00	53.96	54.10
Propanol		2.26	32.48	32.35
Butanol		5.20	13.56	13.55
n-Hexane	Sample 2	1.00	46.22	45.42
n-Heptane		2.60	10.41	10.92
n-Octane		7.09	27.62	28.10
n-Nonane		18.95	8.70	8.82
n-Decane		51.95	7.05	6.70

From Karasek, F. W. and Tiernay, J. M., *J. Chromatogr.*, 89, 31 (1974). With permission.

TABLE 6

Limits of Detection of the Piezoelectric Crystal Detector for Various Compounds Using a Crystal Coating of Carbowax 400

Compound	Minimum detectable quantity (g)
n-Hexane	2.10^{-6}
n-Heptane	7.10^{-7}
n-Octane	4.10^{-7}
n-Nonane	4.10^{-8}
n-Decane	3.10^{-8}
n-Undecane	2.10^{-8}
n-Dodecane	2.10^{-8}
Ethanol	8.10^{-6}
Benzene	4.10^{-7}
o-Xylene	2.10^{-7}
Cumene	3.10^{-8}
Mesitylene	9.10^{-8}
p-Cymene	9.10^{-8}
n-Hexylbenzene	3.10^{-8}
2-Hexanone	2.10^{-7}
2-Heptanone	2.10^{-7}
2-Octanone	2.10^{-7}
2-Nonanone	2.10^{-7}
Ethyl acetate	4.10^{-7}
Ethyl propionate	3.10^{-7}
Ethyl butanoate	2.10^{-7}
Ethyl pentanoate	2.10^{-7}
Ethyl hexanoate	4.10^{-8}

From Karasek, F. W. and Tiernay, J. M., *J. Chromatogr.*, 89, 31 (1974). With permission.

it will take its place alongside the FID and the katharometer.

Gas Density Balance

Measurement of the variation in the density of the gas emerging from a GC column was first described by Claesson.[3] James and Martin later described a more elegant device based on the same principle.[26] Their detector had about the same sensitivity as that of early katharometers but was much more difficult to make and to use. As a consequence, it did not achieve wide use until a simpler version designed by Nerheim[27] and made by Gow-Mac became available.

It was pointed out by Liberti, Conti, and Crescenzi[28] very early in the detector's history that by the use of two different carrier gases the molecular weights of compounds in the GC effluent could be calculated. Guillemin and Auricourt[29] described the advantages of the use of SF$_6$ as one of the carrier gases for this purpose. An instrument is now available[30] which employs two identical columns, two gas density balances, and two different carrier gases simultaneously so that Liberti's procedure can be carried out in one run. Two recent papers describe the performance of this equipment and show that molecular weights up to 400 can be determined with an accuracy of about 1%, although the procedures used can hardly be described as simple.[31,32] The authors of both of these papers point out the usefulness of the gas density balance for the determination of the molecular weight of those compounds which give little or no parent ion when analyzed by mass spectrometry.

The Reaction Coulometer

The reaction coulometer[33] will detect and measure all elements and compounds which will react when passed with oxygen over a heated platinum catalyst.[34] A diagrammatic form of the

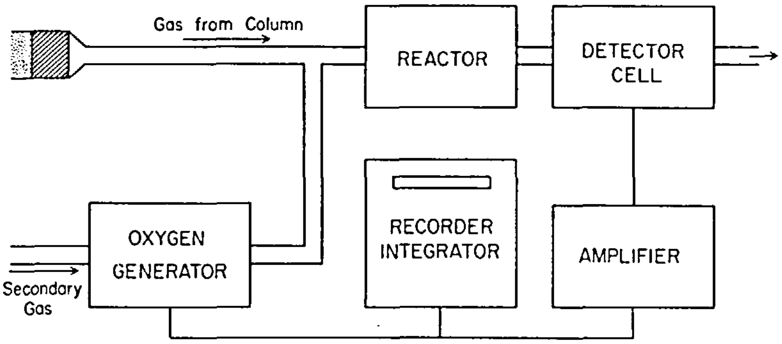

FIGURE 6. Schematic diagram of reaction coulometer. (Courtesy of Reaction Coulometers Ltd.)

coulometer is shown in Figure 6. Carrier gas, usually helium or nitrogen, emerges from the column where it is joined by a second stream of the same gas containing a small amount (100 to 1,000 ppm) of oxygen. The mixed gases pass through a tube containing platinum catalyst heated in a small furnace and thence to an electrolytic cell oxygen detector. When no combustible material emerges from the column, the system is balanced electrically. When an organic compound is eluted, it is burnt to CO_2 and water and the equivalent amount of oxygen required for the combustion is removed. The resulting decrease in oxygen concentration is sensed by the electrolytic detector, which sends a signal to the oxygen generator via a servoamplifier. The generator then produces oxygen until the original concentration of oxygen in the system is restored. The current required to generate the oxygen is displayed on a recorder to produce the familiar elution chromatogram with the important property that the area under each peak is related by Faraday's Law to the weight of the compound eluted. This property makes the reaction coulometer one of the few existing absolute detectors and in this property lies its main advantage. The two main disadvantages of the detector are a relatively slow feedback time constant, so that very sharp peaks may not be measured correctly, and the fact that a large peak may remove all the oxygen and "saturate" the detector. In general, however, the limitations imposed by these constraints are no great handicap in the chromatographic separation of organic mixtures. The sensitivity of the detector is between that of an FID and that of a katharometer, but it does require more routine maintenance than these detectors. Its best use is, therefore, in the calibration of other detectors, the analysis of hydrocarbon gas mixtures (the difficulties of preparing accurate gas blends at low concentrations are well known), and the calibration of sampling loops on gas sampling valves. It can also be used for the analysis of samples known to contain water if the difference between the theoretical and experimental responses is assumed to be due to water.

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