Journal of Chromatography, 167 (1978) 365–380

CHROM. 11,433

PRACTICAL EXPERIENCE WITH A MICROWAVE PLASMA DETECTOR: LIMITS OF MEASUREMENT AND EXAMPLES OF APPLICATIONS*

K. S. BRENNER
BASF AG, WHU-E210, D-6700 Ludwigshafen (G.F.R.)
(First received May 11th, 1978; revised manuscript received August 14th, 1978)

SUMMARY

The properties of a microwave plasma detector, such as sensitivity, selectivity and reproducibility, are demonstrated for practical applications. The main applications are qualitative detection and specific identification of elements in known and unknown compounds, quantitative analysis and trace analysis using one element channel (for example, the sulphur channel) and determination of empirical formulae of compounds in unknown gas chromatographic peaks.

A series of examples are given to show the performance of the MPD 850 detector. Detailed conditions for obtaining accurate empirical formulae and for the exploitation of its full potential are given.

INTRODUCTION

From the viewpoint of information theory, a gas chromatographic (GC) detector can be defined as a converter between the flow of substances that are leaving the separation system and the flow of information that gives, after suitable manipulation, the analytical result (see Fig. 1).

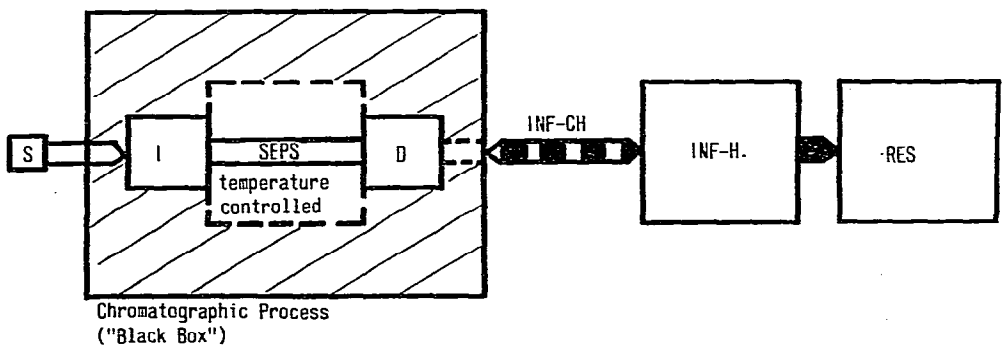


Fig. 1. Chromatographic process and data handling. S = Sample; I = sample inlet; SEPS = separation system (temperature controlled); D = detector; INF-CH = information channel; INF-H = information handling; RES = analytical results.

* Dedicated to Professor Dr. Ernst Otto Fischer on the occasion of his 60th birthday.

The detector is the main source within the chromatographic process where information can be produced and collected by following the rules of electronic measurement and information theory. The subsequent data handling, although often very complex, gives only a small additional gain in information if too much of it has been already lost in the detector itself. A GC detector, therefore, needs to be very sensitive and selective and should be able to produce a comprehensive message.

In addition to the well known selective detectors, such as the electron-capture detector (ECD), the thermionic detector (TID) and the mass spectrometer (MS) (a sensitive and very flexible specific detector), the microwave plasma detector (MPD) has proved to have great potential. Its development was initiated by McCormack *et al.* in 1965 (ref. 1). McLean and co-workers[2–4] later built a versatile instrument for routine applications.

We have been using an MPD in our laboratory for 4 years, and our experience is discussed in this paper.

PRINCIPLE OF MEASUREMENT

The MPD is a combination of microwave plasma excitation and a grating spectrometer. The components eluted from a GC column are fed continuously to a low-pressure helium plasma. At a thermodynamic temperature of about 5000–6000° they are completely atomised and the excited atoms emit their characteristic line spectrum. This emission is focused on a primary slit, through which it enters the grating spectrometer. After dispersion in discrete atom lines a characteristic line is selected for every element under consideration. This line is focused on a photomultiplier window via a secondary slit.

The formation and deposition of carbon or graphite inside the quartz plasma tube is suppressed by the addition of trace amounts of nitrogen or oxygen (scavenger gases) to the helium carrier gas via a cyano radical or carbon oxide cycle (for details, see ref. 2).

EXPERIMENTAL

Apparatus

This work was carried out with an Applied Research Laboratories* (ARL) MPD 850 microwave plasma detector, which we combined with a Perkin-Elmer F22 gas chromatograph. The GC–MPD combination consists of the GC separation system, the interface for coupling with a flame-ionization detector (FID) and a low-pressure (10 Torr) plasma emission source combined with a multi-channel spectrometer (see Fig. 2). Critical points on the instrument combination are the interface and its restrictors, the transfer line to the plasma head and the joints, especially the heated ones. The precise dosage of the small (depending on the problem) amounts of oxygen or nitrogen (range 1–2 ml/min) and their addition to the helium carrier gas as scavenger gases are fundamental for reproducible measurements and the determination of peak ratios.

To obtain precise settings of the operating conditions, to facilitate the change

* At present the instrument is manufactured by Applied Chromatography Systems Ltd.

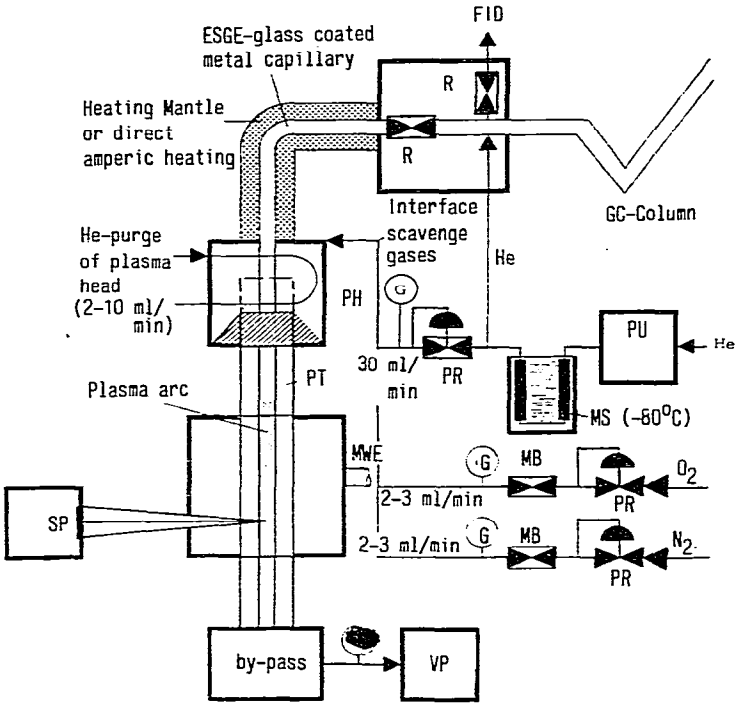


Fig. 2. Schematic diagram of microwave plasma detector. FID = Flame-ionization detector; SP = grating spectrometer with ten different mirror systems and photomultipliers; PR = pressure controller; MB = Laval jet restrictors (Microblende); R = restrictor; G = pressure gauge; PH = plasma head; MWE = microwave energy coupling; PT = plasma tube (quartz); by-pass = by-pass valve for venting peaks that could extinguish the plasma or which exceed the linearity range; V = vacuum gauge; VP = vacuum pump with buffer and vacuum controller; PU = He purifier, loaded with Ti sponge and CuO; MS = molecular sieve, cooled to −80°.

from oxygen to nitrogen as the scavenger gas and to eliminate influences by vacuum and carrier gas fluctuations, we changed several functions on the instrument, in cooperation with ARL Ltd.

For the carrier gas and scavenger gas supplies we used temperature-balanced pressure controllers (type: Druckfeinregler, C 74450-A 294-A 8; Siemens, Karlsruhe, G.F.R.) in combination with special laser-bored Laval jet restrictors (Mikroblende, Siemens, type: hydrogen, for minimum flow-rates of 3–12 ml/min, at 2–10 bar). To avoid any leaks from the large number of connections, we used silver-seal joints (couplings; type: Siemens).

Together with extra purification of the helium carrier gas using a molecular sieve (*ca.* 50 ml; 5 Å, 0.2–0.5 mm), cooled in dry-ice–acetone (*ca.* −80°), the baseline for the oxygen and nitrogen channel can be kept sufficiently low for detection limits of 2 ng/sec to be reached for these two elements. The plasma tube was sealed with Vespel polyimide ferrules on both ends, which allowed a working temperature of 300° to be employed.

The installation of a vacuum controller (type: precision air-pressure regulator;

range from 12 p.s.i. below to 65 p.s.i. above atmospheric pressure; sensitivity 0.025 Torr; Negretti & Zambra, Aylesbury, Great Britian) and a 1-1 vacuum buffer reduced the noise significantly.

A critical parameter, in addition to the dosage of scavenger gas, is the construction of the interface and the preparation of the restrictors. We used an interface that consists of a small three-way joint, which is connected directly to the FID inlet of the gas chromatograph (Fig. 3) to minimize decomposition of compounds by surface effects and to avoid a dead volume.

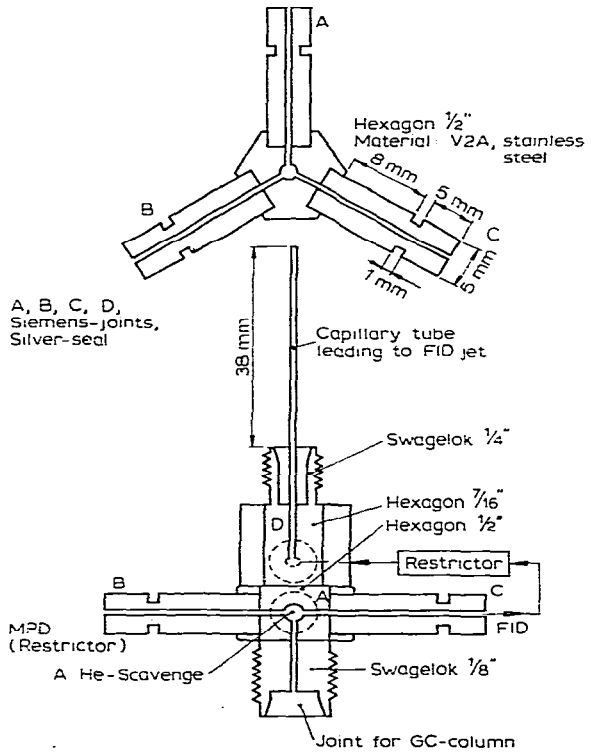


Fig. 3. GC–MPD interface. Perkin-Elmer F22 gas chromatograph.

The restrictors were stainless-steel capillaries about 2 cm long, which were adjusted to the desired splitting ratio between the MPD and the FID. They were adjusted to flow-rates of 40–50 ml/min (for the MPD line) and 80–100 ml/min (for the FID line), which were measured at a pressure difference of 1400 mbar. For analyses with packed columns, carrier gas flow-rates of 10–30 ml/min and a splitting ratio (MPD:FID) of *ca.* 1:1 were usually the optimal conditions. The restrictors were made by squeezing steel capillaries of I.D. 0.3 mm until the desired flow-rate was reached. They were then covered with a protecting steel tube which was soldered on both ends to the restrictor before they were checked again (Fig. 4).

The ESGE glass-coated and electrically-heated transfer line between the interface (situated in the GC oven) and the plasma head (PH) sometimes interferes with analyses of sensitive compounds, such as phosphoric esters and hydroxy compounds.

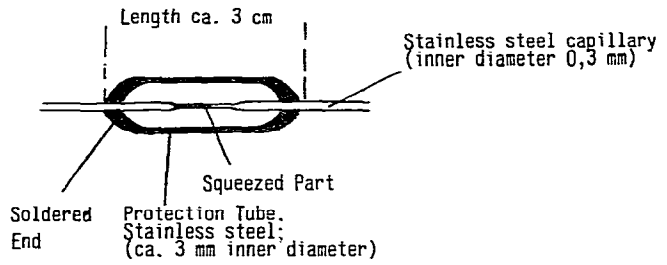


Fig. 4. Restrictor.

At present we are trying to replace this ESGE line with a temperature-controlled glass-capillary connection[5].

Finally, a new plasma stand with Vespel ferrules instead of Viton O-rings allows a rapid change and re-positioning of the quartz plasma tube and leak-free working up to 300–350°.

Conditions

Working with packed columns we used, *e.g.*, the following instrumental conditions. The splitting ratio between the MPD and the FID was *ca.* 1:1. The interface had the same temperature as the GC column; the ESGE line and plasma head (PH) were normally held at the same temperature or at most 50° higher.

Helium is the only gas that can be used as the carrier gas (helium plasma). It should be as pure as possible in order to avoid noise in the hydrogen, oxygen and carbon channels. The purifier will work for several years under these conditions without any changes. The molecular sieve trap has to be regenerated at 150° every 2–4 weeks. This can be easily controlled by the hydrogen channel (water desorption being the most time-consuming step). For the scavenger gas supply we used small pressure bottles with highest purity oxygen and nitrogen (>99.998% O_2; >99.999% N_2; Messer Griesheim, Düsseldorf, G.F.R. or Baker, Deventer, The Netherlands). The gas flow-rates normally used were helium scavenger *ca.* 30 ml/min, *ca.* 4 bar; oxygen/nitrogen scavenger 2–3 ml/min, *ca.* 4 bar; and helium purge (PH) 2–10 ml/min, 0.2–0.5 bar. Microwave energies of 80–120 mA proved optimal; the vacuum is best held in the range 0.5–3 Torr, and fluctuations on the gauge (type Edwards, H 180-42, 0–20 Torr) should be less than 0.1 Torr. The quartz plasma tube in our laboratory lasts for 6–12 weeks, depending on the operating conditions.

The microwave equipment and the spectrometer were handled in accordance with the instructions of the manufacturer. Normally we used four element channels (the carbon and hydrogen channels and two hetero-element channels) simultaneously, depending on the problem.

To avoid errors, before measurement a rough estimation of the mass flow (μg/sec) for every expected peak should be made, to serve as a guide for the amount of sample to be injected or for its appropriate dilution. Overloading of the plasma must be avoided under all circumstances. Peaks that exceed the linearity must be by-passed (see below under linearity).

The linearity, for the determination of empirical formulae, is about 2–3 decades,

especially for the measurement of oxygen:carbon and nitrogen:carbon ratios. Because of their relatively high detection limits (see Table I), a very low baseline and minimum noise must be achieved; this includes low bleeding rates, *e.g.*, of oxygen-containing liquid phases from the column. It is preferable to use high-temperature stationary phases in low concentrations of 1–2%.

TABLE I

LIMITS OF DETECTION

Element	*Wavelength (Å)*	*Limit of detection (ng/sec)*	
		This work	*Manufacturer's measurements*
C	2478	0.06	0.08
H	4861	0.02	0.03
D	6562	—	0.09
O	7772	4.0*	3.00
N	7469	2.8*	2.90
F	6856	0.46	0.06
Cl	4794	0.06	0.06
Br	4705	0.02	0.12
I	5161	—	0.05
S	5454	<0.05	0.09
P	(2536)**	0.005	(0.009)
Si	2881	Not determined	

* Measured with 20% Apiezon grease column.

** Values in parentheses measured by Bache and Lisk, see ref. 3.

For the determination of peak ratios and empirical formulae, the standard (compounds of known composition) should be positioned very close to the unknown peaks in a chromatogram. This eliminates errors caused by drifting baselines. Despite all of these precautions, mutual interferences occur between oxygen and nitrogen, which may be due to a disturbance of the scavenger gas level.

It is also evident, that the sensitivity of the element channels depends on whether oxygen (for nitrogen measurement) or nitrogen (for oxygen measurement) is used as the scavenger gas. With unstable liquid phases such as polyglycols or polyamides we sometimes found negative oxygen or nitrogen peaks (Fig. 5), depending on the nature of the eluted compound. In our opinion, the negative oxygen peaks in the given example (Fig. 5) were caused by the consumption of the high oxygen level in the plasma, which resulted from high polyglycol bleeding. Only dioxane gave a positive peak, owing to its high oxygen content.

Linearity

The linearity of the different element channels, measured as mass of element to signal size, lies between 3 and 4 decades (see ref. 2 and measurements of the manufacturer), with the exception of the elements oxygen, nitrogen and silicon.

Especially for unknown compounds in a gas chromatogram, the determination of oxygen:carbon or nitrogen:carbon ratios is very interesting, because these two hetero-elements are the most important in organic chemistry. As an example, the linearity of the oxygen channel for a low-polarity (diethyl ether) and a polar compound (ethanol) is illustrated in Tables II and III and Figs. 6–8).

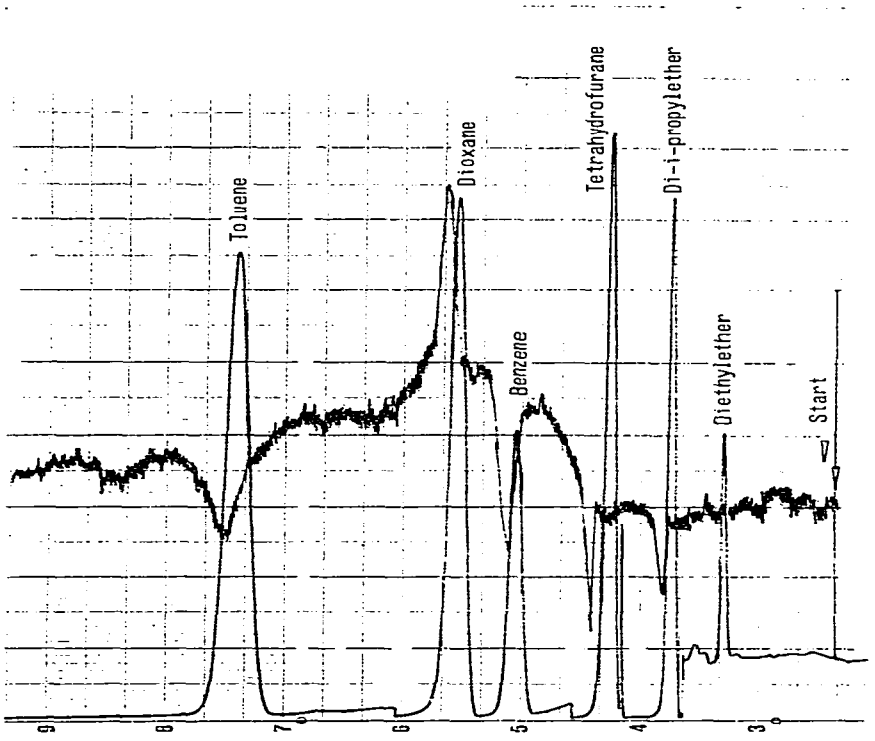


Fig. 5. Negative oxygen signals, caused by high bleeding from polyethyleneglycol phase.

TABLE II

LINEARITY AND DETECTION LIMITS FOR THE OXYGEN CHANNEL

Diethyl ether solution in *n*-propanol.

Mixture	*Ether (ppm)*	*Oxygen (ppm)*	*Oxygen in 1 μl of solution (g)*	*Peak width ~ 5 sec (g O/sec)*	*Peak height (mm)*	*Peak area (mm²)*
1	15290	3306	$3.306 \cdot 10^{-6}$	$6.6 \cdot 10^{-7}$	312	345
2	7645	1653	$1.65 \cdot 10^{-6}$	$3.3 \cdot 10^{-7}$	222	155
3	765	165	$1.65 \cdot 10^{-7}$	$3.3 \cdot 10^{-8}$	38	32
4	382	83	$8.3 \cdot 10^{-8}$	$1.7 \cdot 10^{-8}$	26	26
5	77	16	$1.6 \cdot 10^{-8}$	$3.2 \cdot 10^{-9}$	7	8

TABLE III

LINEARITY AND DETECTION LIMITS FOR THE OXYGEN CHANNEL

Ethanol solution in *n*-propanol.

Mixture	*Ethanol (ppm)*	*Oxygen (ppm)*	*Oxygen in 1 μl of solution (g)*	*Peak width ~ 10 sec (g O/sec)*	*Peak height (mm)*	*Peak area (mm²)*
1	20902	7270	$7.3 \cdot 10^{-6}$	$7.3 \cdot 10^{-7}$	406	734
2	10451	3635	$3.6 \cdot 10^{-6}$	$3.6 \cdot 10^{-7}$	268	528
3	1045	365	$3.6 \cdot 10^{-7}$	$3.6 \cdot 10^{-8}$	34	72
4	523	182	$1.8 \cdot 10^{-7}$	$1.8 \cdot 10^{-8}$	20	40
5	105	37	$3.7 \cdot 10^{-8}$	$3.7 \cdot 10^{-9}$	2	6

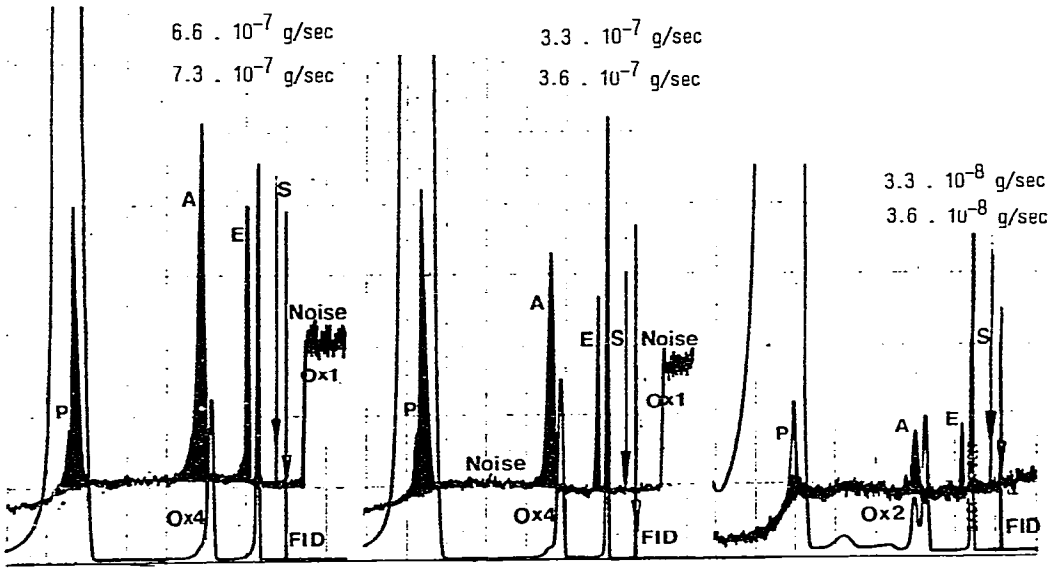


Fig. 6. Linearity of the oxygen channel. Oxygen (O, black) and FID traces for different concentrations of diethyl ether (E) and ethanol (A) in *n*-propanolic solution. P = *n*-propanol peak.

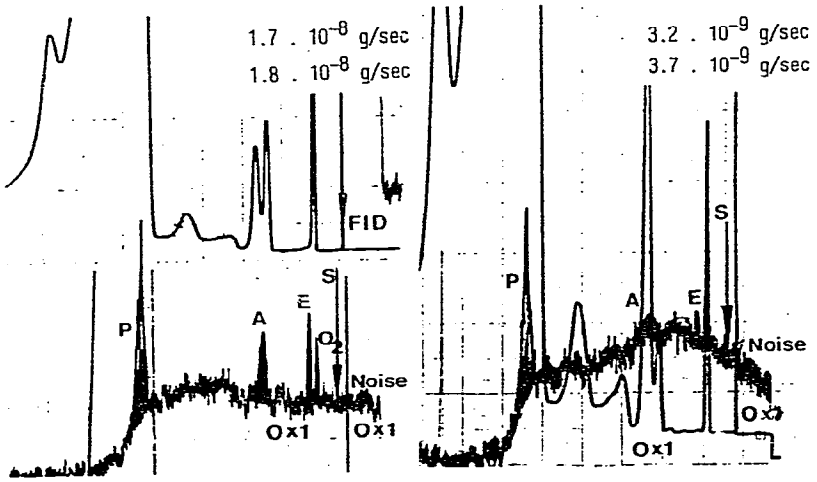
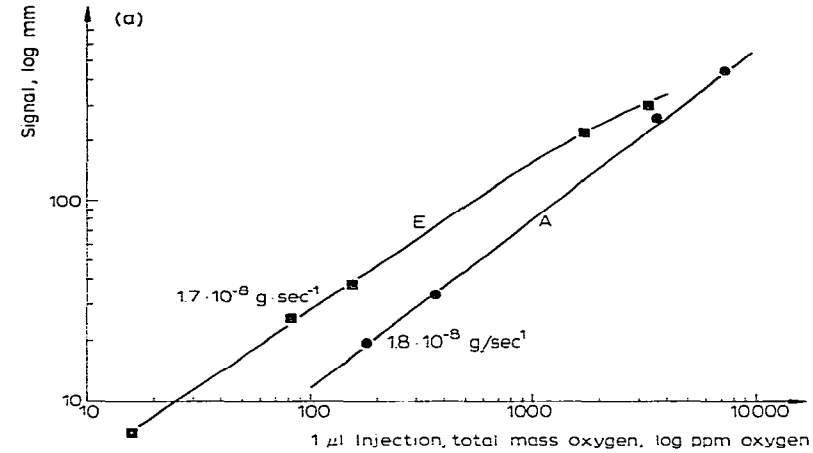


Fig. 7. Linearity of the oxygen channel. See Fig. 6 for details.

Both compounds were dissolved in *n*-propanol at different concentrations (C_E and C_A) such that solutions with about 10^{-8}–10^{-6} g/μl of oxygen resulted (see Tables II and III). A 1-μl volume of these solutions was injected and the size of the oxygen signal (S) was measured as either peak height or peak height × peak width at half-height.

To illustrate a practical application, we used a packed polyglycol column, which is often used in our laboratory for separations of ketones, alcohols and esters and which does not show excessive bleeding at 100°. The measured linearity is there-



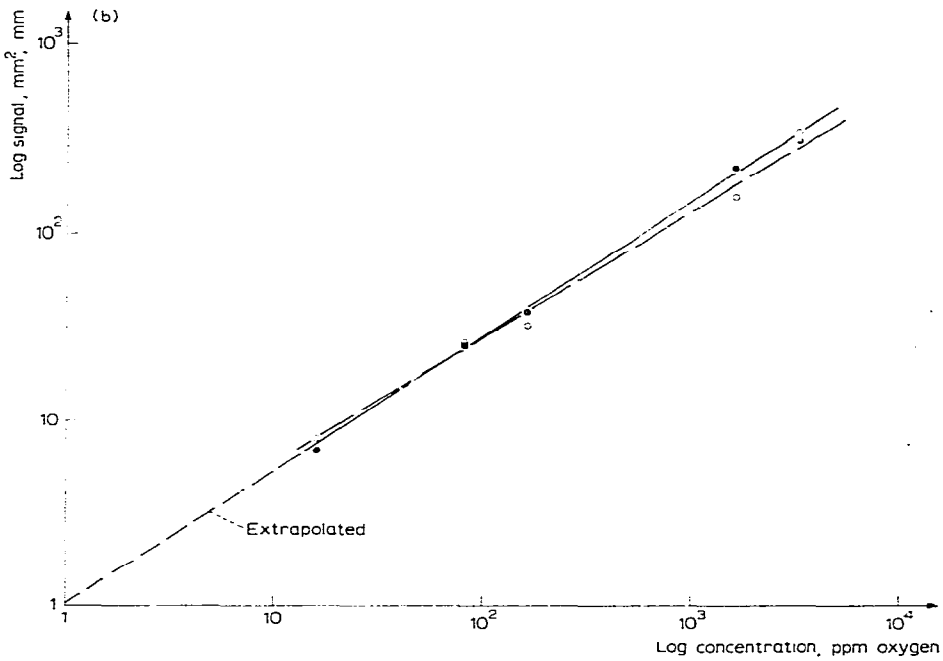


Fig. 8.

(Continued on p. 374)

fore the linearity of the combination gas chromatograph (S+I+SEPS, Fig. 1) plus MPD.

Following the physico-chemical definitions[6,7], the measured values (Tables II and III) are plotted as log S *versus* log c. These plots show a linearity for both compounds (diethyl ether and ethanol) (Fig. 8) of about 3 orders of magnitude. Although the slope (φ) of the line $\Delta S/\Delta c = \tan\varphi$ is not 45°, the detector is linear in the range shown in the graph[7]. The difference from unity is probably caused by spectral and

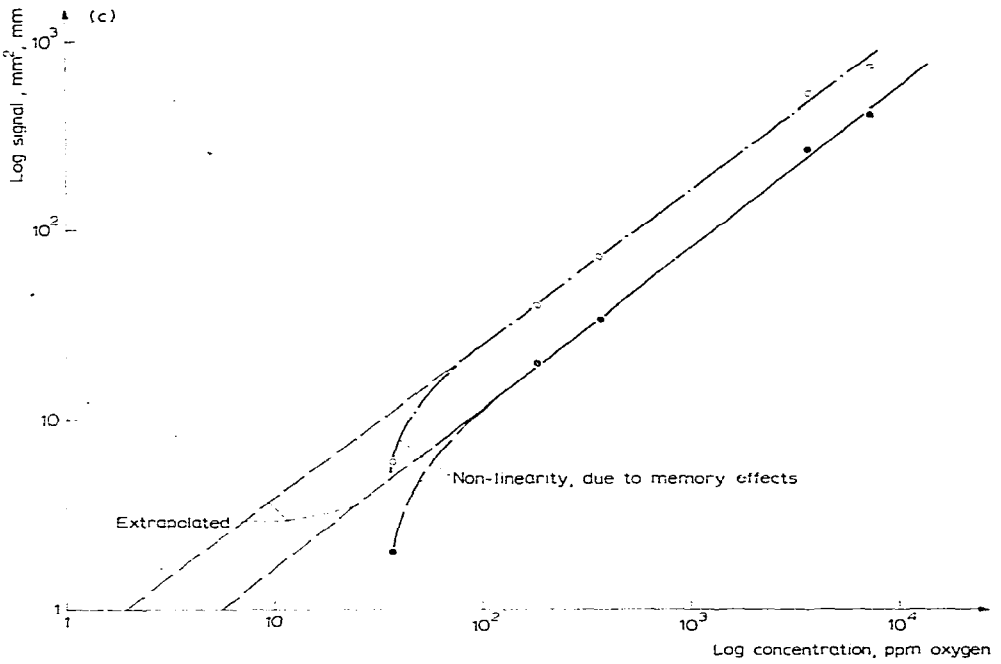


Fig. 8. Linearity of the oxygen channel. (a) ■, Diethyl ether; ●, ethanol. (b) Diethyl ether: ○, peak area measurements; ●, peak height measurements. (c) Ethanol: ○, peak area measurements; ●, peak height measurements.

electronic influences. The intercept on the *S*-axis corresponds to the logarithm of the sensitivity, $\log k \cdot \alpha_A^a$ (k and α_A^a are experimental constants; α_A^a is the value of property a for compound A). This intercept, which limits the sensitivity for oxygen (and similarily for nitrogen), is caused by trace amounts of water injected with the sample, bleeding of polyglycol oligomers from the column and trace amounts of air that enter the separation and detection system at very small leaks.

In Fig. 8b and c the results of two different methods of signal evaluation are demonstrated, namely measurement of peak height and peak height × peak width at half-height (peak area). It can be seen that both methods result in a linear response. As expected, the ethanol signal (Fig. 8c) has a slightly higher sensitivity on measuring the peak areas rather than the peak heights, owing to tailing and memory effects. The latter also cause a strong deviation from linearity close to the detection limit of ethanol ($< 10^{-8}$ g/sec of oxygen), which is not an MPD effect, as can be seen from Fig. 8b, which shows linearity for diethyl ether. The linearity at higher concentrations ($> 10^{-6}$ g/sec of oxygen) was not tested, because this region usually lies beyond practical application.

As the linearity for the carbon channel is between 0.06 and about 1000 ng/sec and the sensitivity for oxygen is much lower (limit of detection 2–4 ng/sec), in most instances only 2–3 decades of linearity for the oxygen channel are necessary. These facts explain why samples have to be diluted to fit these linearity ranges when empirical formulae are to be investigated, and why the concentrations of the standard and the unknown compound should be similar.

Limits of detection

The limits of detection are listed in Table I. They are strongly dependent on spectral noise and particular attention must be paid to the oxygen and nitrogen measurements. The limits of detection lie in the range of nanograms of element per second, *i.e.*, trace components can be analysed qualitatively and quantitatively.

The manufacturer's and our own measurements indicate that hetero elements can be detected in organic compounds with up to 30 carbon atoms. For the more interesting elements (oxygen and nitrogen), the sensitivity of the MPD is high enough to detect them in compounds that contain 18–20 carbon atoms (*e.g.*, octadecanol). The determination of empirical formulae in oxygen- and nitrogen-containing compounds is possible with carbon:hetero element ratios up to 16:1 and for the other hetero elements with ratios between 20:1 and 30:1. Beyond these limits considerable noise and cross-sensitivity from carbon continuum emission interfere. The sensitivity to fluorine, chlorine, bromine, phosphorus, sulphur, carbon and hydrogen is so high that it is sufficient to obtain empirical formulae with a mass flow-rate of 0.1–0.05 μg of substance per second (*i.e.*, trace compounds in concentrations of 250–500 ppm). Trace analyses with one element channel only can be made with chlorine-, bromine-, fluorine- and phosphorus-containing compounds, owing to their low detection limits.

Selectivity

The basis of measurement with the MPD, the atomization of the eluted compounds in a microwave excited plasma (5000–6000°) and the spectrometric analysis of the atomic emission, causes interferences with the different atomic species only with very narrow emission lines (cross-sensitivity). As an example, the deuterium line (6561.00 Å) can be separated from the hydrogen line (6562.81 Å) (ref. 2).

The most important source of incorrect measurements is the carbon continuum emission together with deposition of graphite during plasma overloading. This disturbance is normally suppressed by scavenging with trace amounts of oxygen and nitrogen. The selectivities given in Table IV are defined as the signal ratio of the mass of an element to the signal of the same mass of carbon[2]. For organic compounds this definition is practicable. The selectivities lie in the range from 50:1 to 1000:1 (Table IV).

The plasma tube (quartz) may interfere in the measurement of oxygen and silicon. Oxygen, fluorine and chlorine at high temperatures may initiate a cycle during which silica or silicon–halogen compounds are formed, then oxygen and silicon signals can be simulated.

When using analogue amplifiers with electronic compensating devices, corrections for carbon continuum emission can be made. The last column in Table IV shows the results obtained with this device.

Precision

The precision of the results depends considerably on the selectivity, linearity, purity of the sample (*e.g.*, content of water and polar by-products) and column bleeding. Therefore, no general statements about the precision in determining empirical formulae can be made.

Our experience with the determination of oxygen:carbon ratios, which is

TABLE IV

TOTAL NOISE AND SELECTIVITIES (ELEMENT TO CARBON) FOR THE ELEMENT CHANNELS

Element	*Total noise* on element channel (ng/sec)*	*Selectivity versus n-heptane**	*Our measurements*	
			Selectivity (element:C)	*Selectivity with "ghost correction"*
C	0.81	—	—	—
H	0.22	—	>500:1***	—
D**	0.17	880	—	—
F	0.091	2300	>350:1***	—
Cl	0.16	510 (44)	485:1	~1000:1
Br	0.72	1300 (38)	300:1	~1000:1
I**	0.56	400 (38)	—	—
S	1.1	390 (22)	50:1	~ 500:1***
P	—	— (1000)	Qualitative measurements only	
N	113.0	—	>500:1***	—
O	98.0	—	>500:1***	—
Si	—	—	Qualitative measurements only	

* Data from literature[2-4]; data in parentheses are from Bache and Lisk's publications, see ref. 3.
** Manufacturer's measurements.
*** The measured selectivity was at least 500:1.

a difficult problem, is that the reproducibility lies between 95% and 98%, dependingon the separation conditions, the oxygen content of the compound and the quality of calibration.

RESULTS OF APPLICATION OF THE MPD

Examples of quantitative measurement

The following examples shall give an indication of how the instrument works under the above conditions. It should be mentioned that all of the analysed compounds were incorporated in a matrix of different materials so that a direct microanalysis could not have resolved these problems.

Specific determination of vinylidene chloride. Vinylidene chloride (VDC) had to be determined in tetrahydrofuran solution. The contamination of the solvent by low-boiling trace compounds interfered in the measurement of VDC with an FID. With the chlorine channel a specific determination of VDC was possible down to a concentration of 0.25 ppm on injecting 5 μl of solution.

Polychlorinated biphenyls (PCBs). Extracts containing trace amounts (about 50 ppm) of PCBs were analysed; their presence had to be proved by specific determination of chlorine in each compound and, if possible, by establishing empirical formulae. The results compared with those obtained by GC–MS are given in Table V.

Trace amounts of sulphur compounds in methanol. A sample of methanol containing about 2% of sulphur compounds was examined, and the results are given in Table VI.

Test mixture of various diols. A test mixture of diols was analysed by GC–MPD and GC–MS. The results are compared in Table VII.

TABLE V

RESULTS OF ANALYSIS OF PCBs

Peak No.	*Empirical formulae by GC–MS*	*Empirical formulae by GC–MPD**	
		Measurement 1	*Measurement 2*
8	$C_{12}H_5Cl_5$	$C_{12}H_{7.8}Cl_{4.0}$	$C_{12}H_{10}Cl_{4.2}$
9	$C_{12}H_5Cl_5$	$C_{12}H_{3.5}Cl_{5.2}$	$C_{12}H_{4.7}Cl_{5.6}$
10	$C_{12}H_5Cl_5$	$C_{12}H_{4.9}Cl_{4.8}$	$C_{12}H_{7.1}Cl_{5.5}$
11	$C_{12}H_4Cl_6$	$C_{12}H_{2.7}Cl_{5.5}$	$C_{12}H_{4.5}Cl_{6.0}$
12	$C_{12}H_4Cl_6$	$C_{12}H_{3.4}Cl_{5.8}$	$C_{12}H_{5.3}Cl_{6.5}$
13	$C_{12}H_4Cl_6$	$C_{12}H_{6.1}Cl_{4.9}$	$C_{12}H_{5.1}Cl_{7.3}$

* Measured in duplicate.

TABLE VI

RESULTS OF ANALYSIS OF SULPHUR COMPOUNDS IN METHANOL

Compound	*Concentration (%)*	*Determined empirical formulae*	*Actual empirical formulae*
Dimethyl ether	0.01	$CH_{2.45}O_x$	$C_2H_5O_x$
Methyl mercaptan	0.04	$CH_{5.2}S_{0.95}$	CH_5S
Methanol	98.0	Main product, standard (C, H)	
Dimethyl sulphide	0.01	$CH_3S_{0.5}$	C_2H_6S
Dimethyl disulphide	0.95	$CH_{2.9}S$	$C_2H_{5.8}S_2$

TABLE VII

RESULTS OF ANALYSIS OF TEST MIXTURE OF DIOLS

Approx. concentration	*GC–MPD*		*Compound*	*GC–MS result*
	Found	*Theory*		
0.5%	$C_2H_{4.9}O_{1.8}$	$C_2H_6O_2$	Ethylene glycol	Ethylene glycol
200 ppm	C, H, O	Qualitative	But-2-ene-1,2-diol	Concentration to low
0.5%	$C_4H_{9.2}O_{2.0}$	$C_4H_{10}O_2$	Butane-1,4-diol	Butane-1,4-diol
200 ppm	$C_4H_{7.9}O_{1.6}$	$C_4H_8O_2$	But-2-ene-1,4-diol	Concentration to low

Phthalodinitrile isomers. Phthalodinitrile, terephthalodinitrile and isophthalodinitrile were analysed in a mixture, the last two compounds having a concentration of about 500 ppm. Phthalodinitrile served as a standard. The following empirical formulae (theoretical: $C_8H_4N_2$) in duplicate measurements (A and B values) were found: terephthalodinitrile, (A) $C_8H_{3.2}N_{2.0}$ and (B) $C_8H_{3.1}N_{2.0}$; isophthalodinitrile, (A) $C_8H_{3.3}N_{2.0}$ and (B) $C_8H_{2.9}N_{2.0}$.

This example shows the very good reproducibility for the determination of empirical formulae and the systematic error for the hydrogen values that sometimes occurs (the reasons are dealt with under Experimental).

Determination of yellow phosphorus in phosphorus trichloride. The direct determination of trace amounts of phosphorus in phosphorus trichloride at a level of 100 ppm is possible after separation on a Tenax column.

Examples of qualitative, element-specific measurements; combination with MS results

The rapid, selective identification of hetero elements in GC effluents and the

possibility of calculating empirical formulae often allow the identification of unknown peaks in a chromatogram. The identification is improved considerably by the measurement of retention indices and by the knowledge of all available chemical information about the sample.

In addition, the MPD is a valuable tool for controlling derivatization of organic compounds by subsequent analysis for the functional groups introduced (*e.g.*, TMS-, fluorine-, chlorine-, bromine- or phosphorus-containing groups).

Comparison of GC–MS and GC–MPD measurements. The MPD is a useful and efficient supplement to GC–MS methods. In particular, a mass spectrometer gives specific proof only of the presence of some hetero atoms. The analysis of oxygen- and nitrogen-containing compounds by MS is sometimes difficult if excessive fragmentation occurs and parent peaks are absent.

As an example, the MPD result for an unknown peak was $C_9H_{14-17}O_{2.5}$, which confirmed the formula $C_9H_{16}O_3$ obtained by GC–MS. The latter result had been uncertain because of splitting off of water.

Identification of an unknown halogen-containing solvent. An unknown solvent, the odour of which was similar to a chlorine- (such as chloroform) or bromine-containing compound, had to be identified. The sample was measured on the GC–MPD instrument on the carbon, bromine, fluorine and chlorine channels simultaneously. We found a single GC peak containing chlorine and bromine together with carbon. The identification of the solvent as 1-bromo-2-chloropropane (comparison with catalogue spectra) by a subsequently recorded IR spectrum was a routine step.

Identification of oxygen compounds eluted from capillary columns. The components of an extract from natural products (terpenes and terpene alcohols) were separated on a 100-m capillary column (0.5 mm I.D.) and identified by GC–MS. Unfortunately, some of the oxygen-containing compounds underwent decomposition during MS measurement (splitting off of water) and no parent peak could be measured. By means of the specific determination of oxygen the uncertainty of the results could be eliminated and many alcohols identified.

Oxidation products from tar. Autoxidation products of tar had to be identified. IR spectra of the extract showed high carboxyl and hydroxyl contents, and the GC–MPD results for the methylated sample showed a very high content of oxygen in some of the peaks and a low hydrogen:carbon ratio (Fig. 9a and b). We had expected high molecular weights and polarities and therefore used a 15-cm Dexsil 300 column. With this information, GC–MS analysis on a glass capillary column was easy.

DISCUSSION AND CONCLUSIONS

The MPD can be defined as a multi-dimensional detector following the definition of Schomburg[8]. Its capability of giving simultaneous information about the presence or absence of up to ten elements and about their ratios gives the following advantages.

Its "multi-dimensional" selectivity gives more accurate information about unknown peaks than do most other detectors. The selectivity of the MPD is defined here as[7]

$$\Gamma = \frac{S_j{}^a}{S_k{}^a} = \frac{\alpha_j{}^a}{\alpha_k{}^a}$$

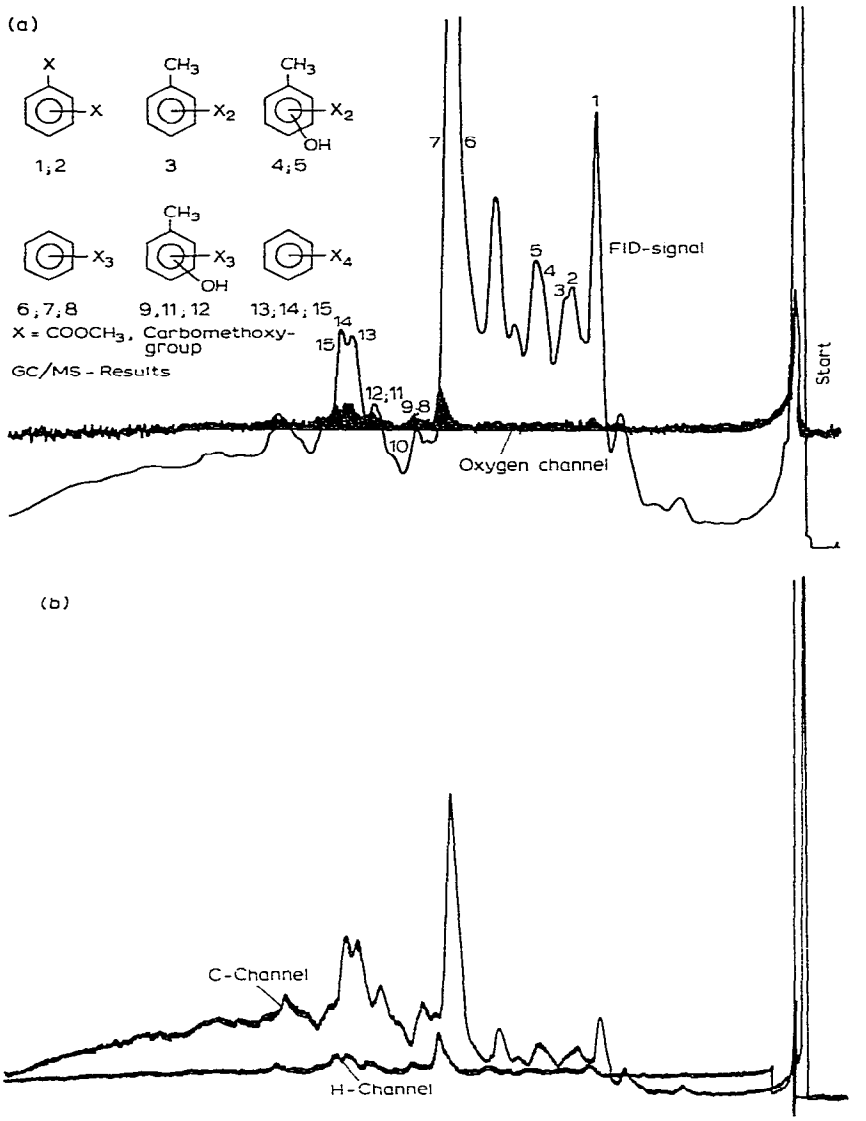


Fig. 9. Oxidation products from tar sample. Column, Dexsil 300, 15 cm; column temperature, 50–300°, programmed at 10°/min; flow-rate of He carrier gas, 30 ml/min. (a) FID and oxygen channel. (b) Carbon and hydrogen channels.

(Jentzsch and Otte[6] use the terms selectivity and sensitivity in the opposite sense), where S_j^a and S_k^a are the signals of the substances J and K to be compared, measured in a detector for property a; a_j^a and a_k^a are the values of the property a for compounds J and K, respectively.

In the element-selective range (element to carbon ratios up to 1000:1, see Table IV) and within the range of linearity the MPD is more selective than the ECD, TID or a conductivity detector, in a complex manner, because the latter measure one

property *a* only. In favourable instances specific determinations are possible with the MPD, for example if a chlorobromoaniline is measured via the chlorine, bromine and nitrogen channels simultaneously.

The determination of element ratios (and thus of empirical formulae) at concentrations down to 100 ppm, and quantitative and selective analysis, for oxygen-, halogen-, nitrogen- or phosphorus-containing compounds etc. are the most important advantages of this detector.

It is very valuable that any kind of reference standard can be used, because all elements in a compound are measured independent of their chemical bonding, according to the mechanism of measurement.

Disadvantages are the influence of the quartz tube on the oxygen, silicon and sometimes the chlorine channels. The sensitivity of the oxygen and nitrogen channels should be higher. Mutual element influences, *e.g.* between oxygen and nitrogen, carbon and oxygen or nitrogen or carbon and chlorine must be eliminated by careful calibration.

Further development seems possible by using a higher energy input to the plasma, which could increase the linearity range and suppress mutual element effects: for this purpose more stable plasma tubes are necessary.

ACKNOWLEDGEMENTS

The author thanks BASF AG for making this work possible and for permission to publish the results, and ARL Ltd. and ACS Ltd. for technical discussions and support. The considerable practical contributions of L. Köhler and R. Mertens and the valuable help of Mrs. K. Keszler with the preparation of the English manuscript are acknowledged.

REFERENCES

1 A. J. McCormack, S. C. Tong, W. D. Cooke, *Anal. Chem.*, 37 (1965) 1470.
2 W. R. McLean, D. L. Stanton and G. E. Penketh, *Analyst (London)*, 98 (1973) 432, and references cited therein.
3 M. Krejči and M. Dressler, *Chromatogr. Rev.*, 13 (1970) 35.
4 W. R. McLean, *Proc. Soc.Anal. Chem.*, 10 (1973) 144.
5 D. Henneberg, Max-Planck-Institut für Kohlenforschung, Mühlheim-Ruhr (G.F.R.), personal communication.
6 D. Jentzsch and E. Otte, *Detektoren in der Gas-Chromatographie*, Akademische Verlagsgesellschaft, Frankfurt/Main, 1970.
7 J. Ševčik, *Detectors in Gas Chromatography*, Elsevier, Amsterdam, Oxford, New York, 1976.