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Characterization of an element-specific detector for combined gas chromatography–atomic emission detection

András Gelencsér, János Szépvölgyi and József Hlavay*

Department of Analytical Chemistry, University of Veszprém, P.O. Box 158, 8201 Veszprém (Hungary)

ABSTRACT

An element-specific detector using a capacitively coupled plasma developed recently for gas chromatography was characterized according to the accepted terms of gas chromatographic detectors. The most important detector parameters, sensitivity, linearity, limit of detection, linear range and selectivity, were determined for channels of four elements, carbon, chlorine, bromine and sulphur, with a view to potential applications. The parameters obtained were compared, as permitted by the different mechanisms of operation, with some common gas chromatographic detectors of similar application. The characteristics of the detector were evaluated independently of application.

INTRODUCTION

Element-selective chromatographic detectors play an important role in separation science for compound identification. Element-selective detection methods commonly used in gas chromatography (GC) are nitrogen–phosphorus detection (NPD), flame photometric detection (FPD), which is selective for sulphur and phosphorus, and Hall electrolytic conductivity detection (HECD), which is selective for halogens, nitrogen or sulphur [1]. Three types of atomic spectrometry have been applied for GC detection: atomic absorption, flame emission and atomic plasma emission spectrometry. Atomic emission detectors have just recently been introduced to GC [2,3]. Their application as GC detectors is based on the fact that a multitude of elements, C, H, D, O, N, S, P and the halogens, give

intense emission signals in the plasma, thus making the detector perfectly suited for the analysis of organic compounds.

For GC detection, microwave-induced plasmas are generally used. The molecules entering the plasma are atomized and the atoms are excited at high temperature, emitting at given emission lines which represent their characteristic spectra. By measuring the signal at a given emission line, a signal proportional to the concentration of the given element can be obtained irrespective of the type of molecule.

The element-specific detector was developed by Anton Paar (Graz, Austria) [4]. In contrast to other atomic emission GC detectors, it utilizes a capacitively coupled, stabilized plasma which is made up from helium plasma gas and oxygen dopant gas in a water-cooled fused-silica discharge tube. Helium is used as the plasma gas because it gives a simpler background spectrum, provides higher excitation energy and yields a broader linear range than does argon. For the four elements studied (C, Cl, Br and S), oxygen
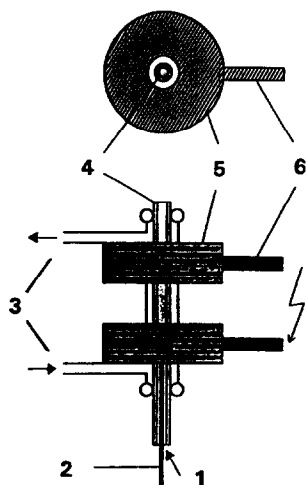
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* Corresponding author.

Fig. 1. ESD torch design. 1 = Plasma gas in; 2 = chromatographic column; 3 = water cooling; 4 = discharge tube; 5 = annular electrode; 6 = HF contact.

was the most suitable dopant gas. The scheme of the discharge tube is depicted in Fig. 1.

The discharge tube is held in the plasma generator unit mounted on the detector position of the gas chromatograph. The light emitted is directed through fibre optics to the spectrometer, where light is resolved by interference filters and detected by photodiodes in four separate units for the four elements. The aim of this paper was to determine the fundamental detector parameters for the individual channels, to make a broad comparison of the parameters with those of the corresponding common GC detectors and to evaluate the characteristics of the detector independently of application.

Basic parameters of gas chromatographic detectors

There has been continuing debate in the literature about the interpretation of certain parameters of gas chromatographic detectors. Apart from the different mechanisms of operation and their consequences, it aggravates the difficulties in comparing the performances of different detectors independently of application. Therefore, the most critical detector parameters are briefly addressed below.

Linearity of detectors is often defined in the literature with linear coordinates. Detectors are classified as linear and non-linear. As non-linear behaviour may either result from the operating principle of the detector or the electronics, the calibration graph should always be plotted with logarithmic coordinates. Linearity is defined as the proportionality constant between the logarithm of the signal and the logarithm of the amount eluted.

Limit of detection has been a subject of much controversy. For this paper, the considerations given in ref. 5 were accepted.

The selectivity for an element-specific detector can be quantified as the amount of a given element that yields a chromatographic peak on the channel of another element or disturbs its baseline to such an extent that determination of a co-eluting compound on that channel is no longer feasible. In the former instance, the degree of interference may also be expressed by the selectivity ratio as defined in ref. 5.

EXPERIMENTAL

Chemicals

n-hexane was obtained from Carlo Erba, n-decane from Fluka, tert.-pentanethiol and n-hexanethiol from Polyscience, bromobenzene, carbon tetrachloride and chlorobenzene from Supelco and tetrachloroethylene, bromoform and 2-bromochlorobenzene from Aldrich. All the chemicals were used as received without further purification.

For the determination of the fundamental detector parameters, four model solutions of different concentrations were prepared with n-decane as internal standard at a concentration of 0.9 μmol/ml. The concentrations of the compounds in the model solutions are listed in Table I. For the determination of C:X mole ratios, carbon tetrachloride, bromoform, bromobenzene and chlorobenzene were applied at concentrations of 1.35, 1.43, 1.15 and 1.10 μmol/ml, respectively (solution 1) and in a tenfold dilution of solution 1 (solution 2). All solutions were thoroughly homogenized in an ultrasonic bath. Peak areas were considered as signals after normalization by the signal of the internal standard. For preparation of the calibration graph, nine measurements were carried out. The ex-

TABLE I

AMOUNTS OF THE COMPOUNDS IN 1 ml OF THE MODEL SOLUTIONS

Compound	Solution 1 (μmol)	Solution 2 (μmol)	Solution 3 (μmol)	Solution 4 (μmol)
tert.-Pentanethiol	9.20	0.84	91.3	11.1
n-Hexanethiol	8.08	0.78	80.0	9.7
Tetrachloroethylene	8.81	0.80	87.2	10.6
Bromoform	11.45	1.04	113.4	13.7
1-Bromochlorobenzene	7.27	0.66	72.0	8.7

perimental conditions were kept at their optimum values, except when the dependence of sensitivity values on experimental parameters was determined.

Instrumental conditions

The gas chromatograph used was a Carlo Erba MEGA 5300, equipped with a split/splitless injector (temperature 250°C). The column was SPB-20 (30 m × 0.32 mm I.D., 0.25 μm film thickness) (Supelco) and the carrier gas was helium (T55, Messer Griesheim). The column was held at 40°C for 2 min, then programmed to 220°C at 10°C/min and held at 220°C for 5 min. The detector was an element-specific detector (Anton Paar) with a stabilized capacitive plasma (generator frequency 27.12 MHz; plasma power 150 W). The selected emission lines were 940.6, 837.6, 827.4 and 921.4 nm for carbon, chlorine, bromine and sulphur, respectively.

RESULTS AND DISCUSSION

The sensitivity, linearity, linear range, limit of detection and selectivity found for each channel are summarized in Table II.

Sensitivity

If the amounts of the elements entering the detector are measured in picomoles and the signal is expressed in peak- area units, the sensitivities listed in Table II are obtained for the channels. As can be seen, the sensitivities of the different channels are very similar. This phenomenon may be surprising in the light of the fact that the four elements have different plasma-chemical behaviours and the emission intensities of the measuring lines and the efficiencies of the filters are different. The sensitivities of the channels are dependent on the experimental parameters, particularly on the flow-rate of the plasma and dopant gases. It can be considered that a change in the flow-rate of the gases affects the local thermal equilibrium of the plasma and hence the number of atoms excited.

Linearity

The data in Table II clearly indicate that the carbon, chlorine and bromine channels can be considered as linear detectors but the sulphur channel shows non-linear behaviour. On the basis of the operating principle of the detector, linear behaviour would also be expected for this

TABLE II

FUNDAMENTAL DETECTOR PARAMETERS OF THE CHANNELS

Parameter	Carbon	Chlorine	Bromine	Sulphur
Sensitivity	3.32	3.41	3.06	2.77
Linearity	1.0	1.0	1.0	1.4
Linear range	4.0	4.5	4.6	4.2
Limit of detection (pg/s)	7	14	25	6

channel, so the result indicates that the reaction producing the excited S atoms is not a simple first-order reaction. As sulphur tends to participate in a series of bimolecular reactions in flames [6], the reaction leading to the excited S atoms may also be fairly complex in the plasma. The observed phenomenon, however, calls for further investigations.

Linear range

As can be seen from the data in Table 2, the values for the channels are fairly similar to each other. It is more informative, however, to compare these values with those of GC detectors of similar application.

The outstanding figure for flame ionization detection (FID, 10^7) [7] exceeds the linear range of the carbon channel of the element-specific detector. This is not surprising, however, as FID is unsurpassed among GC detection methods in terms of its linear range. The comparison of the linear ranges of the chlorine and bromine channels with that of ECD is not so straightforward. In ECD the linear range is strongly dependent on the mode of operation (constant-current or constant-frequency mode). In the constant-current mode this value can be as high as 10^4–10^5, similar to those of the Cl and Br channels, with a concomitant decrease in sensitivity and the disadvantage that for compounds with ultrafast electron attachment rate constants ($2.8 \cdot 10^{-7}$–$4.6 \cdot 10^{-7}$ ml/molecule·s; Cl_4, SF_6, $CFCl_3$, CH_3I) the detector shows non-linear response behaviour. In the constant-frequency mode the linear range of ECD is not more than 100 [6].

The linear range of the sulphur channel of the element-specific detector can be compared with that of the flame photometric detector which has values between 500 and 1000 depending on the structure of the functional group containing the sulphur atom [7].

An additional comment on the comparison of the linear ranges of the different detectors is worthy of note. For a conventional GC detector the value is usually given with integers, as it is strongly dependent on the type of compound being analysed. For the element-specific detector, however, the response is proportional only to the number of atoms of a given element

irrespective of the type of substance, hence the second digit may also be significant.

Limit of detection

Although in theory the element-specific detector is a mass flow-sensitive GC detector, in contrast to the electron-capture detector, which has a concentration dependent response, direct comparison of the detection limits is feasible. In practice, calibration and the subsequent quantitative analysis are always carried out under constant, optimized experimental conditions. In this case the limits of detection can be expressed in mass/time or number of moles/time units for both types of detector. A chromatographic peak given by 14 pg/s of chlorine on the chlorine channel is depicted in Fig. 2.

Each of these values is worth comparing with those given a common GC detector or similar application, taking into account the differences in the mechanisms of their operation. The limit of detection of the carbon channel of the element-specific detector is of the same order of magnitude as that for FID (2–5 pg/s). As a consequence of the operating principle of the FID instrument, its response is proportional to the number of "effective" carbon atoms capable of hydrogenation. The signal is the largest for hydrocarbons, truly proportional to the number of carbon atoms, whereas compounds containing
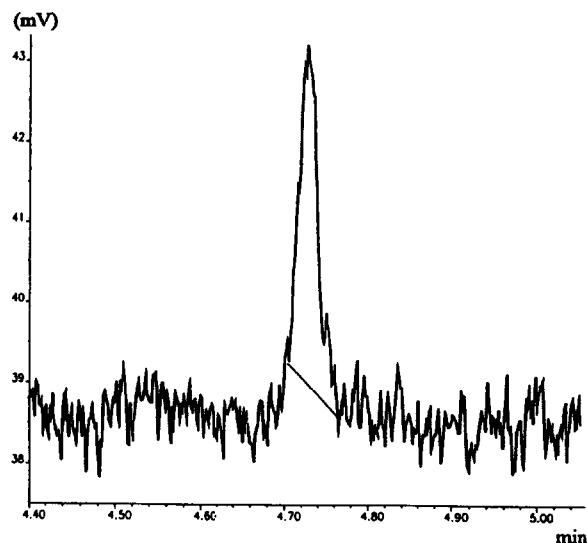

Fig. 2. Signal for 14 pg/s of chlorine on the chlorine channel.

nitrogen, sulphur or halogens yield smaller responses depending on the character of the heteroatom and the electron affinity of the combustion products. The effective carbon number can be estimated from the contributions of carbon atoms and other elements. The detection limit in FID is most often given for members of the n-alkanes (e.g., n-butane), for which direct comparison with that of the carbon channel is feasible.

The detection limits of the chlorine and bromine channels of the element-specific detector can be compared with that for ECD. The fundamentally different operation principle and selectivity of the electron-capture detector (the latter covers six orders of magnitude) and the differences between their operation modes and the strong dependence on experimental parameters make this comparison ambiguous. The detection limit in ECD is most often quoted for lindane (hexachlorocyclohexane) (50 fg/s). The detection limit obtained for the chlorine channel can be re-calculated for this compound, yielding a value of 20 pg/s. In this respect the element-specific detector can only be competitive with ECD for compounds containing one (or two) chlorine or bromine atom(s).

The detection limit of the sulphur channel can be compared with that in flame photometric detection (FPD). The value obtained for the element-specific detector is normally lower than those reported for FPD (5–50 pg/s). The response for FPD, however, depends slightly on the substance to be determined.

Selectivity

For the definition of selectivity, the cross-interactions of the different channels should be considered in the form of a matrix. Quantification of these effects, however, is hampered by the fact that the disturbance on a given channel may reflect the contributions of all the atoms in the detector and not only of those giving signals on the other channels.

Therefore, the selectivity of the different channels of the element-specific detector, in fact the only one among the parameters of the detector, depends on the type of interfering substance,

hence its determination is mostly linked to a particular application.

The most important effect among the cross-interactions is the effect of hydrocarbons on each of the selective channels. During the elution of the solvent peak, especially when a larger sample volume is injected at a low splitting ratio, the change in the physical conditions of the plasma is noticeable with concomitant disturbances on the selective channels. This region of the chromatogram is best avoided by optimizing the conditions of separation and selecting a suitable programme for the detector.

Apart from the peak of the solvent, hydrocarbons have little effect on the other channels with the exception of the sulphur channel. During the elution of 11 nmol/s carbon atom a distinct chromatographic peak appears on the sulphur channel, giving a selectivity ratio of 550. This value is poor compared with the similar parameter in FPD (10^4–10^5) and raises serious doubts about the applicability of this channel for more complex samples.

In addition, considerable cross-effects can be observed between the selective channels of the element-specific detector; 1.5 nmol/s of chlorine atom (in tetrachloroethylene) yielded a chromatographic peak on the bromine channel, whereas 1.1 nmol/s of bromine atom (in bromoform) gave a peak on the chlorine channel. Above these critical amounts the selectivity ratios for chlorine/bromine and bromine/chlorine were *ca.* 600 and 400, respectively. Sulphur gave a signal on the chlorine channel in amounts as low as 400 pmol/s with a selectivity ratio of 800. These cross-effects are illustrated in Fig. 3.

The carbon channel shows the elution of n-hexanethiol (6.9 min) and bromoform (7.1 min) with baseline resolution. The amounts of carbon atoms entering the detector were 7.13 and 1.68 nmol, respectively. Their effects on the chlorine channel clearly reflect that pseudo-peaks primarily result from the effects of the sulphur and bromine atoms. The ratio of the two pseudo-peaks can be accounted for by the amounts of the two elements and the corresponding selectivity ratios. These phenomena may be interpreted as follows. First, there may be some overlap between the emission lines of different
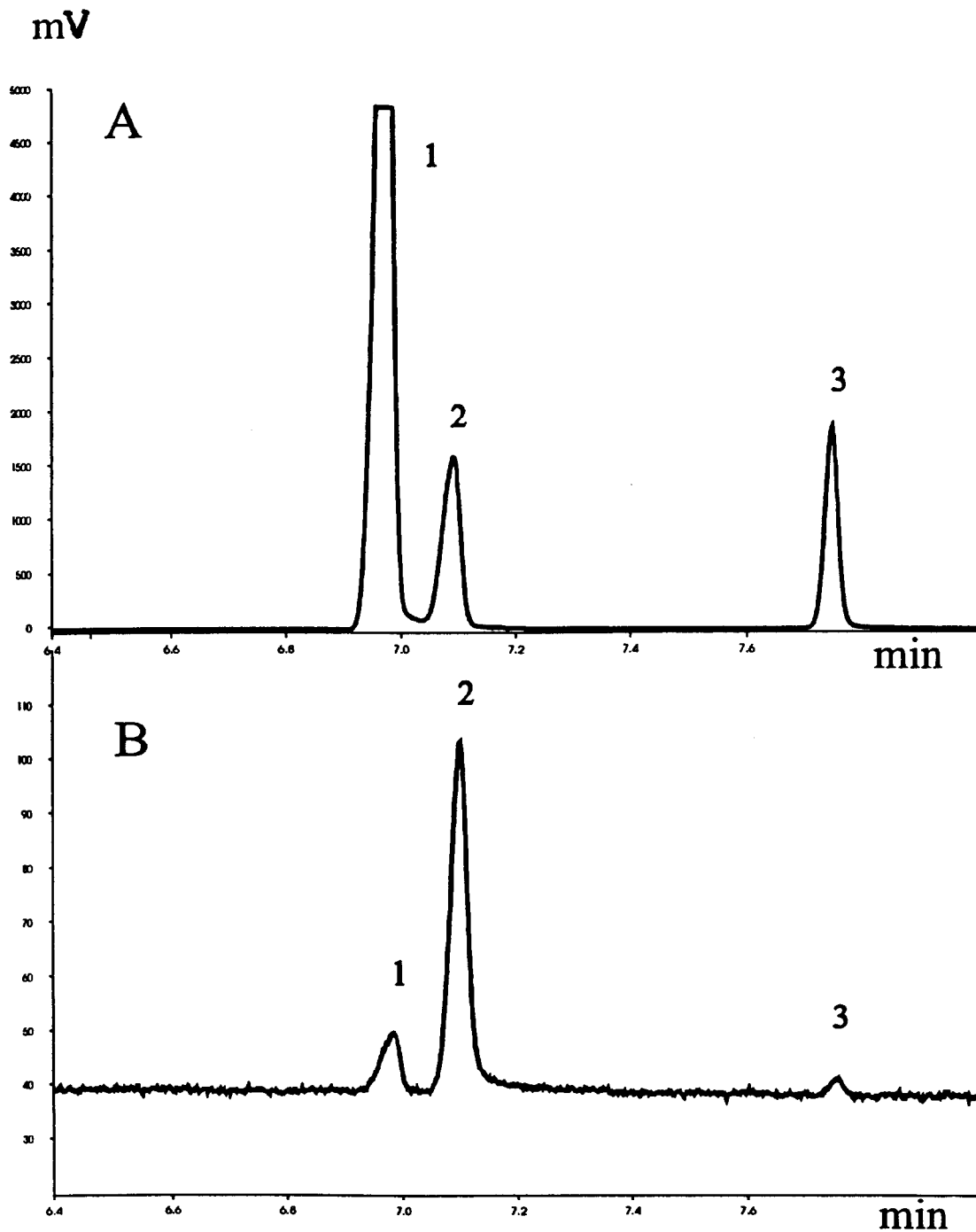
Fig. 3. Effect of sulphur and bromine on the chlorine channel. (A) Carbon channel; (B) chlorine channel. Peaks: 1 = *tert.-*pentanethiol; 2 = bromoform; 3 = *n*-decane.

elements. For example, chlorine gives an emission line at 827.4 nm whereas the bromine signal is measured at 827.2 nm. Similarly, bromine gives an emission line at 836.2 nm in the vicinity of the selected line for chlorine (837.2 nm). Second, some cross-effects may be experienced through a change in the chemical conditions in the plasma. The evaluation of these effects, however, is fairly academic. On a high-resolution fused-silica capillary column, two compounds containing different heteroatoms can probably be separated from each other. From practical considerations, only the selectivity with respect to hydrocarbons is of importance, which is normally good for the selective channels except the sulphur channel.

Advantages of the element-specific detector in qualitative and quantitative analyses

One of the most important advantages of the element-specific detector is that the detector is capable of the truly simultaneous acquisition of four virtually independent chromatograms without splitting of the flow. Therefore, the amount of information supplied by the detector is unsurpassed among conventional GC detectors. The fact that the signal is proportional to the amount of the element gives the detector unique selectivity and helps in the identification of the compounds. From the signal of the different channels the mole ratios of the elements can be calculated, allowing the determination of molecular formulae and increasing the probability of positive identification of the unknown compounds.

Experimental C:X mole ratios were calculated for four halogenated compounds at two concentration levels (see Experimental). The number of moles were determined from the corresponding calibration graphs and their ratios were calculated. The results are given in Table III. Although the values found are different from the theoretical values, they can still be related to the correct integers. The departures from the theoretical values can partly be explained by the fact that calibration graphs for the elements chlorine and carbon were established using compounds not included in Table III. In addition, the fact that the ratios are closer to the theoretical values

TABLE III

EXPERIMENTAL C:X MOLE RATIOS AT TWO CONCENTRATION LEVELS

Compound	Solution 2	Solution 1
Carbon tetrachloride	1:3.83	1:3.91
Tribromomethane	1:3.07	1:3.03
Bromobenzene	5.78:1	5.81:1
Chlorobenzene	6.11:1	5.99:1

at higher concentrations may imply that the amounts in solution 2 are fairly close to the lower end of the calibration graph, introducing a larger bias to the determination of mole ratios.

As, in theory, the signal of each channel is directly proportional to the amount of the element and independent of the structure of the compounds, a single standard for each element should be appropriate for determining the concentration of any compounds containing the given element. This assumption was tested with a model solution containing four halogenated compounds. The concentrations were determined using the previously established calibration graphs. The results of the single standard measurements are given in Table IV.

The results are in fairly good agreement with the true concentrations except for 2-bromochlorobenzene (on both the chlorine and bromine channels), where the interferences between chlorine and bromine (as discussed with respect to the selectivity of the detector) can be held responsible for the observed bias. The good accuracy of the single standard measurements implies that there is no need to run calibration samples in order to determine the response factors of the individual compounds. This is a great advantage over the conventional GC detectors where the determination of response factors in a separate set of calibration experiments for each compound to be quantified is essential.

The parameters of the detector allocate the potential field of application where its advantages can be fully exploited. In laboratories where samples of changing character are frequently encountered, the element-specific detector may be superior to conventional GC detec-

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TABLE IV

RESULTS OF QUANTIFICATION WITH A SINGLE STANDARD PER CHANNEL

Compound	Concentration found (μg/l)[a]	True concentration (μg/l)
Carbon tetrachloride	457 ± 23	470
Tribromomethane	1261 ± 49	1320
2-Bromochlorobenzene[b]	2031 ± 198	1615
2-Bromochlorobenzene[c]	2124 ± 182	1615
Chlorobenzene	752 ± 15	740

[a] Mean ± standard deviation ($n = 6$).
[b] Determined on bromine channel.
[c] Determined on the chlorine channel.

tors as it may considerably reduce the efforts required for the preparation of calibration solutions and their measurements and evaluation.

In addition, the element-specific detection can be simultaneously operated as a universal or selective detector. It is uniquely versatile, responding quickly to incoming samples requiring different types of detectors without instrumental modification or extensive calibration measurements. All these facets can be achieved without any compromise in quantitative analysis within the framework allocated by the parameters of the detector.

CONCLUSIONS

The most important parameters of GC detectors were determined for the four channels (C, Cl, Br, S) of the element-specific detector. Each parameter of the channels was compared with the performance of a common GC detector of similar application with regard to the basic differences in the operational mechanisms.

The sensitivities were found to be nearly identical for all channels. The values were dependent on the flow-rates of the plasma and dopant gases. The responses of the carbon, chlorine and bromine channels were linear whereas the sulphur channel showed non-linear characteristics, its linearity parameter being 1.4. This finding calls for further investigation. The linear ranges for all channels covered 4–5 orders of magnitude. The values were worse than the corresponding parameter for FID but generally exceeded the values for other selective detection methods (ECD, FPD).

For detection limits the standard classification of GC detectors were neglected (mass flow- or concentration-sensitive detectors) and limits of detection were determined at the optimum experimental parameters. The detection limit of the carbon channel (7 pg/s) was similar to that of FID. For the chlorine and bromine channels (14 and 25 pg/s, respectively) these parameters were generally worse than those of ECD. The detection limit obtained for the sulphur channel was usually lower than that of FPD. The selectivities of the channels towards hydrocarbons were exceptionally good for the chlorine and bromine channels whereas it was poor for the sulphur channel, limiting its applicability in the case of complex samples. In contrast, there were considerable cross-effects between the selective channels. The selectivity ratios varied between 400 and 1600, but these effects are rather academic.

The fact that the detector is capable of acquiring four different, universal and selective chromatograms at the same time considerably increases the probability of positive identification of analyte compounds. As the signal on each channel is directly proportional to the amount of the given element, the concentration of any compound can be determined with a single standard without the need to determine response factors in separate calibration measurements.

The element-specific detector is a versatile

instrument for laboratories encountering a flow of samples requiring different types of detectors even with a single gas chromatograph.

ACKNOWLEDGEMENTS

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