A SEMI-SPECIFIC FLAME-IONIZATION DETECTION SYSTEM

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SUMMARY

A modification of the flame-ionization detector (FID) has been designed, based on the change in the detection mechanism due to a pre-reaction zone containing a heated hydrogen path and the simultaneous handling of the signal by parallel combination with a normal-mode FID. Owing to the reactions in the pre-flame zone, organic substances are cracked and the reactions lead to higher yields of radicals, in addition to hydrogenation reactions.

The simultaneous use of a normal FID together with this modified FID, which is called an EFID (thermally and chemically energized) permits the identification of organic substances by means of numerical factors related to the structure and particular behaviour of the EFID. These numerical factors are, within the linear dynamic range of the detectors, highly reproducible, because of the exclusion of all chromatographic errors and sampling problems.

The parallel use of the EFID/FID system is demonstrated with examples and some results are reported.

This simultaneous EFID/FID is especially useful for the analysis of compounds of similar structure and gives more information about one sample than highly specific detectors of the element-sensing type such as the NID, SID and PID, halogen detectors and the oxygen-sensing FID.

INTRODUCTION

The flame-ionization detector (FID) is widely used in gas chromatography (GC) and its underlying mechanism is the subject of continuous research. The normal FID uses a diffusion flame, the eluate and hydrogen being mixed after the GC column. It has been found that only this arrangement gives a constant response related to the CH_2 groups of organic substances[1]. It has also been shown that temperature has an important effect on the magnitude of the FID signal.

On the basis of our earlier results[2], we can state that the ionization efficiency of FID increases rapidly with the number of CH_3 functional groups present in organic molecules and that the proportion of $CH_3 \cdot$ radicals is correlated with the resulting FID ion current.
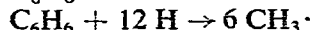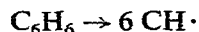
The mechanism of the FID is based on two steps:

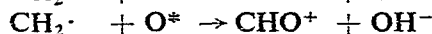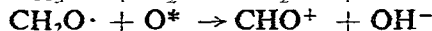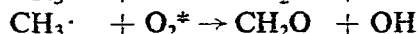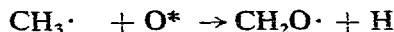(1) radical formation, requiring the absence of oxygen;

(2) chemical ionization of radicals formed by excited atomic or molecular oxygen states.

It is possible to change the resulting ion current due to reactions that decrease the yield of the recombiantion reaction. By changing the radical formation in step 1, we can obtain a higher yield of $CH_3\cdot$ radicals and, as the $CH_3\cdot$ radical has at least a 10 times higher ionization efficiency than the $CH\cdot$ radical, the magnitude of the FID signal is increased[2].
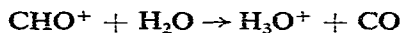
The equations involved in step 1 are:

$$C-C-C-C-OH \rightarrow 1\ CH_3\cdot + 3\ CH_2\cdot + OH\cdot$$
$$C-C-C-C-OH + H \rightarrow 4\ CH_3\cdot + OH\cdot$$
$$C_6H_6 \rightarrow 6\ CH\cdot$$
$$C_6H_6 + 12\ H \rightarrow 6\ CH_3\cdot$$

The equations involved in step 2 are

$$CH_3\cdot\ \ + O^* \rightarrow CH_2O\cdot + H$$
$$CH_3\cdot\ \ + O_2^* \rightarrow CH_2O\ + OH$$
$$CH_2O\cdot + O^* \rightarrow CHO^+ + OH^-$$
$$CH_2\cdot\ \ + O^* \rightarrow CHO^+ + OH^-$$

In an atmosphere of water vapour, the primary CHO^+ ions formed react rapidly and a hydrated proton is formed[3,4]:

$$CHO^+ + H_2O \rightarrow H_3O^+ + CO$$

and the probability of recombination increases.

EXPERIMENTAL

The measurements were carried out on the apparatus shown schematically in Fig. 1. The eluate from the column was split into two streams, to one of which hydrogen at a flow-rate of about 50–100 cm^3/min was added before the EFID inlet. The materials used were stainless steel, nickel and nickel in platinum–iridium alloy tubes.

The tubing of the EFID was heated by an external heating coil to 200–550°. The whole arrangement was mounted within a Model F 22 gas chromatograph (Perkin-Elmer Bodenseewerh), allowing both the EFID and FID signals to be measured simultaneously and independently. Separations were carried out on various micropacked glass columns in separation cassettes (IfC), 2–3 m in length and 0.8 mm I.D., packed with 80–100-mesh synthetic carrier material (Merck, Darmstadt, G.F.R.) and OV-101, UCON 50 HB 5100 and OV-225 as liquid phases.

The signal was handled off-line by measuring the peak height data from the recorded chromatogram as well as integrated areas from a Spectra Physics System 1 integrator and a Spectra Physics Minigrator for the double-channel signals. Direct conversion of simultaneous signal to peak ratios by a multi-integration system such as the Spectra Physics 4000 would be the best solution to the problem, but this is not yet possible.
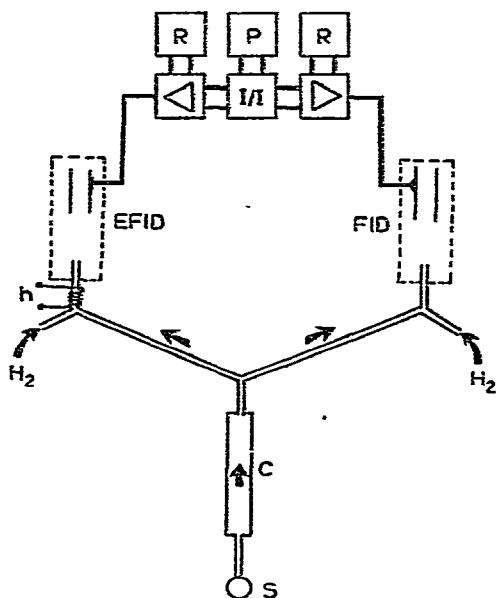
Fig. 1. Schematic diagram of EFID–FID combination. S = sample inlet; C = column; h = heating device; R = recorder; I/I = double-channel integrator with signal relation capability for channel one/channel two; P = printer for relative adjusted retention time data $k' = (t_{ms} - t_m)/t_m$, area correction and quantitation from FID channel and together with the k' data s_x number presentation.

RESULTS AND DISCUSSION

The changes in ionization efficiencies are based on cracking reactions in front of the flame, termed the pre-reaction zone. It was assumed that the radical formation changes owing to the change in temperature. At low temperatures, the formation of $CH_3 \cdot$ radicals does not occur and therefore there is no difference in the signals in the normal FID and the EFID modes. If electronegative groups or atoms are present, the EFID signal must be smaller than the FID signal owing to an increased probability of electron recombination.

With increasing temperature, the yield of $CH_3 \cdot$ radicals is increased and, owing to its higher ionization efficiency, the EFID signal must be higher than that of FID.

The signal of a compound X in an FID can be written as S_X^{FID} and we can write

$$S_X^{FID} = q_X^{FID} \cdot \frac{c}{n}$$

where q_X^{FID} is the ionization efficiency of substance X in the FID mode, c is the concentration in the effective detector volume or flow-rate in grams per second and n is the number of carbon atoms in one molecule of X. The resulting signal of the same compound X in the EFID can be written as

$$S_X^{EFID} = q_X^{EFID} \cdot \frac{c}{n}$$

A simultaneous but not identical flow of X into both detectors will remain constant, when the pressure, temperature, flow-rate, etc. remain constant.

If we use methane as a normalizing compound, the relationship of the CH_4 signal (FID) to the CH_4 signal (EFID) will remain constant and acts as an equalization factor, as

$$q_{CH_4}^{FID} = q_{CH_4}^{EFID}$$

Therefore

$$\frac{S_{CH4}^{FID}}{S_{CH4}^{EFID}} \cdot \frac{S_X^{EFID}}{S_X^{EFID}} = \frac{q_X^{EFID}}{q_X^{FID}} = s_X \tag{1}$$

s_X is a numerical factor, that corresponds to the structure of a compound under given conditions of the EFID–FID detection system.

s_X is independent of the concentration or flow-rate of X, provided that both detectors remain in their linear dynamic range. Therefore, s_X is a function only of the different ionization efficiencies in the simultaneously operating detectors and is an identification number, independent of all possible errors of sampling, vaporization, separation, column polarity and disproportionation at the inlet splitter, if present. Of course, for s_X to offer precise information for identification purposes, a complete separation into individual compounds is necessary.

It has long been known that relative response factors can be useful in making qualitative identifications. However, they cannot act as identification numbers, for instance in hydrocarbon class identifications, nor are highly specific detectors, used simultaneously with non-specific detectors, a real help in identifications, for instance in the trace level range, as the differences in the q factors are often too large. It is the semi- or moderate specifity of the EFID together with a normal FID that can help analysts to solve qualitative analysis problems in GC. There are many possibilities for changing the specifity of the EFID, but only slight changes are of interest in order to help positively with identification. For instance, temperature effects change the q to q relationship (see eqn. 1).

Temperature effects

Temperature effects were studied in the range 20–750°. Between 20° and 200°, s_X changes significantly for substances that contain electronegative atoms in their molecules. At 500°, most of the structure-dependent quantitative reactions are stabilized to constant values. Above 500°, futher effects become dominant and the materials of tubes tend to have a greater influence.

Fig. 2 illustrates as an example the effect of temperature at the EFID inlet, and Table I gives further data.

Effect of material used for the reaction tube

Stainless steel, nickel and nickel in platinum–iridium alloy (75:25%, w/w) were examined and the results are given in Table II. The lifetime of nickel tubes does not permit their use without an inert environment.
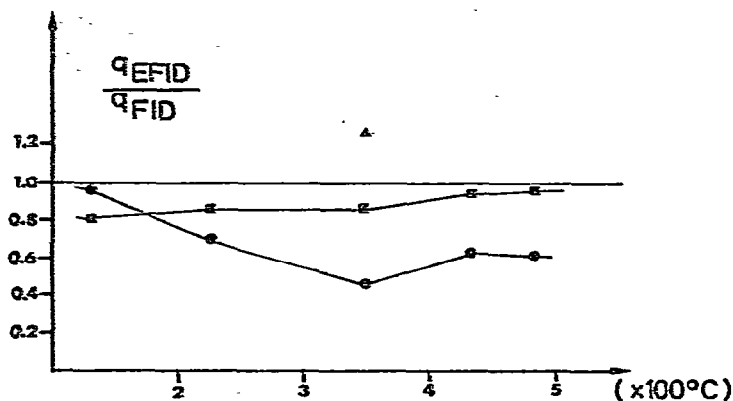
Fig. 2. Dependence of ionization efficiency ratio (q_{EFID}/q_{FID}) on the temperature applied to the EFID inlet. ▲, 1-propene; ●, methyl chloride; ■, 2-methyl-1-propene.

TABLE I

EFFECT OF EFID TEMPERATURE ON THE STRUCTURE FACTOR (s_x)

Conditions: stainless-steel tube, 140-mm heated zone, 0.8 mm I.D.

Compound	s_x			
	100°	200°	400°	500°
n-Heptane	1.00	1.00	1.00	
Benzene	1.01	0.98	0.91	
Methyl propyl ketone	1.00	0.33	0.28	
n-Nonane	1.00		0.99	
n-butanol	1.01	0.286	0.29	
n-Decane	1.01	0.83?	0.98	
Pyridine	1.01		0.42	
	Coefficient of variation: ± 0.3%			
Ethanol			0.467	
2-Propanol			0.885	
1-Propanol			0.676	
2-Methyl-1-butanol			0.833	

TABLE II

EFFECT OF TUBE MATERIAL ON s_x

Tubing material	s_x at 400°			
	n-Butane	2-Methyl-1-propene	1-Butene	Methyl chloride
Stainless steel	0.625 ± 0.008	0.763 ± 0.011	0.774 ± 0.008	0.683 ± 0.007
Nickel	1.186 ± 0.011	1.030 ± 0.046	1.279 ± 0.025	0.600 ± 0.008

We consider that metallic traces on the inner surface of the tubes are of importance, and a precisely known surface quality is essential.

TABLE III

PARAMETERS OF EFID AND FID

Mode	Compound	Linearity	Linear dynamic range	Lowest detectable amount (g)
EFID	CH_4	0.588	6	2.8×10^{-11}
	CH_2Cl_2	8	8	6.3×10^{-12}
FID	CH_4	0.629	4.7	1.6×10^{-11}
	CH_2Cl_2	0.503	5	8.6×10^{-11}

Linearity, linear dynamic range, detection limit (lowest detectable amount, LDA)

The logarithmic dilution flask method was used. Measurements were carried out with methane and methylene chloride and the results are given in Table III.

The calculation of the detector parameters is based on eqns. 1–4 below[5]. For measurements of the linearity (*l*) of detectors, eqn. 1 holds:

$$l = \frac{\log n \cdot S^{EFID} - \log q_X^{EFID}}{\log w} \tag{1}$$

where n = number of carbon atoms: S = signal for X in amperes; q_X is the ionization efficiency of X in ampere·seconds per gram; and w is the amount of compound X in grams per second.

For the linear dynamic range $(\alpha_2 - \alpha_1)$ of detectors, eqn. 2 holds:

$$\alpha_2 - \alpha_1 = \log S_{\alpha_1}^{EFID} - \log S_{\alpha_2}^{EFID} \tag{2}$$

when the amount of substance is changed in the interval from $10^{-\alpha_2}$ to $10^{-\alpha_1}$ and in which the linearity (*l*) is constant.

For the lowest detectable amount, (w_{LDA}) eqn. 3 holds:

$$\log w_{LDA} = \frac{\log \Delta S^{EFID} - \log q_X^{EFID}}{l} \tag{3}$$

where $\Delta S^{EFID} = 2K(S_{noise})$ (4)

and K is the chosen probability constant[5], which is as follows:

n	K for 95% probability	K for 99% probability
3	5.2	12.04
5	2.04	3.36
10	1	1.32

where n is the time range for noise measurements and $n = 3.40$ times the peak width at half-height for substance X.

On the basis of the results obtained, the hydrogenation of eluted substances plays an important but not the only role. The magnitude of the EFID signal depends on temperature and the material used, which has an important catalytic effect.

In the mechanism of EFID, two phenomena are dominant: cracking leads to radical formation, and in the presence of electronegative groups or atoms there is a higher probability of recombination. This phenomenon is demonstrated with alcohols. Isoalcohols generally produce a higher signal than n-alcohols, as they have more CH_3 groups per molecule. When the substances do not carry electronegative atoms, the EFID signal is determined by the yield of $CH_3\cdot$ radicals. If hydrogenation of unsaturated hydrocarbons was the only reaction in the EFID mechanism, the resulting signal could not be higher than that of saturated hydrocarbons. The experimental results, however, show higher signals for unsaturated hydrocarbons, and $CH_3\cdot$ formation is therefore probable.

The repeatibility of the data for s_X is high, as demonstrated by the value of estimated standard deviations. Values of s_X are generally lower for substances with electronegative atoms, but the EFID tested showed a broader linear dynamic range and a smaller lowest detectable amount when compared with the normal FID (same type electronics, geometry, manufacturer, materials, etc.).

These preliminary results should serve as a basis on which further development will continue.

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