

# STUDIES ON THE FLAME IONIZATION DETECTOR SIGNAL IN THE PRESENCE OF ORGANOSILICON COMPOUNDS

## A METHOD FOR THE REGISTRATION OF THE DETECTOR PERFORMANCE

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### INTRODUCTION

An outline has been given, in an earlier communication from this laboratory<sup>1</sup>, of the observations made on the anomalous behaviour of the flame ionization detector (FID) in the presence of organometallic compounds. It was found that, under conditions which gave normal or even ideal detector performance for organic compounds, inversion of the gas chromatographic peaks occurred with organosilicon, organogermanium and organotin compounds. This phenomenon was observed with both types of detectors used in the experiments. The experiments reported in this paper were restricted to organosilicon compounds.

According to our experience, the inversion of peaks had no relation to the slight deposition of  $\text{SiO}_2$  on the electrodes.

The inversion of the peak, *i.e.* the decrease of the ion current at increasing mass flow rates takes place when the silicon mass flow rate exceeds a critical value in the flame. On the basis of our previous experiments it has been stated that the critical values of the silicon mass flow rate, as well as the maximum ion current, depend on the following factors: detector geometry, detector voltage, the flow rates of the carrier-, fuel- and scavenging gases and the actual carbon mass flow rate in the flame, the extent of which is determined by the composition of the organosilicon compound tested. Except this last factor, these are the same as those which influence the sensitivity and the linearity range of an FID when measuring organic compounds. All experimental conditions being constant, the maximum height of the inverted peak depends only on the carbon/silicon molar ratio of the test substance.

In our previous communication<sup>1</sup>, the application of an FID operating with a mixed hydrocarbon-hydrogen flame was also described. This arrangement detects organometallic or other volatile metallic compounds by a decrease of the ion current.

Following these observations, a more detailed investigation of the peak inversion seemed to be reasonable. A number of experiments was needed to afford the possibility of making a comparison between detector signal produced by organic and organosilicon compounds under different conditions.

Plotting of response curves, *i.e.* detector signal *vs.* mass flow rate, was chosen as the basis of the comparative examinations, as described by BRUDERECK *et al.*<sup>2</sup>. Con-

sequently the following terms will be used in the subsequent discussion for characterising the performance of the FID:

The *response factor* ( $r$ ), the proportionality factor in the equation  $I = r \cdot g(C) \cdot t^{-1}$ . Since the numerical value of " $r$ " is equal to the ion current ( $I$ ) produced by the unit of carbon mass flow rate, MFC [ $g(C) \cdot t^{-1}$ ] in the flame, it is a measure of the detector sensitivity. For convenience, " $r$ " is usually expressed in millicoulombs/gram carbon.

The *linearity range* is defined by the constancy of the response factor. The value of the ion current and the carbon mass flow rate at the upper limit of the linearity range are designated as " $I_{linear}$ " and " $MFC_{linear}$ ", respectively.

It is obvious from the foregoing discussion that under those circumstances when peak inversion takes place, the response curves display a maximum. For this reason, further characteristics of the detector performance had to be introduced in the case of organosilicon compounds: the value of the ordinate at the maximum of the curve is called the "*limiting ion current*" ( $I_{lim}$ ), while the abscissa, called the "*limiting mass flow rate*", represents the mass flow rate at which the inversion of the peak takes place. This may be expressed either in terms of carbon mass flow rate ( $MFC_{lim}$ ) or in silicon mass flow rate ( $MFSi_{lim}$ ).

The dependence of these parameters on the operating variables of the FID had to be subjected to systematic investigation in order to explain the anomalies observed in the presence of organometallic compounds.

A method is presented in the first part of this paper, by means of which a record of the response curves for different substances may be obtained from a single chromatogram with great relative accuracy. In the second part a discussion of some experimental results illustrates the efficiency of this method.

#### PRINCIPLES OF THE AUTOMATIC RECORDING OF RESPONSE CURVES

The usual way of determining response characteristics of a mass flow rate sensitive detector is to measure the ion current at different known levels of continuous mass flow through the detector<sup>3</sup>. However, the application of a continuous mass flow proved to be impracticable in the case of organosilicon compounds, in consequence of the deposition of a considerable quantity of  $SiO_2$  on the electrodes.

In the experiments already reported<sup>1</sup>, the response curves were obtained by recording series of chromatograms. Increasing quantities of a mixture of known composition were injected and the values of the ion current at the peak maxima were plotted against the corresponding mass flow rates, calculated as follows.

At a first approach, the peak was assumed to be a triangle, the height of which—representing the maximum mass flow rate ( $MF_{max}$ )—may be expressed by the equation:

$$MF_{max} = \frac{2G}{t}$$

If  $G$  represents the weight of the sample in micrograms and  $t$  the peak width at the base expressed in seconds, then  $MF_{max}$ , the mass flow rate at the peak maximum is obtained in microgram/seconds. As second approach, the  $MF_{max}$  values were then multiplied by a correction factor of 0.81, originating from the assumed Gaussian shape. The MFC terms used were derived from these corrected  $MF_{max}$  values.

This method was rather time-consuming and involved some uncertainties, partly arising from the limited accuracy of determining the sample quantity, but mainly from the distortion of the peaks, occurring with large sample quantities. This factor was rather considerable in the case of inverted peaks, so that in the very region of the anomalous responses the response curves became unreliable. The slight deviation of the shape of the peak from a Gaussian one, occurring at low sample quantities, may be regarded as the reason for uncertainties in determining MFC values in the linear range. The accuracy of the " $\gamma$ " values derived from these MFC values was  $\pm 2.5\%$  when introducing small samples in the column.

In addition, the situation of the maximum of the response curves could only be determined by a fairly inaccurate graphical method as a consequence of the discontinuous method in plotting the curves.

The principles of the new method for the recording of the response curves may be summarized as follows.

A chromatographic peak is essentially a continuous recording of the ion current values, pertaining to mass flow rates varying from zero to a maximum value, defined by the quantity of the sample and the width of the chromatographic band. If the momentary values of the mass flow rate were known at any moment during the elution of the band, it would be possible to plot the response curve on the basis of a single chromatographic peak. Having, however, a detector which is supposed to function linearly throughout the whole range of mass flow rates occurring in the peak, the momentary values of the mass flow rates could be calculated at any point of the peak from the detector signal and the characteristic " $\gamma$ " value of the detector.

Providing that a perfectly synchronous change of the mass flow rate can be obtained in two FID-s with different performances, one of them being a reference detector (FID<sub>RX</sub>) with constant response, and the other one the detector to be investigated (FID<sub>IY</sub>), the signal of the latter may be recorded as a function of the reference detector signal by means of an X-Y recorder, the two channels of which are controlled by the signals of the FID<sub>RX</sub> and the FID<sub>IY</sub>, respectively.

The abscissa of the X-Y diagram thus obtained represents the ion current of the FID<sub>RX</sub>. If the " $\gamma$ " factor in the FID<sub>RX</sub> is known from independent measurements, the ion current data on the abscissa may be converted into mass flow rate values, and the diagram will represent the response curve of the FID<sub>IY</sub>. In fact, the method employed earlier and already reported was the only way to derive the " $\gamma$ " factors needed.

#### APPARATUS AND TECHNIQUE

The experiments were carried out with a Carlo Erba Fractovap C type PAID/ff dual column gas chromatograph equipped with two flame ionization detectors. Some modification of the apparatus was needed for the special purpose of the present investigation.

The original detectors were of the parallel electrode type, connected with opposite polarity to the PAID/ff electrometer amplifier, in order to give difference signals. One of them was replaced by a detector in which the jet was functioning as anode, the cathode being a platinum cylinder of 8 mm diameter and 10 mm height. This arrangement served as reference detector. In the other detector the electrodes

were parallel platinum plates, situated laterally to the flame. Variation of the electrode gap was afforded by means of screws. This detector was disconnected from the circuit of the PAID/ff instrument and operated independently, in connection with a Vibron electrometer. The two channels of a Philips PR 2220 A/00 X-Y recorder were controlled by the signals of the PAID/ff electrometer and by the Vibron electrometer, respectively. In addition, the detector signals were fed also into two Speedomax G recorders, so the chromatograms and their X-Y diagram were recorded at the same time. The Vibron electrometer used for measuring the ion current of the FID<sub>IV</sub> was supplemented with the necessary attenuating and compensating circuits in order to equalize the measuring ranges of the EA 1 and EA 2 electrometers. Thus it was possible to set the scales equal on both ordinates of the X-Y recorder. The schematic circuit diagram is shown in Fig. 1.

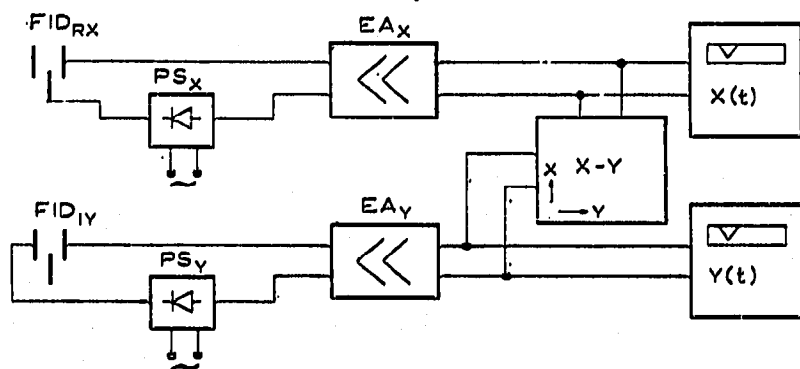


Fig. 1. Schematic circuit diagram. FID<sub>RX</sub> = Reference detector (jet-electrode type); FID<sub>IV</sub> = detector investigated (parallel-electrode type); PS<sub>X</sub> = power supply of the Carlo Erba Chromatograph, 150 V; PS<sub>Y</sub> = power supply, Solartron SRS 151 A, 20-500 V stab.; EA<sub>X</sub> = Carlo Erba Electrometer Amplifier  $5 \cdot 10^{-12}$ - $10^{-7}$  A.f.s.; EA<sub>Y</sub> = Electrometer Amplifier Vibron Mod. 33 C; A 33 C  $10^{-12}$ - $10^{-7}$  A.f.s.; X(t) Y(t) Speedomax G Recorders 1 mV f.s.; 1 sec. X-Y: X-Y Recorder Philips PR 2220 A/00.

In order to obtain a synchronous change of mass flow rates in the two detectors, a single chromatographic column was used for the separation. The column effluent was divided into two equal streams. These were conducted through capillary resistances to the detectors. Uncoated stainless steel capillaries of about 50 cm length and 0.1 mm diam. were used for this purpose. The length of the capillaries was adjusted so that the dead volumes and flow resistances between the junction point and the burner jet were the same in both branches. Fig. 2 shows the schematic flow diagram of the system.

There were two main points which had to be ensured before starting the experiments: (1) the synchronisation of the mass flow rates in the two detectors, and (2) the linear performances of the FID<sub>RX</sub>.

In order to verify that the mass flow rate of the sample eluted from the column was varying synchronously in both branches, the detectors were connected with opposite polarity to the same electrometer amplifier circuit and the difference of the two signals was recorded. The length of the capillary resistances was altered until a small symmetrical peak was obtained as difference-signal. If mass flow rates varied asynchronously in the two detectors, asymmetrical difference signals were recorded as shown in Fig. 3a-d. The small symmetrical peak shown in Fig. 3e indicates the

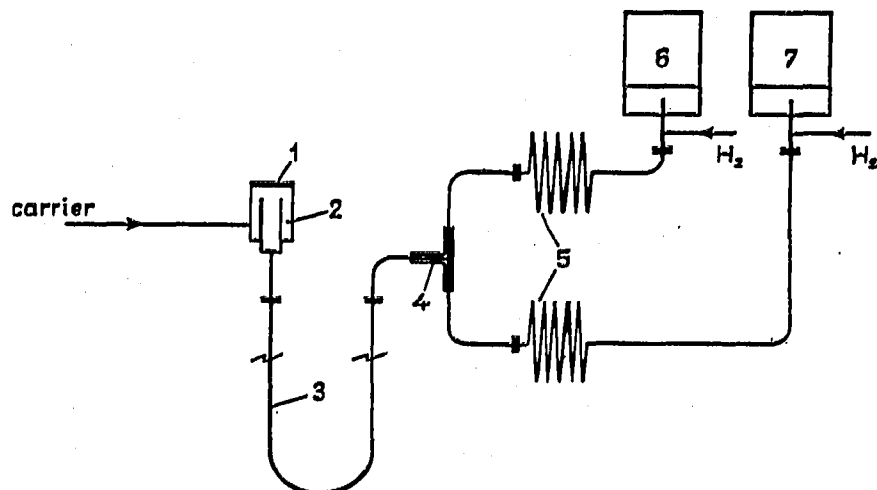


Fig. 2. Schematic flow diagram. 1 = Injection port; 2 = evaporator; 3 = chromatographic column; 4 = capillary splitter; 5 = capillary resistances; 6 = reference detector  $FID_{RX}$ ; 7 = detector investigated  $FID_{IV}$ .

synchronous mass flow in two detectors having slightly different sensitivities. In the case of two detectors of the same sensitivity, the difference signal would be zero, of course. Another possibility was also furnished in the course of the experiments for controlling the synchronism of the mass flow rates; under these conditions, where both of the detectors were functioning linearly, the response curves recorded were straight lines starting from the origin.

The geometric features and other operating variables of the  $FID_{RX}$  were arranged so as to ensure its linear functioning up to the highest possible mass flow rates. For each component of the mixture used in these experiments the response curves of the  $FID_{RX}$  were plotted by means of the method described earlier. These curves proved to be linear up to mass flow rates as high as  $1.3-1.5 \cdot 10^{-6}$  g C/sec for each component. Above these MFC values, a unidirectional deviation exceeding 2.5% of the "r" factors was noticed. As the linear performance of the  $FID_{RX}$  is a requirement of great importance, the mass flow rates were always kept far below the linearity limit during the runs.  $1.0 \mu\text{l}$  and in some cases  $1.2 \mu\text{l}$ , quantities of the mixture tested were introduced in practice to ensure that the MFC values occurring in the flame should not exceed  $1.0 \cdot 10^{-6}$  g C/sec.

In order to get information on the effect of the C/Si ratio of the sample detected, the mixture was made up in such a way as to contain several organosilicon compounds

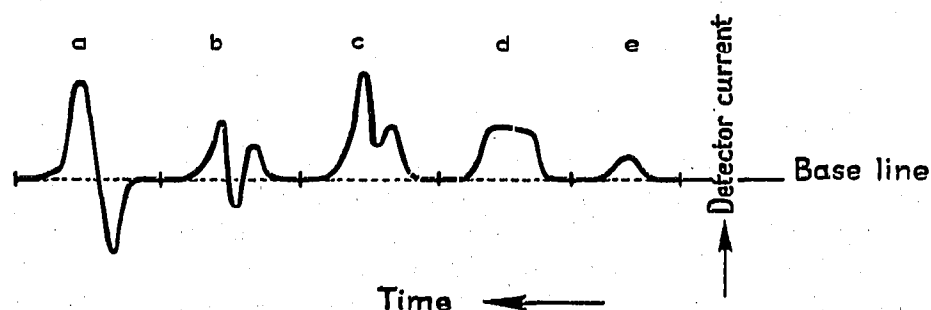


Fig. 3. Difference chromatograms of *n*-hexane.

of different C/Si ratio, and in addition a hydrocarbon, at the same time taking into account the requirement of a good separation. The components of the mixture are listed in Table I.

TABLE I  
COMPOSITION OF TEST MIXTURE CONTAINING ORGANOSILICON COMPOUNDS

Number	Compound	Concentration %	C/Si molar ratio
1	Benzene	60.5	—
2	Trimethyl-butenylsilane	3.9	7
3	Hexamethyl-cyclotrisiloxane	13.7	2
4	Divinyl-tetramethyldisiloxane	11.4	4
5	<i>o</i> -Xylene	10.5	—

The numbers in Figs. 4–8 refer to the same compounds as in Table I. Benzene served only for the dilution of the mixture to the required extent, therefore neither the peaks on the chromatograms, nor the response curves referring to benzene were recorded.

The mixture was separated on a chromatographic column of 3 m length and 2 mm I.D., containing 6 % of SE-30 silicon elastomer on Chromosorb W, thermostated to 56°. Nitrogen was used as carrier gas, at a flow rate of 19.2 ml/min. The electrodes of both detectors were cleaned with hydrogen fluoride solution after every 2 or 3 runs, in order to minimize the effect of the slight deposition of SiO<sub>2</sub>. The operating variables of the FID<sub>RX</sub> were as follows:

Carrier gas: 9.6 ml/min,

Hydrogen: 19.5 ml/min,

Oxygen: 200 ml/min,

Detector voltage: 150 V.

Response factors of the FID<sub>RX</sub> for the compounds used were calculated from series of chromatograms by the method described previously, and are listed in Table II.

As can be seen from the data in Table II, there is a pronounced difference between the individual response values. This fact has been taken into account when calculating the MFC values of the components in FID<sub>IY</sub> from the ion current measured in the FID<sub>RX</sub>.

TABLE II  
RESPONSE FACTORS OF THE FID<sub>RX</sub>

Compound	" <i>r</i> " (mC per g carbon)
Hexamethyl-cyclotrisiloxane	50.6
Xylene	47.0
Divinyl-tetramethyldisiloxane	47.5
Trimethyl-butenylsilane	46.4

The conversion of the  $FID_{RX}$  signal into MFC values, is based on " $r$ " factors computed by the method used in our previous work. Consequently, the absolute values of carbon mass flow rates attributable to the abscissa of the X-Y diagrams as well as the " $r$ " factors of the  $FID_{IY}$  may be assumed to have an error of  $\pm 2.5\%$ , this also being the accuracy in estimating the " $r$ " factors of the  $FID_{RX}$ , when operating linearly. If, however, constancy of the reference detector response and synchronism of the mass flow rates in the detectors, are assured, then the distances on the abscissa of the X-Y diagram are exactly proportional to the mass flow rates, even in the non-linear region of the  $FID_{IY}$  response curve where the mass flow rates could not have been computed otherwise, owing to the inversion of the peaks. Consequently, the shape of the response curves recorded continuously is always correct, *i.e.* its relative accuracy is no longer charged with the uncertainties arising from the method in calculating  $FID_{RX}$  " $r$ " factors.

During these experiments, the operating conditions of the  $FID_{RX}$  were kept constant, while those of the  $FID_{IY}$  were varied. Thus the influence of the operating variables on the characteristic parameters of the detector performance— $I_{lim}$ ,  $MFC'_{lim}$ ,  $MFSi'_{lim}$  and " $r$ "—could always be related to a fixed MFC scale on the abscissa. In this sense, the relative accuracy of these data was limited only by the precision of the electric equipment, which means 0.5%.

This great relative accuracy does not refer, of course, to the comparison of the components in a chromatogram, considering that the individual " $r$ " factors measured in  $FID_{RX}$  do not bear equally the uncertainties involved in the method of determination.

An indisputable advantage of the method is that the uncertainties arising from the graphical determination of the maximum on the plotted response curves are eliminated by the continuous recording.

TABLE III

CHARACTERISTIC DATA OF THE RESPONSE CURVES, OBTAINED AT VARIOUS OPERATING VARIABLES OF THE  $FID_{IY}$

No.	Detector voltage	% $H_2$	Electrode gap (mm)	Xylene			Hexamethyl-cyclotrisiloxane			
				$r$ (mcoul./gC)	$I$ linear ( $mA \times 10^{-5}$ )	MFC linear (gC/sec $\times 10^{-6}$ )	$r$	$I_{lim}$	$MFC'_{lim}$	$MFSi'_{lim}$
4	60	62	4.5	34.8	0.12	0.04	40.7	0.185	0.052	0.061
7	100	62	4.5	35.3	0.67	0.17	41.0	0.434	0.124	0.145
5	150	62	4.5	34.7	1.3	0.42	41.2	0.65	0.15	0.175
6	220	62	4.5	35.0	2.7	0.7	40.5	1.35	0.30	0.351
16	400	62	4.5	39.0	*	—	43.0	*	—	—
10	150	54	4.5	21.6	1.18	0.48	27.6	0.485	0.175	0.204
5	150	62	4.5	34.7	1.30	0.42	41.6	0.65	0.15	0.175
14	150	65.6	4.5	38.6	1.81	0.46	43.7	1.07	0.224	0.262
8	150	70	4.5	42.9	2.19	0.48	46.9	1.34	0.284	0.332
17	150	65.6	5.5	36.9	1.23	0.33	41.3	0.78	0.116	0.194
18	150	70.7	5.5	42.2	1.35	0.32	46.2	1.09	0.198	0.232
19	150	73.2	5.5	43.4	1.46	0.32	50.1	1.39	0.236	0.276

\* Not reached under the experimental conditions.

The application of this procedure is not limited, of course, to the study of the anomalous behaviour of the FID. With an appropriate selection of the reference detector it provides a quick and reliable method for studying the sensitivity, linearity and the optimal operating conditions of a gas chromatographic detector of any kind.

#### EXPERIMENTAL RESULTS

Response curves of the parallel-electrode type detector were recorded in three series:

(1) The detector voltage was varied with constant electrode gap and constant gas flow rates.

(2) The flow rate of hydrogen gas was varied with constant electrode gap and detector voltage.

(3) Variation of the hydrogen gas flow rate was repeated at the same detector voltage, but with a different electrode gap from that employed in case (2).

The operating parameters of the detector and the characteristic data of the response curves are listed in Table III. The actual gas flow rates are characterized by the percentage of hydrogen in the mixture emerging from the burner jet, calculated from the volumetric flow rates of nitrogen and hydrogen. The flow rate of the carrier gas was maintained at 10 ml/min in all experiments and pure oxygen was always used as scavenging gas at a flow rate of 200 ml/min. In agreement with the observations of STERNBERG *et al.*<sup>4</sup>, it was found that the response characteristics depend to a great extent upon the partial pressure of H<sub>2</sub> in the reaction zone of the flame.

Some of the response curves recorded are shown as examples in Fig. 5 I-VI, while Fig. 4 shows two chromatograms recorded synchronously, corresponding to

<i>Trimethyl-butenylsilane</i>				<i>Divinyl-tetramethyldisiloxane</i>			
$r$	$I_{um}$	$MFC'_{um}$	$MFSi'_{um}$	$r$	$I_{um}$	$MFC'_{um}$	$MFSi'_{um}$
32.0	0.294	0.114	0.038	~ 38	0.227	0.072	0.04
32.5	0.63	0.218	0.073	~ 38	0.535	0.143	0.083
31.4	0.97	0.32	0.107	~ 38	0.755	0.22	0.128
31.8	1.98	0.59	0.179	~ 38	1.58	0.415	0.242
38.0	*	—	—	~ 40	*	—	—
18.8	0.715	0.336	0.112	~ 24.5	0.585	0.236	0.137
31.4	0.97	0.32	0.107	~ 38	0.755	0.22	0.128
36.2	1.69	0.45	0.150	~ 41	1.3	0.299	0.174
40.7	2.27	0.58	0.19	~ 45	1.7	0.388	0.226
34.7	1.23	0.325	0.108	~ 39	0.98	0.232	0.135
40.0	1.72	0.385	0.128	~ 44	1.35	0.229	0.133
40.5	2.1	0.432	0.114	~ 46	1.67	0.318	0.185



run No. 18 in Table III. The measuring ranges of the EA1 and EA2 electrometers were set in such a way as to obtain a full-scale deflection of  $8 \cdot 10^{-5}$  mA on the abscissa and of  $4.21 \cdot 10^{-5}$  on the ordinate. (In Fig. 5:  $20 \cdot 0.40 \cdot 10^{-5}$  mA and  $10 \cdot 0.421 \cdot 10^{-5}$  mA, respectively.)

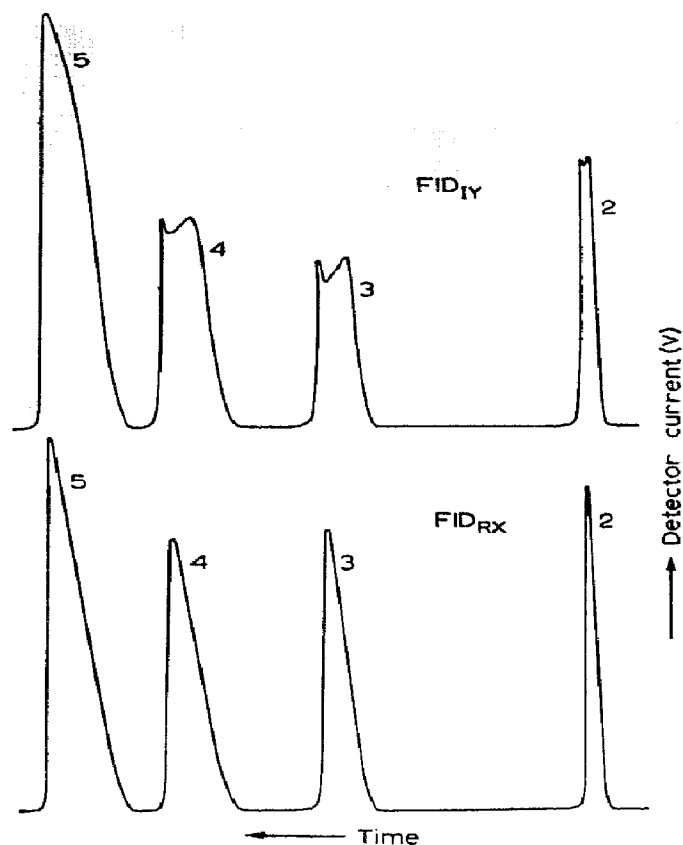


Fig. 4. Chromatograms referring to experiment No. 18. Sample quantity:  $1.2 \mu\text{l}$ . Sample composition, see Table I. FID<sub>RX</sub> operating variables, see text. FID<sub>IX</sub> operating variables: detector voltage 150 V; electrode gap 5.5 mm; gas flow rates:  $\text{N}_2$  10.1 ml/min;  $\text{H}_2$  24.4 ml/min;  $\text{O}_2$  200 ml/min.

Under the conditions corresponding to diagram I, the FID<sub>IX</sub> was functioning linearly, similarly to the FID<sub>RX</sub>. The relation of the two detector signals is represented by straight lines. The slightly different slopes of these lines are a consequence of the individual " $\gamma$ " factors of the test substances in FID<sub>IX</sub>. A decrease of the detector voltage—other conditions being the same—resulted in the successive diminution of the linearity limit of the hydrocarbon component and in the appearance of peak inversion of the organosilicon components (see diagrams II and III). At the same time the slope of the initial linear part of the curves remained unaltered. The effect of the  $\text{H}_2$  partial pressure becomes manifested by the comparison of diagrams IV and V. The limiting values—both  $\text{MFC}_{11\text{m}}$  and  $I_{11\text{m}}$ —are considerably higher in diagram V, corresponding to an increased hydrogen content. In contrast to the variation of the detector voltage, a variation of the percentage of  $\text{H}_2$  also affected the response factors, *i.e.* the slopes of the linear parts of the curves. A comparison of diagrams V and

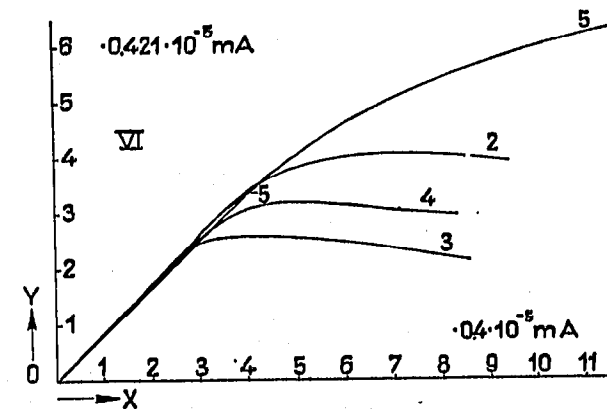
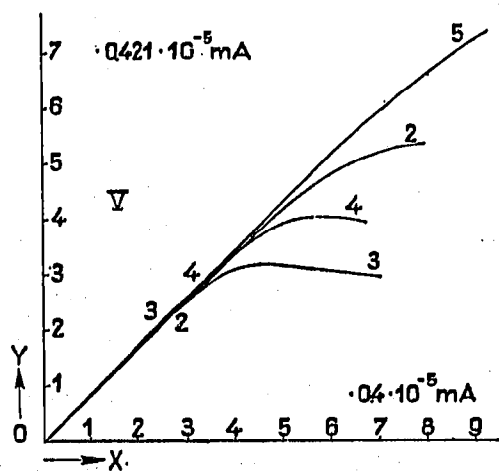
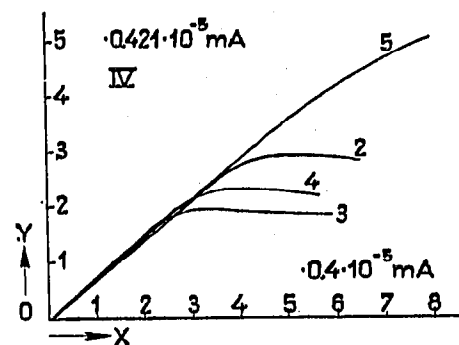
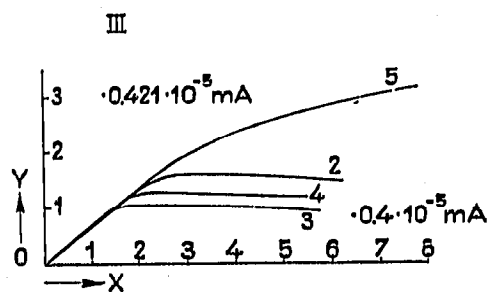
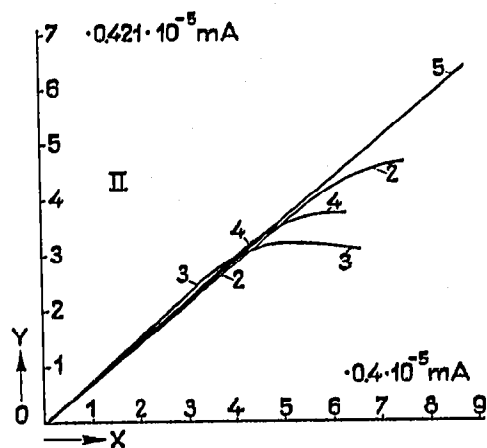
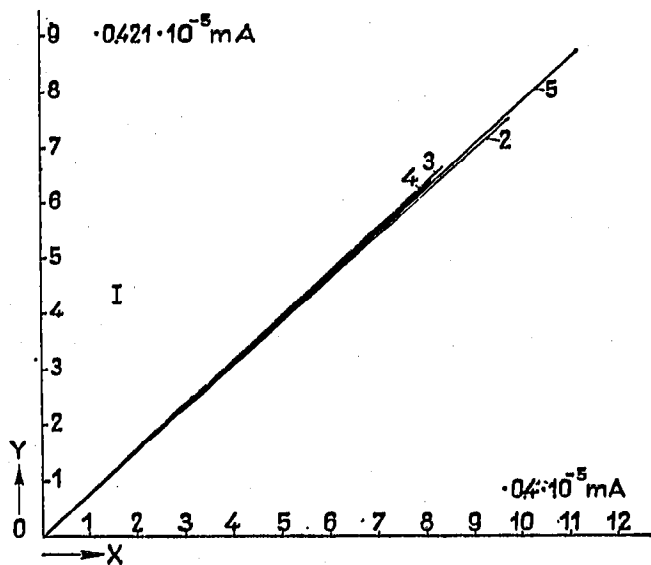


Fig. 5. Response curves, obtained with the "X-Y Recorder". Sample quantity: I and VI, 1.2  $\mu$ l; II, III, IV and V, 1.0  $\mu$ l. Sample composition, see Table I. FID<sub>RX</sub> operating variables, see text. FID<sub>IV</sub> operating variables, see Table III. Diagram I refers to Expt. 16; II to Expt. 6; III to Expt. 7; IV to Expt. 5; V to Expt. 8; VI to Expt. 18.

VI is representative of the effect of the electrode gap, an increase of which resulted in a decrease of the limiting values, while the response factors remained constant.

In general, the shape of the response curves draws attention to the fact that there is a fairly wide linearity range of the  $FID_{IV}$  signal with respect to organosilicons, under all operating conditions examined. Within this range the corresponding " $\gamma$ " factors do not differ considerably from the " $\gamma$ " values of a hydrocarbon. Hexamethyl-cyclotrisiloxane and divinyl-tetramethyl-disiloxane showed an " $\gamma$ " factor slightly higher, while trimethyl-butenyl-silane an " $\gamma$ " factor slightly lower than xylene. This observation indicates that the silicon does not exert any lowering effect on the ion current below a critical  $MFSi$ , in fact some increment of the ion current may be attributed to the Si-C bond.

As shown Fig. 5, the response curves of organosilicons may be divided into different regions. There is always an initial linear region followed by a non-linear one and, in some cases, this is also followed by a region of constancy. Finally, if conditions are favourable for peak inversion, a descending region is observed. The length of these regions as well as the slopes of the descending region depend to a great extent on the operating conditions.

The experimental results obtained hitherto by recording response curves are summarized in the diagrams of Figs. 6, 7 and 8 and in Table III.

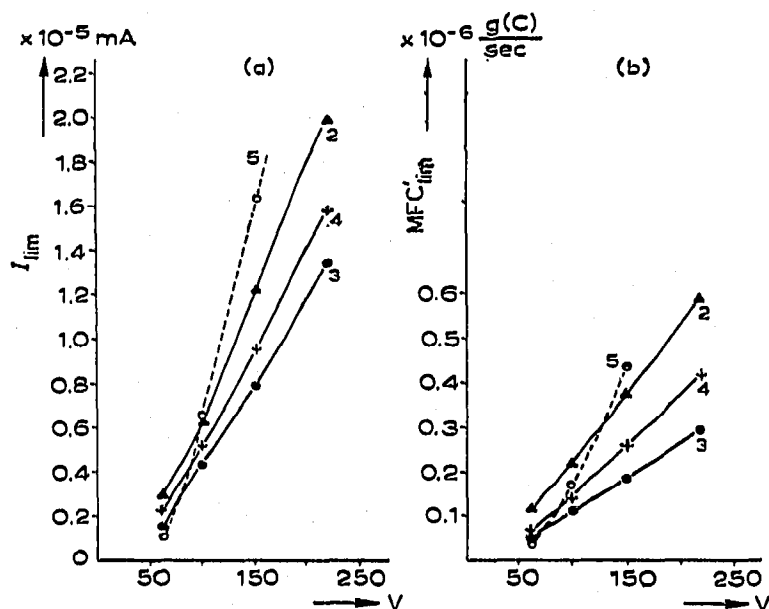


Fig. 6. Effect of detector voltage on (a)  $I_{lim}$  (solid lines) and linear  $I$  (dotted lines), and (b)  $MFC_{lim}$  (solid lines) and linear  $MFC$  (dotted lines) at a constant electrode gap (4.5 mm) and constant gas flow rates ( $H_2$ : 62.4 %). 2 = Trimethyl-butenyl-silane; 3 = hexamethyl-cyclotrisiloxane; 4 = divinyl-tetramethyl-disiloxane; 5 = *o*-xylene.

The following conventions were used for the evaluation of the characteristic data of the response curves listed in Table III.

As the determination of the abscissa of the maximum proved to be unreliable or even impossible in many cases because of the flat maximum or constant region of the curve, the initial linear region of the response curve was elongated and a horizontal line was drawn at the height of the maximum ion current ( $I_{lim}$ ). The abscissa of

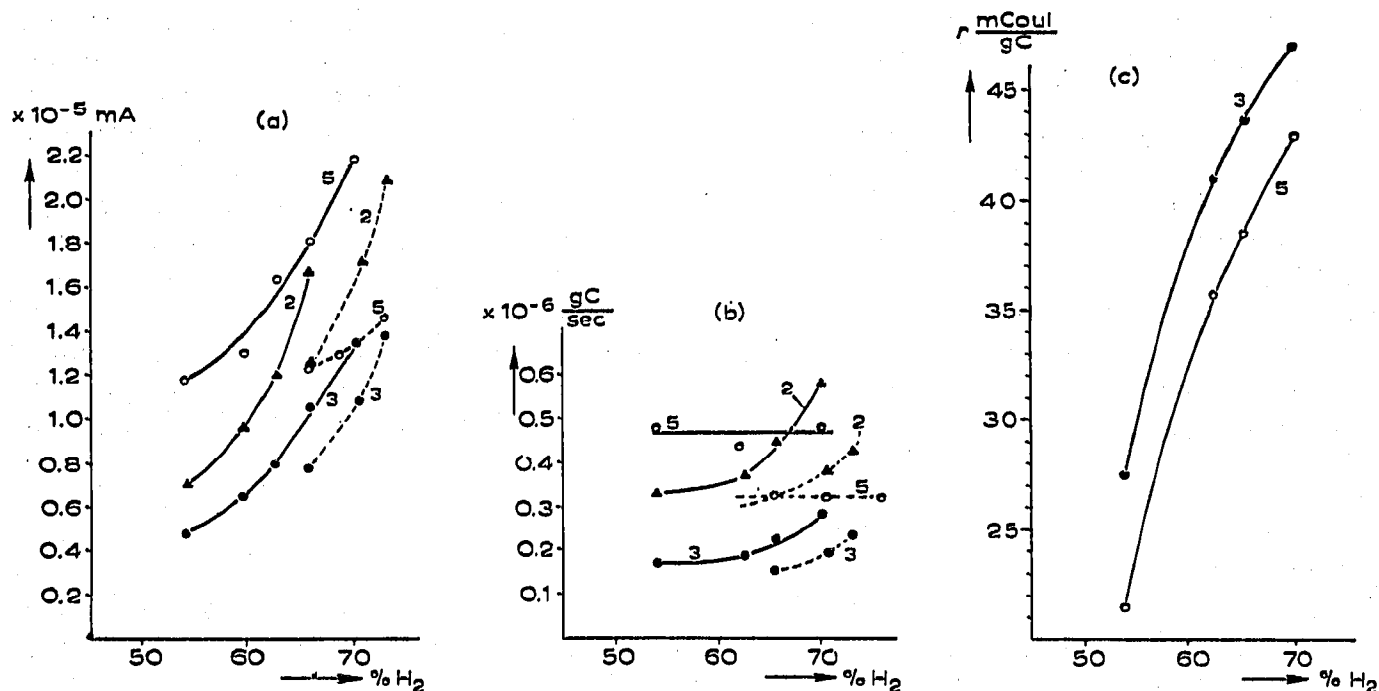


Fig. 7. Effect of the hydrogen percentage on  $I_{11m}$  and linear  $I$  (a), on  $MFC'_{11m}$  and linear MFC (b), and on " $\gamma$ " factors (c), with an electrode gap of 4.5 mm (solid lines) and 5.5 mm [dotted lines in (a) and (b)] and a constant detector voltage of 150 V. For an explanation of the numbers see Table I.

the intersection of the two straight lines is called the extrapolated limiting carbon mass flow rate ( $MFC'_{11m}$ ). Presuming the constancy of " $\gamma$ " up to the maximum of the curve, this value would represent the MFC pertaining to the limiting ion current  $I_{11m}$ .

Another convention had to be used for the evaluation of the linearity limit on the response curves of xylene. Here again the linear section of the curve was extrapolated. That point of the curve where the deviation of the recorded curve from the elongated line reached 0.5 % of the actual ion current was considered to be the linearity limit, since the precision of the recorder was 0.5 %.

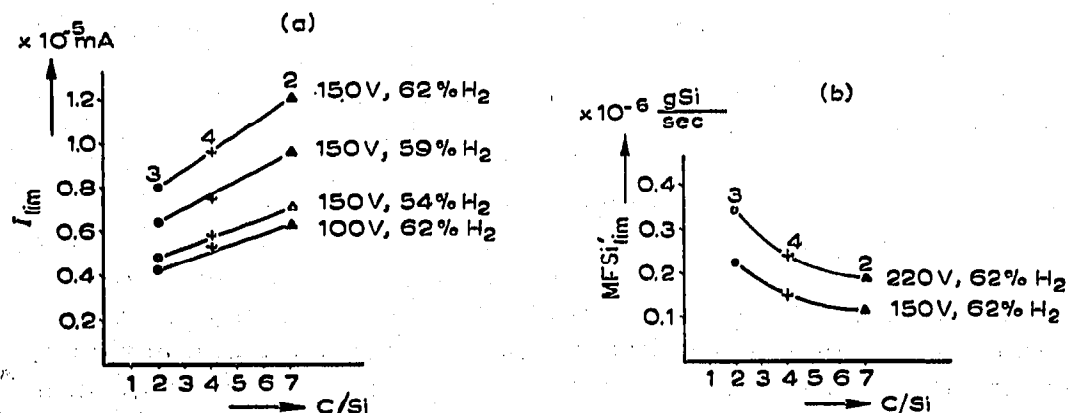


Fig. 8. Effect of the C/Si molar ratio of the test substance on the critical values  $I_{11m}$  (a) and  $MFSi'_{11m}$  (b). For an explanation of the numbers see Table I.

In accordance with the data in the literature, these experiments show that the response factors both of hydrocarbons and organosilicons are independent of the detector voltage within the range of 60–400 V. The extrapolated limiting carbon mass flow rates of organosilicons show a linear increase with increasing detector voltage as illustrated in Fig. 6 b. The “ $\gamma$ ” factor being constant, the same relation is also valid for the limiting ion currents (Fig. 6 a). The effect of the detector voltage on the linearity limit of xylene is still more pronounced (see dotted lines in Figs. 6 a and b).

An increase in the concentration of hydrogen, within the range of 50–70%  $H_2$ , causes a rapid increase of the “ $\gamma$ ” factor both for xylene and for organosilicons (5 and 3 in Fig. 7 c). At the same time an increase in the limiting mass flow rates— $MFC'_{11m}$ —of the organosilicons is to be seen in Fig. 7 b with increasing  $H_2$  concentration. Consequently, the dependence of the limiting ion current— $I_{11m}$ —on the hydrogen concentration shows a still more rapid increase within the range of the present measurements, as illustrated in Fig. 7 a. Fig. 7 b draws attention to a rather interesting fact: in contrast to the  $MFC'_{11m}$  values of organosilicons the linearity limit of the carbon mass flow rate (linear MFC) of xylene does not change with the percentage of hydrogen. Consequently, the increase of the linearity limit in ion current (linear  $I$ ) is not so steep in the case of xylene as the increase of  $I_{11m}$  values in the case of organosilicons.

Figs. 7 a and b also illustrate the effect of the electrode gap. The limits of both linearity and of inversion expressed in both MFC and ion current values, decrease with increasing electrode gap. Fig. 8 a shows a relationship of practical importance: the limiting ion currents of organosilicons are varying linearly with the carbon/silicon molar ratio of the compound within the investigated range of 2–7 C/Si. The diagram in Fig. 8 b demonstrates that the  $MFSi'_{11m}$  values are as a first approximation inversely proportional to the actual MFC values.

## CONCLUSIONS

The experiments reported do not afford sufficient data to explain the anomalous response of the FID for organometallic compounds. However, it seems unquestionable that these anomalies have no relation to the deposition of solid combustion products on the electrodes.

Deviations from the linear relationship between the ion current and carbon mass flow rate always imply the process of ion recombination. The dependence of the recombination rate upon the electric field strength and carbon mass flow rate in hydrogen flames containing small amounts of organic material has been the subject of detailed studies<sup>4,5</sup>.

The combustion of organometallic (organosilicon) compounds introduces a new parameter which must be taken into account as a cause of recombination. According to our observations this parameter proved to be a critical metal concentration in the flame, the extent of which is a function of the actual carbon mass flow rate, besides the operating variables of the detector. The rate of recombination is affected much more markedly by this factor than by all the others. It is remarkable that the increase of the metal concentration does not result in a continuous diminution of the ionization efficiency. Below the critical mass flow rate the “ $\gamma$ ” factor is of the

same magnitude or even higher than in the case of a hydrocarbon. The relatively elevated response factors of hexamethyl-trisiloxane and divinyl-tetramethyldisiloxane may be quoted as examples. A possible explanation is given by the higher ionizability of the Si-C bond than that of the C-C bond.

The observation that the recombination is unaffected by small amounts of silicon may be explained if it is assumed that the recombination takes place on the surface of solid combustion products floating in the reaction zone, and that the formation of solid particles of sufficient size requires a critical silicon concentration. This assumption is also supported by an experiment where small amounts of Freon were added to the fuel gas, in order to prevent the formation of solid SiO<sub>2</sub> in the flame. In this experiment peak inversion did not occur. However, the dependence of the critical silicon mass flow rate upon the actual carbon mass flow rate is inconsistent with this simplified theory.

Apart from these still unsolved problems, the relationship between  $I_{11m}$  and the C/Si ratio is a valuable result of the experiments reported. This relationship affords the possibility of estimating the C/Si ratio of an unknown compound from the maximal height of its inverted peak. Further investigations are still needed in order to make statements concerning the accuracy and practicability of information of this kind.

#### SUMMARY

A method is described by means of which the response curves of a flame ionization detector may be recorded on the basis of a single chromatogram. The column effluent is divided into two equal streams which simultaneously enter a reference detector and the detector being examined. The relation between the two detector signals is recorded with the aid of an X-Y recorder. Providing that the performance of the reference detector is linear, and by determining its response factor, the abscissa of the X-Y diagram represents a scale of mass flow rates, and the diagram itself the response curve of the detector tested. The method was used for the investigation of the FID performance when detecting organosilicon compounds. Inversion of the gas chromatographic peaks takes place and the response curves display a maximum under certain operating conditions. The shape of the response curves, the height and situation of the maximum depend on the detector voltage, the electrode gap, the flow rate of gases and the carbon/silicon ratio of the compound detected. The estimation of the carbon/silicon ratio on the basis of the maximum ion current is suggested.

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