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GAS CHROMATOGRAPHY OF ALKYL IODIDES

II. INFLUENCE OF STRUCTURE ON RETENTION TIME AND SENSITIVITY TO ELECTRON CAPTURE DETECTOR*

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SUMMARY

Several linear and branched iodoalkanes were synthesised and analysed by gas chromatography with tricresylphosphate columns and an electron capture detector.

The behaviour of retention times and retention indices was examined as a function of the number of carbon atoms, the position of the iodine in the molecule, and the number and position of branchings.

Also the sensitivity of the electron capture detector to alkyl iodides was studied, and the capture coefficient, the absolute molar response and the relative molar response were determined.

While all these values depend on several parameters, the relative molar response depends only on standing current, and therefore can be easily used for standardisation.

INTRODUCTION

In a previous paper¹, the gas chromatographic (GC) analysis of alkyl iodides was performed using tricresylphosphate columns, and a regular behaviour of retention times and sensitivities to electron capture detector (ECD) was found for the homologous series of 1-iodoalkanes.

The linear dependence of $\log t_a$ (where t_a is the adjusted retention time) (ref. 2) on the number of carbon atoms in the linear molecule, allowed the introduction of retention indices relative to 1-iodoalkanes (I_{ni}) as means of identification for all the branched-chain alkyl iodides. These retention indices are quite similar to the retention indices proposed by Kováts³.

The values of I_{ni} for some branched iodoalkanes, as determined in the work cited¹, have only shown that branched-chain and 2-iodo compounds have a lower retention time than 1-iodoalkanes.

A greater number of branched and linear iodoalkanes were synthesised and

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analysed in the present work in order to investigate the correlations between structure, retention time and sensitivity.

EXPERIMENTAL

In addition to the products cited in ref. 1, several products were synthesised and are listed in Table I. They were generally prepared from the corresponding alcohol, by treatment with constant boiling point hydriodic acid (57 %) (ref. 4). Only 3-iodo-2,2,4-trimethylpentane was obtained from the alcohol by reaction with purified red phosphorus and iodine⁵.

Some products, whose syntheses were impossible due to the lack of the corresponding starting compound, were obtained by irradiation of the congruent hydrocarbon with γ rays in the presence of iodine.

TABLE I

PHYSICAL CONSTANTS OF SYNTHESISED AND ANALYSED COMPOUNDS

Unless otherwise specified, boiling points are at 760 Torr, index of refraction and density at 20°C.

No.	Alkyl iodides	Boiling point (°C)	Index of refraction	Density (g/ml)
1	2-Iodopropane	89.5	1.5026	1.70
2	2-Iodobutane	120	1.4991	1.5984
3	2-Iodopentane	144-145	1.4954	1.53
4	3-Iodopentane	145-146	1.4967	1.52
5	2-Iodohexane	90-91 (70 Torr)	1.4911 (25°C)	1.4269 (15°C)
6	3-Iodohexane	110 (70 Torr)	1.4933	1.45
7	2-Iodoheptane	100 (50 Torr)	1.4827	1.304
8	3-Iodoheptane	88.9 (30 Torr)	1.4901	1.3675 (25°C)
9	4-Iodoheptane	185	1.4915	1.39
10	1-Iodo-2-methylbutane	148	1.4977	1.53
11	1-Iodo-3-methylbutane	147	1.4939	1.51
12	2-Iodo-2-methylbutane	124.3-125.5	1.50	1.49
13	2-Iodo-3-methylbutane	141	1.4965	1.5026
14	1-Iodo-2-methylpentane	72 (22 Torr)	1.4938	1.44
15	1-Iodo-3-methylpentane	170	1.4925	1.46
16	1-Iodo-4-methylpentane	173.2	1.4892	1.4283
17	2-Iodo-2-methylpentane	142	1.4940	1.41
18	2-Iodo-3-methylpentane	83 (65 Torr)	1.484	1.451 (18°C)
19	2-Iodo-4-methylpentane	160	1.4900	1.4713
20	3-Iodo-2-methylpentane	147	1.477	1.31
21	3-Iodo-3-methylpentane	120 (vacuum)	1.4930	1.37
22	1-Iodo-2-ethylbutane	—	1.4975	1.46
23	1-Iodo-2,2-dimethylbutane	110 (vacuum)	1.4960	1.45
24	1-Iodo-3,3-dimethylbutane	162	1.4315	1.34
25	2-Iodo-3,3-dimethylbutane	145	1.4973	1.42
26	1-Iodo-2,3-dimethylbutane ^a	—	—	—
27	2-Iodo-2,3-dimethylbutane	145	1.4895	1.39
28	2-Iodo-2,4-dimethylpentane	140-142	1.4690	1.08
29	1-Iodo-2,2,4-trimethylpentane	131	1.4770	1.22
30	3-Iodo-2,2,4-trimethylpentane	126	1.4894	1.23
31	1-Iodo-2,4,4-trimethylpentane ^a	—	—	—
32	4-Iodo-2-methyl-7-ethylnonane	170	1.4726	1.0805
33	4-Iodo-2,6,8-trimethylnonane	140 (vacuum)	1.4590	1.0201
34	2,2,7,7-tetramethyl-iodooctane ^a	—	—	—

^a Prepared by γ -irradiation (see text).

The analyses were made using a Varian Aerograph Model 500-D electrometer and a separate column oven Model 550-B, to allow for better temperature control. A 3 m \times 1/8 in. glass column, filled with 15 % tricresylphosphate on DMCS-treated Chromosorb W (80-110 mesh) was used. The detector was an electron capture of the concentric type, containing 250 mCi of titanium tritide; the polarising voltage was 90 V d.c. Ultrapure nitrogen was used as carrier gas. The sample, about 1 μ l of iodoalkane solution in purified *n*-hexane, was directly injected on-column to minimise decomposition.

RESULTS

In Table II are reported the adjusted retention times (t_a), obtained by subtracting the gas hold-up time t_a from the total retention time t_r , and the retention indices relative to the linear 1-iodoalkanes (I_{ni}).

TABLE II

ADJUSTED RETENTION TIMES AND RETENTION INDICES RELATIVES TO *n*-IODIDES OF SOME ISOMERIC ALKYL IODIDES

No.		t_a (min)	I_{ni}	δI_{ni}	$\delta I_{ni}\%$
1	2-Iodopropane	1.84	245	55	18.33
2	2-Iodobutane	3.93	359.5	40.5	10.12
3	2-Iodopentane	7.00	444	66	13.20
4	3-Iodopentane	7.73	458	42	8.40
5	2-Iodohexane	13.53	540	60	10.00
6	3-Iodohexane	13.58	540.5	59.5	9.92
7	2-Iodoheptane	29.55	636	64	9.14
8	3-Iodoheptane	29.05	633.5	66.5	9.50
9	4-Iodoheptane	26.44	619.5	81.5	11.64
10	1-Iodo-2-methylbutane	8.22	467	33	6.60
11	1-Iodo-3-methylbutane	7.33	451	49	9.80
12	2-Iodo-2-methylbutane	7.04	445	55	11.00
13	2-Iodo-3-methylbutane	6.99	444	56	11.20
14	1-Iodo-2-methylpentane	15.12	556	44	7.33
15	1-Iodo-3-methylpentane	15.60	561	39	6.50
16	1-Iodo-4-methylpentane	15.42	559	41	6.83
17	2-Iodo-2-methylpentane	13.21	538	62	10.33
18	2-Iodo-3-methylpentane	13.67	541.5	58.5	9.75
19	2-Iodo-4-methylpentane	13.23	537	63	10.50
20	3-Iodo-2-methylpentane	13.17	536	64	10.67
21	3-Iodo-3-methylpentane	13.72	542	58	9.67
22	1-Iodo-2-ethylbutane	15.15	557	43	7.17

The behaviour of I_{ni} vs. the number of carbon atoms for straight-chain iodoalkanes is reported in Fig. 1. The plot is obviously linear for 1-iodoalkanes, but it is interesting to observe that also 2- and 3-iodoalkanes show a similar relationship. As only one 4-iodoalkane was synthesised, it was not possible to determine the corresponding function.

The following equation for 1-, 2- and 3-iodoalkanes can therefore be written:

$$I_{ni} = A_0 + A_1 n$$

using the least square method, the coefficient A_0 and A_1 were calculated and are reported in Table III.

Behaviour of 2-iodoalkanes parallels that of 1-iodoalkanes, while 3-iodoalkanes have a minor slope. It is probable that by increasing the length of the chain the slope of 3-iodoalkanes will increase.

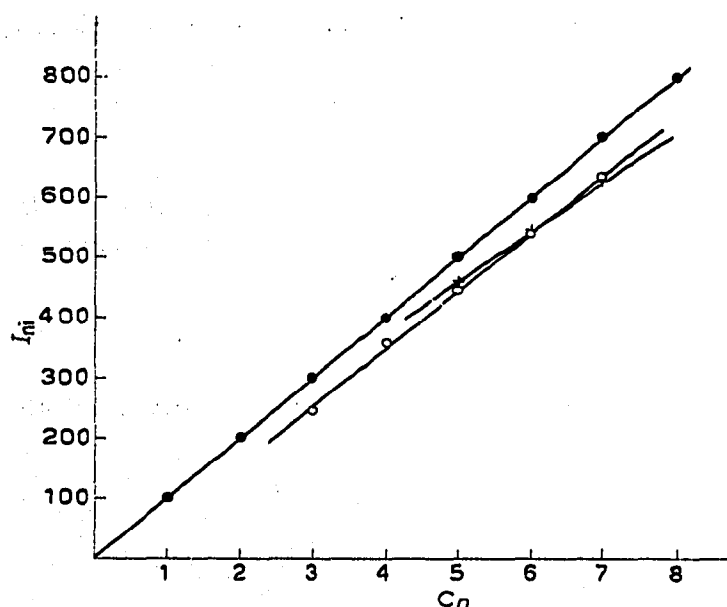


Fig. 1. Retention indices relative to n -iodoalkanes as a function of the number of carbon atoms for 1-iodo, 2-iodo and 3-iodo straight-chain alkanes. ●, 1-Iodoalkanes; ○, 2-iodoalkanes; +, 3-iodoalkanes.

TABLE III

COEFFICIENT OF EQUATION $I_{ni} = A_0 + A_1n$ CALCULATED BY THE LEAST-SQUARE METHOD FROM DATA OF TABLE II AND FIG. 1. FOR STRAIGHT-CHAIN IODOALKANES

	A_0	A_1
1 Iodo	0	100
2 Iodo	-50.38	98.42
3 Iodo	+33.33	85.75

If the iodine is substituted on one of the carbon atoms internal to the chain, a smaller I_{ni} than that of the 1-iodoalkanes is therefore obtained. Differences between the various internal positions are of minor importance, as can be seen from Fig. 2, where the I_{ni} of straight-chain iodoalkanes is plotted vs. the position of iodine in the molecule. When iodine is at the end of the chain, the I_{ni} is obviously a multiple of 100. When iodine is connected to a methylenic carbon atom, the decrease of I_{ni} is approximately the same, independent of the length of chain and of the position. This behaviour of I_{ni} for straight-chain iodides is very similar to that of boiling points. By changing the iodine position in branched-chain compounds, as 2-methyl-iodobutanes, 2-methyl-iodopentanes and 3-methyl-iodopentanes, a similar behaviour can be seen.

In Table II are reported, as δI_{ni} and $\delta I_{ni} \%$, the differences between the I_{ni} of the linear 1-iodoalkanes (by definition equal to multiples of 100) and those of each isomeric compound, respectively, in index units and in percent values. If the iodine atom is substituted on the first carbon atom of the chain, we can observe a $\delta I_{ni} \%$ of about 7%. If the iodine is internal to the chain, it produces a larger decrease of I_{ni} . In fact, the average $\delta I_{ni} \%$ is about 11% for 2-iodo-2-methylbutane and 2-iodo-3-methylbutane, 10.5% for 2-methyl-iodopentanes and 9.7% for 3-methyl-iodopentanes with iodine in positions 2 and 3. From these values it seems that the decrease in the retention time is relatively more important for short chains and larger if the methyl group is substituted in position 2.

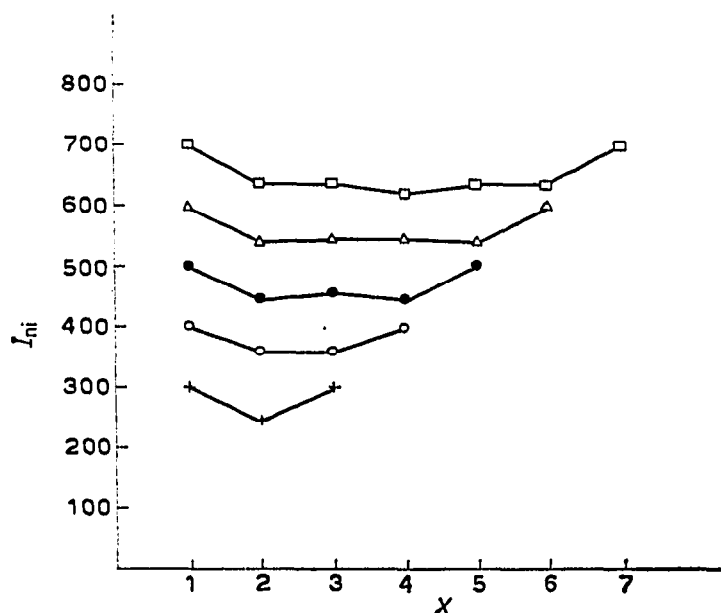


Fig. 2. I_{ni} of straight-chain iodoalkanes as a function of the position of iodine in the molecule. □, *n*-Iodoheptanes; △, *n*-iodohexanes; ●, *n*-iodopentanes; ○, *n*-iodobutanes; +, *n*-iodopropanes.

It is now interesting to investigate the effect of the different positions of the methyl group in compounds with the same position of the iodine. In the three parts of Fig. 3 are plotted the values of I_{ni} for alkyl iodides with iodine in positions 1, 2 and 3, respectively. Values on the abscissa indicate the methyl group position. One should observe that, to compare products with the same basic structure, 2-iodo-*n*-alkanes may be considered as 1-iodo-1-methylalkanes, 3-iodoalkanes as 2-iodo-1-methylalkanes, etc. For example, to see the effects of methyl substitution on the various carbon atoms of the 1-iodopentane, we can consider the 2-iodohexane as the first member of the series of general formula 1-iodo-*x*-methylpentane, etc. The compounds without methyl substitution are therefore plotted at abscissa zero (*i.e.*, as an example, 1-iodohexane, 2-iodohexane and 3-iodohexane for the three parts of Fig. 3).

In Table IV are reported the retention indices I_{ni} of various compounds with a branched skeleton. The increase in branching causes a decrease in I_{ni} . This effect increases for compounds with a higher number of carbon atoms, but the small number of possible isomers analysed does not allow a general law to be deduced. Notwithstanding this, the behaviour of C_{12} methyl-branched iodoalkanes is interesting; di-

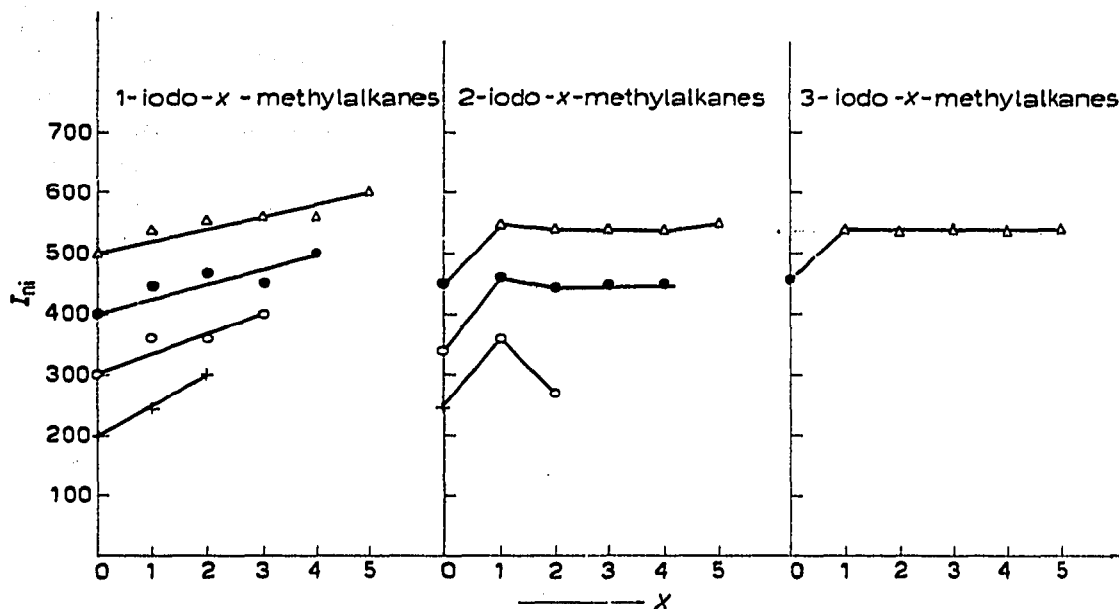


Fig. 3. I_{ni} of branched-chain iodoalkanes as a function of the different positions of iodine and methyl group. Number of carbon atoms in basic chain: + = 2; O = 3; ● = 4; Δ = 5.

TABLE IV

RETENTION INDICES I_{ni} OF BRANCHED-CHAIN ALKYL IODIDES

No.		I_{ni}	δI_{ni}	$\delta I_{ni}\%$	$\delta I_{ni}^{(branch)}$
23	1-Iodo-2,2-dimethylbutane	540	60	10.00	30
24	1-Iodo-3,3-dimethylbutane	496	104	17.33	49.5
25	2-Iodo-3,3-dimethylbutane	501	99	16.50	52
26	1-Iodo-2,3-dimethylbutane ^a	538	62	10.33	31
27	2-Iodo-2,3-dimethylbutane	501	99	16.50	49
28	2-Iodo-2,4-dimethylpentane	604	96	13.71	48
29	1-Iodo-2,2,4-trimethylpentane	665	135	16.87	45
30	3-Iodo-2,2,4-trimethylpentane	662	138	17.25	46
31	1-Iodo-2,4,4-trimethylpentane ^a	695	105	13.12	35
32	4-Iodo-2-methyl-7-ethylnonane	964	236	19.67	118
33	4-Iodo-2,6,8-trimethylnonane	858	342	28.50	114
34	2,2,7,7-Tetramethyl-iodo-octane ^a	700	500	41.66	125

^a Prepared by γ -irradiation (see text).

viding δI_{ni} by the number of branches, a constant value is obtained. It seems that for compounds with a great number of carbon atoms, the effect of iodine is small compared to that of the chain branching and that every new branch produces the same decrease in retention time. From the experimental data reported above, a general trend for the separation of alkyl iodides on tricresylphosphate columns can be obtained: the retention time decreases when the branching of the molecule increases and when the iodine is substituted on carbon atoms internal to the molecule.

On the basis of these observation, a reasonable explanation of the separation

mechanism can be the fact that tricresylphosphate is a polar stationary phase and that the great retention time of alkyl iodides is due to their dipole moment. The separation between isomeric alkyl iodides with small differences in the boiling points is probably due to different dipole moments.

SENSITIVITY

The sensitivity as a function of structure can be studied using as measuring unit the K (capture coefficient) (refs. 6–8) defined by:

$$K = \frac{I_b - I_c}{I_c} \frac{(V + a)}{c} \quad (1)$$

where I_b is the standing current, as measured from the difference between the detector signals with and without applied field, that takes into account the reduction due to column bleeding;

I_c is the decreased current observed on the introduction of a capturing species into the detector;

$I_b - I_c$ is therefore the detector signal;

c is the instantaneous concentration of the capturing species;

V is the voltage of the field applied to the detector;

a is a constant characteristic of the detector used and is equal to the ratio L/K_t between the leakage of electrons from the reaction volume and the electron mobility under electrical field.

According to ZLATKIS AND PETTITT⁸ the K can be calculated with the following practical formula:

$$K = \left(\frac{I_b - I_c}{I_c} \right) (W/2) \frac{F}{ZM} \quad (2)$$

where:

$(W/2)$ is the width of the chromatographic peak at half height (in seconds);

F is the gas flow (in ml/sec);

Z is the sample size;

M is the molar concentration of the sample injected.

The temperature dependence of the capture coefficient K gives information about the mechanism taking place in the detector. According to WENTWORTH AND CHEN⁶ four paths for the mechanism of electron attachment phenomena to alkyl iodides RI can be written:



Mechanism A represents attachment by a nondissociative mechanism to form a stable negative ion. B and C represent attachment with immediate or following

dissociation. Mechanism C is assumed to have lower activation energy. Mechanism D can be excluded, as it is unlikely with alkyl iodides. The choice between mechanisms A and B or C may be made taking into account the fact that mechanism A must theoretically show an increase of $\ln KT^{3/2}$ versus $1/T$, while mechanisms B and C must show a decrease or a constant behaviour.

In Fig. 4 and in Table V the values of $\ln KT^{3/2}$ in function of $1/T$ for some alkyl iodides, representative of various skeletal structures, are reported. With the exception of 2-iodo-2-methylalkanes, one can observe a decrease in or a constant behaviour of these values, which seem to confirm a reaction of the B or C type. These mechanisms are highly probable, due to the fact that alkyl iodides tend to cleave at the carbon-iodine bond, with formation of an I^- and an alkyl radical R^\cdot .

The observed increase of $\ln KT^{3/2}$ vs. $1/T$ for 2-iodo-2-methylalkanes seems to

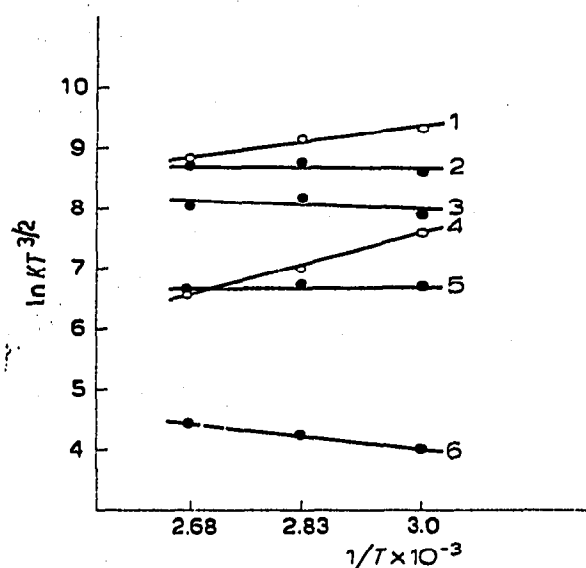


Fig. 4. Values of $\ln KT^{3/2}$ in function of the reciprocal of absolute temperature. 1 = 2-Iodo-2-methylpropane; 2 = 1-iodo-2-methylpropane; 3 = 1-iodopropane; 4 = 2-iodo-2-methylbutane; 5 = 1-iodo-3,3-dimethylbutane; 6 = 2-iodopropane.

TABLE V

VALUES OF $\ln KT^{3/2}$ FOR VARIOUS ALKYL IODIDES AT DIFFERENT TEMPERATURES (COLUMN *a*, *b*, *c*) After 10 days of aging of the standard solution (column *d*), and difference between values of columns *c* and *d*.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>c-d</i>
	333°K	353°K	373°K	373°K	373°K
1-Iodopropane	7.981	8.188	8.027	8.024	0.003
2-Iodopropane	4.002	4.255	4.340	4.241	0.099
Diiodomethane	—	—	5.878	5.839	0.039
1-Iodo-2-methylpropane	8.602	8.786	8.699	8.707	0.008
2-Iodo-2-methylpropane	9.338	9.154	8.776	8.694	0.082
2-Iodo-2-methylbutane	7.636	6.992	6.640	6.540	0.100
1-Iodo-3,3-dimethylbutane	6.693	6.716	6.640	6.630	0.010
1-Iodo-2,2,4-trimethylpentane	—	—	5.336	5.336	0.000

indicate a mechanism of type A. This is improbable because the tendency to formation of I^- and $R\cdot$ with mechanism B or C increases, going from primary to secondary and tertiary alkyl iodides. To explain the observed increase, one must take into account the fact that the compounds with iodine on secondary and tertiary carbon atoms show little stability during synthesis and storage. An increase of $\ln KT^{3/2}$ vs. $1/T$ may only show that at higher temperatures a greater decomposition takes place. The greater slope of the 2-iodo-2-methylbutane plot is in accordance to the fact that this compound is less stable than 2-iodo-2-methylpropane. To confirm this fact, in the last column of Table V are reported the values obtained from analysis of the same standard solution (about 1 p.p.m. per compound) used for the analysis reported in the other columns, after 10 days of storing at 0°C .

Temperature was the same (373°K) as in the third column. While other compounds give quite constant values, the decrease for 2-iodoalkanes and for diiodomethane can be easily observed. Note that, as previously observed, the decomposition of very dilute solutions (from 0.5 to 2.5 p.p.m.) is slow in comparison with these of pure compounds. The decomposition with time of products different from 1-iodoalkanes makes the quantitative analysis very difficult, as it is impossible to store for a long period the synthesised standards.

The absolute molar responses (AMR), suggested in the previous work¹, can be used for quantitative work if analytical parameters are the same, as the AMR were found to be characteristic of every compound. If any of the analytical parameters (temperature, column length, percent of stationary phase) will change, the molar

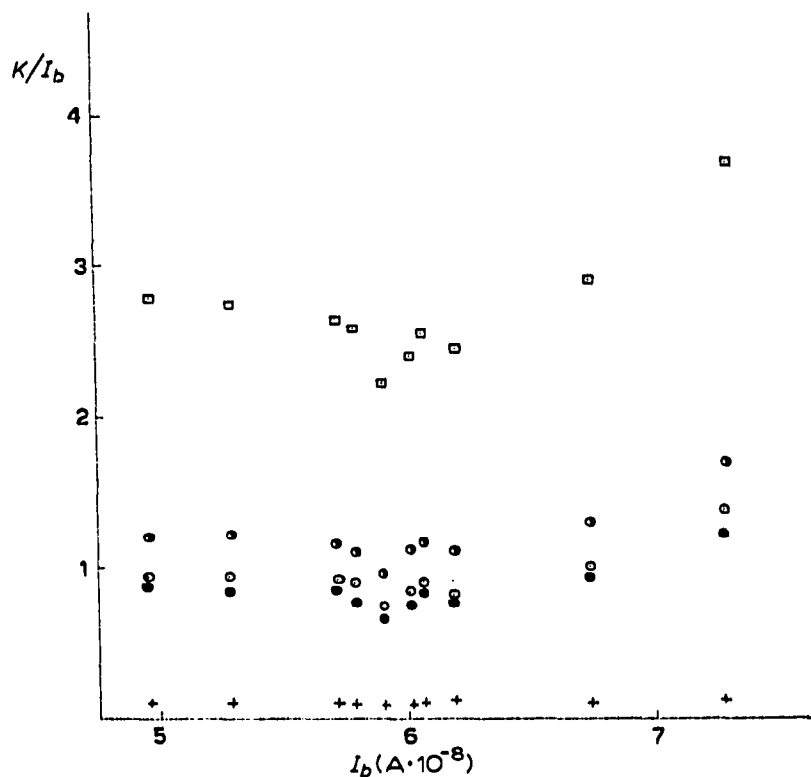


Fig. 5. Variation of ratio K/I_b in function of I_b during a long time of detector use. \odot , 1-Iodo-propane; $+$, 2-iodopropane; \bullet , 1-iodo-2-methylpropane; \square , 2-iodo-2-methylpropane; \bullet , 1-iodo-3,3-dimethylbutane.

response relative (RMR) to 1-iodopropane can be used. Only one condition must be satisfied in this case: the standing current I_b must be constant, as RMR values depend on it.

Theoretically, the best way to know the sensitivity for each compound is the knowledge of its capture coefficient K . In fact, from Eqn. 1, taking into account that c is an instantaneous concentration and that the time that it takes for the sample to pass through the detector is inversely proportional to the gas flow rate through the detector, determination of sample quantity should be made from knowledge of I_b , I_c and K . Unfortunately, the variation of the standing current during detector life depends on many factors⁷ whose effect is competitive. While temperature, pressure,

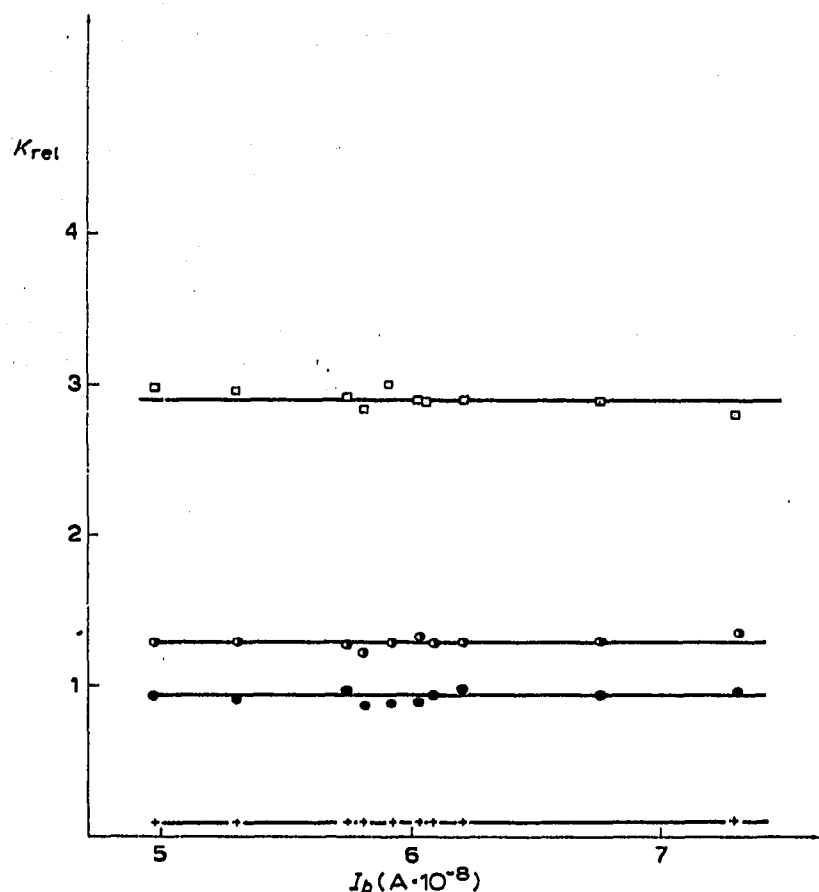


Fig. 6. Capture coefficient relative to 1-iodopropane (K_{rel}) in function of the standing current I_b . +, 2-Iodopropane; \circ , 1-iodo-2-methylpropane; \bullet , 1-iodo-3,3-dimethylbutane; \square , 2-iodo-2-methylpropane.

flow can be easily maintained constant, column bleeding and contamination cannot be controlled. Therefore, values of K have non-regular behaviour in function of the standing current. In Fig. 6 are reported the values of K/I_b vs. I_b obtained during a long time (about 1 month) of detector use. Variation of I_b due to contamination causes non-linear variation of K , also when temperature, pressure and flow are identical. A constant value is obtained if, instead of K , one takes as a measure of sensitivity the K_{rel} , ratio between the K of every compound and the K of 1-iodopropane (Fig. 6).

TABLE VI

CAPTURE COEFFICIENT RELATIVE TO I-IODOPROPANE (K_{rel}) AND RELATIVE STANDARD DEVIATION

<i>Alkyl iodide</i>	K_{rel}	$\bar{\sigma}_{rel}$
2-Iodopropane	0.096	$\pm 4.0\%$
1-Iodo-2-methylpropane	1.30	$\pm 3.7\%$
2-Iodo-2-methylpropane	2.89	$\pm 2.5\%$
1-Iodo-3,3-dimethylbutane	0.93	$\pm 5.0\%$

In Table VI are reported the values of K_{rel} for the compounds of Figs. 6 and 7, and the corresponding σ_{rel} . The constancy of these values is satisfactory. K_{rel} can therefore be used as a measure of the sensitivity to the various compounds, and the values obtained from freshly prepared standard solutions can be applied to quantitative analysis, thus avoiding the difficulty due to decomposition. In fact, addition of a stable compound (1-iodopropane) as internal standard will allow a rapid calculation of the amount of other iodides present in the mixture. The values of Table VI are indicative, as it is clear that the reported values of K_{rel} cannot be used by other workers with different types of detectors or different columns and that a series of K_{rel} must be determined *una tantum* with the parameters selected for the analysis.

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