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THE DEPENDENCE OF FLAME IONISATION DETECTOR RELATIVE RESPONSE FACTORS ON THE CONFIGURATION OF THE ELECTRODES

J. NOVÁK, P. BOČEK, L. KEPRT AND J. JANÁK

Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

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SUMMARY

Results obtained by quantitative evaluation of chromatograms of a model mixture chromatographed on seven different commercial gas chromatographs were processed statistically by analysis of variance. Flame ionisation detectors with two parallel electrodes and a floating jet were shown to have relative ionisation efficiencies per 1 gram atom of carbon generally dependent on both the construction of the detector and the type of hydrocarbon. No significant variations in the above relative ionisation efficiency were found with detectors in which the jet served as a polarising electrode, even when the detectors differed substantially from each other in overall geometry and in the shape and position of the collecting electrode.

INTRODUCTION

It is already a well established fact that the performance of the flame ionisation detector (FID) is strongly affected by many experimental variables. On the other hand, the FID has excellent properties when operated under properly chosen and stabilised conditions. This explains why the FID has received so much attention since its advent[1,2]. Along with numerous works affording basic information on the constructional and geometrical aspects[3-13], effects of various experimental parameters on the detector performance[4,6,7,14-19], and the behaviour of the FID under varying normal working conditions[20], papers have also been published stating that the relative response factors are dependent on the experimental parameters[19,21]. Furthermore, recent findings by DEANS[22] show that the relative response factors also depend on the type of apparatus.

In the present work, an attempt has been made to find a conclusive cause of the above phenomenon. The essence of the work is a statistical analysis of the results obtained by evaluating the chromatograms of a model mixture obtained on several commercial gas chromatographs under identical conditions.

DESIGN OF THE EXPERIMENTS

The results obtained from the chromatograms were processed by the analysis of variance, namely, by factorial experiments[23]. In order to make maximum use of the data measured, the latter were expressed in the form of relative ionisation efficiency which is defined as the ratio of the ionisation efficiencies of one gram atom of carbon in the substance under consideration and that in a reference substance. This makes it possible to determine not only whether there are differences in the relative response factors measured with different flame ionisation detectors for a given pair of substances, but also whether the kind of model substance plays some role and whether a change in the nature of the substance brings about the same or different changes in the relative response factor with different detectors.

The ionisation efficiency, q, as quoted above, may be defined by the relation

$$q = AM/K(\Sigma C)w \tag{1}$$

where A is the peak area of the substance chromatographed, as measured in the chromatogram, w is the corresponding weight of the substance contained in the charge injected, M and (ΣC) are the molecular weight and the number of carbon atoms pertaining to the substance, and K is an apparatus constant. Denoting the quantities corresponding to the substance in question and to the reference substance by subscripts i and s, it is possible to write, in compliance with eqn. 1,

$$q_{is} = q_i/q_s = A_iM_i(\Sigma C)_s w_s/A_sM_s(\Sigma C)_i w_i \tag{2}$$

where q_{is} designates the above mentioned relative ionisation efficiency. As the corresponding relative weight response, RWR_{is}, is given by

$$RWR_{is} = A_i w_s/A_s w_i \tag{3}$$

the relationship between RWR_{is} and q_{is} can be written:

$$RWR_{is} = q_{is}\, M_s(\Sigma C)_i/M_i(\Sigma C)_s \tag{4}$$

In eqns. 2 and 3, the ratios A_i/A_s and w_i/w_s may obviously be substituted by the corresponding ratios of the peak area and weight fractions.

The analysis proper is based on the presumption that the relative ionisation efficiency with a detector a and substance i may be regarded as a sum of additive contributions, *i.e.*,

$$q_{is} = q_{is}^0 + \varepsilon_a + \varepsilon_i + \varepsilon_{ai} + \varepsilon_r$$

where q_{is}^0 is a relative ionisation efficiency value identical for all the detectors tested, ε_a and ε_i are the contributions accounting for the differences in the detectors and kinds of substance, respectively, ε_{ai} is the interaction contribution, and ε_r is the random error. The above contributions were processed in the form of the respective variances, S_a^2, S_i^2, S_{ai}^2, and S_r^2. The statistical significance of the variances S_a^2, S_i^2, and S_{ai}^2 was tested by comparing them with the residual variance S_r^2 by means of the SNEDECOR criterion[23].

EXPERIMENTAL

In order to be able to compare the results, the components of the model mixture as well as the column stationary phase were the same as those used in the work by DEANS. In order to reduce the number of variable factors, one and the same column was used with all the gas chromatographs employed, and it was operated at the same temperature and carrier gas flow rate. In addition, a Servogor RE 512 recorder (Goerz Electro, G.m.b.H., Austria) was used in all cases, thus eliminating the possible variability in peak distortion due to the recorder. Under the above conditions, changes in relative response factors may be considered as incidental only to variations in the detector parameters. The following gas chromatographs were employed in the measurements:

(i) Becker Multigraph, Type 409, Delft, The Netherlands.
(ii) CHROM 2, Laboratory Instruments, n.e., Prague, Czechoslovakia.
(iii) CHROM 4, Laboratory Instruments, n.e., Prague, Czechoslovakia.
(iv) Carlo Erba Fractovap, Model C, Type AID/f, Milan, Italy.
(v) Giede Hochtemperatur Gas Chromatograph, Model GCHF 18.3, Betriebskontrollgeräte KG, Berlin, D.D.R.
(vi) Hewlett-Packard High Efficiency Gas Chromatograph, Model 402, U.S.A.
(vii) Shimadzu Gas Chromatograph, Model GC-4A PTF, Kyoto, Japan.

The column was a 150 cm long stainless steel tube of 3 mm inner diameter, packed with 5.40 g of Chromosorb W 80–100 mesh coated with 10% (by weight) Apiezon L. In all cases, the carrier gas (N_2) flow rate was 0.13 ml/sec, and the column and injection block temperatures were 100 and 200°, respectively. The hydrogen flow rates were set at values giving a maximum sensitivity with each apparatus under the above conditions, the air flow rate amounting to about 600 ml/min.

The model mixture contained 22.92, 29.00, 25.00, and 23.08 wt. % of hexane, benzene, methyl cyclohexane, and octane, respectively. All the components were of an analytical grade purity (B.D.H. Ltd., Great Britain). 0.5 μl samples of the above

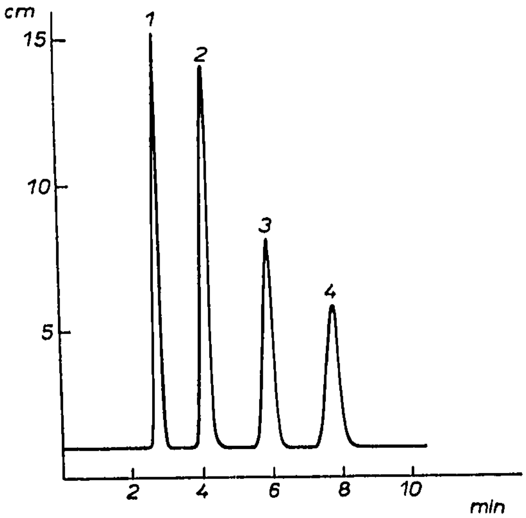

Fig. 1. A chromatogram of the model mixture; 1 = hexane; 2 = benzene; 3 = methyl cyclohexane; 4 = octane.

mixture were injected with a Hamilton 7001 (1 μl) syringe (Hamilton Co. Inc., Whittier, U.S.A.); the sensitivity attenuation necessary to obtain chromatograms of comparable sizes with different chromatographs varied between 1×10^4 and 4×10^4, except with the Giede apparatus where the attenuation had to be 2×10^3. The data such as retention times, intervals of elution, etc., are apparent from the chromatogram in Fig. 1 (obtained on the Becker Multigraph 409). The chromatograms were evaluated by measuring the peak areas as the multiples of the peak height and peak width at half height.

TABLE I

RELATIVE IONISATION EFFICIENCY (q_{is}) VALUES OBTAINED WITH INDIVIDUAL INSTRUMENTS FOR THE COMPONENTS OF THE MODEL MIXTURE

Apparatus	*Relative ionisation efficiency*		
	Benzene	*Methyl cyclohexane*	*Octane*
Becker	1.078	1.040	0.979
CHROM 2	0.996	1.057	1.035
CHROM 4	1.041	0.960	0.895
Carlo Erba	1.113	1.012	0.891
Giede	1.119	0.916	0.703
Hewlett-Packard	1.050	1.024	0.957
Shimadzu	1.085	1.186	1.114

TABLE II

SIGNIFICANCE OF THE INDIVIDUAL FACTORS INVESTIGATED

Factor	$F_{exptl.}$	$F_{crit.}$	*Significance*
Instruments	54.93	2.16	+
Substances	127.7	3.06	+
Interactions	26.83	1.82	+

RESULTS AND DISCUSSION

The experimental values of the relative ionisation efficiencies for the individual chromatographs and substances are summarised in Table I, the hexane carbon ionisation efficiency has been used as a reference throughout. All the data represent the average values of 10 measurements; the standard deviation of the averages varied within approximately 0.005–0.03. A comparison of the significance of the individual factors is shown in Table II where $F_{exptl.}$ stands for the experimental $S_a{}^2/S_r{}^2$, $S_t{}^2/S_r{}^2$, and $S_{at}{}^2/S_r{}^2$ ratios and $F_{crit.}$ represents the tabulated values of the Snedecor distribution $F_\alpha(\nu_1,\nu_2)$ for the confidence level and degrees of freedom ν_1 and ν_2; for the instruments, substances, and interactions, the ν_1 values are given by $k - 1$, $l - 1$, and $(k - 1)$ $(l - 1)$, respectively, where k and l are the number of instruments (7) and the number of substances (3), and the ν_2 is equal to $kl(n - 1)$ where n is the number of replicate chromatographic runs (10). All the data have been expressed for a 0.05 confidence level.

It can be seen from the data in Table II that all the effects investigated are statistically significant, which confirms, in the main, the findings by DEANS[22]. However, the situation affords a further analysis of the data. It is possible to calculate from the residual variance the interval of confidence, I_a, which allows the significance of the differences between the line averages in Table I to be tested. Thus for the above interval:

$$I_a = t_a(\nu_2)S_r(2/nl)^{\frac{1}{2}} = 0.02491$$

where t is the Student coefficient, $\alpha = 0.05$, $\nu_2 = 189$, $S_r = 0.04897$, and $nl = 30$. By applying this test, it is possible to place the individual instruments into several groups in such a way that there is no significant difference between the individual instruments within a group, but significant differences between the groups. Thus, in accordance with the results in Table I, the Giede, CHROM 4, Carlo Erba, and Shimadzu gas chromatographs represent by themselves particular groups in the above sense, while the Hewlett-Packard, Becker Multigraph, and CHROM 2 instruments form a single group.

It should be pointed out that all the instruments falling into the common group have detectors with the burner jet serving as a polarising electrode. In this case, neither a passage from one apparatus to another nor changes in the testing substances used brought about any significant variations in the relative ionisation efficiency, despite the fact that all the three detectors differed appreciably from each other in their geometry. The other groups are formed by instruments having detectors with two parallel electrodes and floating jets; these detectors showed significant differences in the relative ionisation efficiencies with respect to both the kind of detector and the kind of substance.

Provided the detectors with two parallel electrodes are considered as a single group, it is possible to carry out a comparison of the detectors having parallel electrodes and floating jets with those in which the jet serves as an electrode. This may be done by means of the method of linear contrast[23]. In this method, $F_{\text{exptl.}}$, given by $S_{\text{contrast}}^2/S_r^2$, is compared with $F_{\text{crit.}}$; $F_{\text{exptl.}} > F_{\text{crit.}}$ implies a statistically significant difference between the groups under comparison. In our case, $F_{\text{exptl.}}$ amounted to 37.43 ($S_{\text{contrast}}^2 = 0.08975$ and $S_r^2 = 0.002398$) while $F_{\text{crit.}}$ was 3.90, so that the groups differ significantly from each other.

CONCLUSION

Flame ionisation detectors have proved to be classifiable into two groups from the point of view of their performance, detectors with two parallel electrodes situated symmetrically with respect to the flame axis, and detectors in which one of the electrodes consists of the burner jet. In the first case, not only the absolute ionisation efficiency with a given substance, but also relative response factors showed a considerable dependence on the overall detector geometry. Moreover, the ionisation efficiency of a carbon in a hydrocarbon depended on the type of substance used. Detectors with the burner jet as a polarising electrode did not display any of the above unfavourable effects even when the shape and position of the collecting electrode differed appreciably.

Thus, it seems to be of little use listing FID relative response factors measured with detectors of the first type or to employ tabulated relative response factors when working with such a detector. The above problems may be avoided by choosing a detector with the burner jet as a polarising electrode.

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