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GAS CHROMATOGRAPHIC IDENTIFICATION OF SOME INDOOR AIR POLLUTANTS USING CORRELATION EQUATIONS

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SUMMARY

A calculation method for the identification of indoor air pollutants analysed by gas chromatography is described. It is based on correlation between the retention and the molecular properties of a substance. The equation

$$r_{1,2}^{calc} = A + B \cdot t_b^r + C/V_{mol}^r$$

where t_b^r is the relative boiling point, V_{mol}^r the relative molecular volume and A, B and C are constants gives values of the relative retention, $r_{1,2}^{calc}$, that differ from the experimental values by only ± 0.02 unit.

INTRODUCTION

The gas chromatographic (GC) identification of indoor air pollutants could be difficult and time consuming, because of the great variety of pollutants present. The certainity of their identification when only retention data are used could be increased by comparing the values with those obtained by some calculation method. The application of several calculation methods[1–5] to indoor air analyses showed, however, unacceptable discrepancies between the calculated and experimental retention values. The method[6] employing the vapour pressure (p^0) and molecular volume (V_{mol}) of the substances of interest is relatively reliable but it is difficult to obtain p^0.

In this work, the correlation between relative retention ($r_{1,2}$) and relative boiling point (t_b^r) and any relative molecular property of the compound was studied as a possible solution of this problem. Freshly painted surfaces produce an air pollutant mixture of solvents and diluents, such as aromatic hydrocarbons, aliphatic alcohols and acetates. Mixtures containing representatives of these classes were used in this study.

All investigations were based on the assumption that there exists a linear correlation of the type

$$r_{1,2} = A + B \cdot t_b^r + C \cdot MP + D \qquad (1)$$

where *MP* is any molecular property, *D* is the difference between the calculated and experimental relative retentions and *A*, *B* and *C* are constants. The value of *D* is the criterion to be used in selecting a suitable molecular property and we aimed at arriving at a *D* value equal to or less than 0.02 unit.

EXPERIMENTAL

The compounds chosen for the investigation and their properties are listed in Table I.

TABLE I

PROPERTIES OF AROMATIC HYDROCARBONS, ALIPHATIC ALCOHOLS AND ACETATES USED IN THE CORRELATION ANALYSIS

Compound	t_b (°C)	*Mol. wt.*	*Specific gravity*	V_{mol}
Benzene	80.1	78.0	0.879	88.7
Toluene	110.8	92.1	0.866	106.1
Ethylbenzene	136.2	106.2	0.867	122.5
p- and *m*-xylene	138.5	106.2	0.862	123.0
o-Xylene	144.4	106.2	0.880	120.6
Ethanol	78.3	46.1	0.789	58.4
Isobutanol	108.0	74.0	0.803	92.0
sec.-Butanol	100.0	74.0	0.806	92.0
n-Butanol	117.5	74.0	0.810	91.5
Isopentanol	132.0	88.1	0.812	108.6
Ethyl acetate	77.1	88.1	0.901	97.8
Isobutyl acetate	118.0	116.2	0.875	134.3
n-Butyl acetate	126.1	136.2	0.881	131.7
Isoamyl acetate	142.0	130.2	0.876	149.7

We studied one apolar phase, Apiezon L (ApL), a phase of moderate polarity, benzyldiphenyl (BDP), and a polar phase, polyethylene glycol 20M (PEG 20M). In addition, Chromosorb 101 was included, as it is very useful in the separation of alcohols and other polar compounds. The columns used had different lengths, the support was Chromosorb W, at least two amounts of each stationary phase were studied and the temperature was varied within $\pm 20°$ of the optimal. For every column length, amount of stationary phase and temperature, at least three values of the retention time were measured. The dead volume was determined before and after every analysis. An amount of 0.2 μl of mixtures containing only one class of substance and a standard was injected. A Pye Unicam Series 104 chromatograph with a flame-ionization detector with sensitivity 100 and 5000 was used. *o*-Xylene was chosen as the standard as it gives an individual peak in the separations examined with the columns used.

RESULTS AND DISCUSSION

The solution of a correlation matrix showed that the best correlation between $r_{1,2}$ and the substance property existed when t_b^r and $1/V_{mol}^r$ were used:

$$r_{1,2} = A + B \cdot t_b^r + C/V_{mol}^r + D \qquad (2)$$

TABLE II

VALUES OF CONSTANTS IN EQN. 2

Stationary phase	*Aromatic hydrocarbons*			*Aliphatic alcohols*			*Acetates*		
	Constants	*Difference between* $r_{1,2}^{calc}$ *and* $r_{1,2}^{exp}$		*Constants*	*Difference between* $r_{1,2}^{calc}$ *and* $r_{1,2}^{exp}$		*Constants*	*Difference between* $r_{1,2}^{calc}$ *and* $r_{1,2}^{exp}$	
		Average	*Maximum*		*Average*	*Maximum*		*Average*	*Maximum*
ApL	$A = -8.95$ $B = 5.71_5$ $C = 4.42$	0.02	0.03	$A = -1.05$ $B = 1.23$ $C = 0.36_5$	0.01	0.02	$A = -0.67$ $B = 0.84_5$ $C = 0.14_5$	0.02	0.03
BDP	$A = -8.77$ $B = 5.49_5$ $C = 4.35_5$	0.01	0.02	$A = 0.59$ $B = 0.83$ $C = 0.11$	0.03	0.04	$A = -1.65_5$ $B = 1.82_5$ $C = 0.64_5$	0.02	0.03
PEG 20M	$A = -6.14_5$ $B = 4.09$ $C = 3.05$	0.00	0.01	$A = -1.55$ $B = 1.72$ $C = 0.64$	0.01	0.02	$A = -1.97_5$ $B = 2.78$ $C = 0.32_5$	0.03	0.04
Chromosorb 101	$A = -5.74$ $B = 3.96$ $C = 2.85$	0.00	0.01	$A = -0.88$ $B = 1.38$ $C = 0.22_5$	0.02	0.03	$A = -0.34_5$ $B = 0.74_5$ $C = 0.00$	0.02	0.03

The solution of eqn. 2 for the aromatic hydrocarbons, aliphatic alcohols and acetates for the stationary phases examined gave values of the constants A, B and C shown in Table II). It can be seen that the average difference between $r_{1,2}^{calc}$ and $r_{1,2}^{exp}$ was about 0.02 unit or less, the greatest difference being 0.04 unit. The accuracy achieved permits the identification of very closely situated peaks.

As a practical illustration, air from inside a furniture plant was examined. From the nature of the plant, we would have expected as pollutants toluene, *m*- and *p*-xylene, ethanol, isobutanol and *n*- and isobutyl acetate. GC analysis on Chromosorb 101 at 200° showed, however, more peaks on the chromatogram (Table III). As all of the unknown peaks occurred before that of toluene, if there were any aromatic hydrocarbons present it could have been only benzene. The $r_{1,2}^{calc}$ value for benzene is 0.30 unit, which corresponds to $r_{1,2}^{exp}$ of peak X_3. Hence peak X_3 was identified as benzene. The next peaks could be either alcohols or ethyl acetate. The $r_{1,2}^{calc}$ values for the possible compounds are as follows: ethyl acetate, 0.14, *n*-butanol, 0.26 and isobutanol, 0.17. It is evident that peak X_1 belongs to *sec.*-butanol, while peak X_2 seems to be *n*-butanol.

TABLE III

EXPERIMENTAL AND CALCULATED RELATIVE RETENTIONS FOR POLLUTANTS IN A REAL INDOOR AIR

Retention time, t_R (sec)	$r_{1,2}^{exp}$	$r_{1,2}^{calc}$	*Pollutant*
63	0.07	0.06	Ethanol
103	0.17	(0.17)	X_1 (*sec.*-butanol)
113	0.20	0.21	Isobutanol
128	0.23	(0.26)	X_2 (*n*-butanol)
153	0.30	(0.30)	X_3 (benzene)
196	0.41	0.44	Isobut-l acetate
235	0.51	0.51	Toluene
365	0.85	0.84	*p*- + *m*-x-lene
426	1.00	1.00	*o*-X-lene (standard)

In more complicated instances, the use of the method of Dimov and Schopov[6] allows such changes in the temperature of analysis to be made that lead to reliable identification. In more common instances, however, the method proposed above provides a sufficiently accurate identification in a very easy and convenient way.

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