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QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS WITH AND WITHOUT PURE COMPONENTS OF ANALYSED MIXTURES

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SUMMARY

Multicomponent mixtures of acetone, methanol, propanol and butanol were analysed using calibration mixtures, constant area factors and a linear relationship. The latter is simple to apply and, compared with the former methods, gives satisfactory accuracy.

INTRODUCTION

No general gas chromatographic method for quantitative analysis exists due to the small range in which the detector responds linearly to the concentration of components and to the differences in area factor values of compounds. Thus it was recommended that calibration mixtures having compositions nearly identical qualitatively and quantitatively to those of analysed mixtures (method of calibration mixtures, CM)[1] be prepared. This method, although very accurate, is tedious and time consuming. Therefore, for routine analysis, the area factors are calculated from one or more calibration mixtures and the mean is used to calculate the percentage concentration of components of analysed mixtures (method of constant area factors, CAF)[1]. If all the components of the mixtures are not available as chromatographically pure substances or if one or more components are adsorbed in the column, then an external standard to which concentrations can be related is used. The concentrations can be normalised only if all the components of an analysed mixture are available. The disadvantage of all these methods is that it is necessary to have all the components of the analysed mixture in which one is interested. Calculation of area factors while having no pure components has been previously described (method of linear relationship, LR)[2].

The aim of this paper is to show the usefulness and to compare the accuracy of the LR method with that obtained by the methods of calibration mixtures and constant area factors in the case of internal normalisation (CMN and CAFN, respectively) and in the case of relation of concentrations to external standard (CMS and CAFS, respectively).

EXPERIMENTAL

Materials

Acetone A.R. grade (Chemical Works Oświęcim); methanol A.R. grade (Chemical Works Oświęcim); n-propanol A.R. grade (Isopharm); n-butanol A.R. grade (Isopharm); polyethylene glycol M.W. 1000 (Shell); and Chromosorb W (Johns-Manville Prod. Corp.) were used.

TABLE I

COMPOSITION OF MIXTURES AND PEAK AREAS

Sample no.	Injection	Weight m_i (g)				Sample weight m^a	Areas P_i of peaks (cm²)			
		Acetone (i = 1)	Methanol (i = 2)	n-Propanol (i = 3)	n-Butanol (i = 4)		Acetone (i = 1)	Methanol (i = 2)	n-Propanol (i = 3)	n-Butanol (i = 4)
1	a	2.2914	2.3678	2.4510	2.3841	7.1102	1.33	1.03	1.82	1.91
	b						1.17	0.92	1.56	1.69
	d						1.68	1.13	2.24	2.37
	e						1.66	1.16	2.18	2.31
	c	—	—	—	1.4278	5.6928	1.34	1.09	1.86	4.03
2	a	6.8668	0.6394	0.1510	2.6760	7.6572	3.31	0.31	0.13	2.02
	b						3.32	0.30	0.08	1.88
	c	—	—	—	1.8206	4.8871	2.61	0.22	0.12	3.59
3	a	0.1706	0.1498	7.7120	2.6142	8.0324	0.12	0.08	4.70	1.68
	b						0.14	0.09	5.88	2.28
	c	—	—	—	1.9953	5.0182	0.09	0.07	3.77	3.81
4	a	1.5600	2.3886	4.0242	2.6288	7.9728	0.80	1.02	2.59	2.01
	b						0.80	0.95	2.60	1.90
	c	—	—	—	1.5945	5.0333	0.66	0.82	2.20	3.53
5	a	5.4758	0.8406	1.5932	2.7080	7.9096	3.65	0.36	1.20	2.17
	b						2.62	0.27	0.75	1.60
	c	—	—	—	1.6199	5.0292	3.77	0.33	1.22	5.35
6	a	1.9756	3.8292	2.0204	1.3520	7.8252	1.52	1.91	1.82	1.40
	b						1.35	1.70	1.62	1.15
	c	—	—	—	0.6571	4.4584	1.32	1.72	1.68	2.47
7	a	0.7963	5.5102	1.6118	2.6349	7.9183	0.51	2.53	1.36	2.51
	b						0.55	2.39	1.30	2.30
	c	—	—	—	1.7888	5.1452	0.38	1.92	1.00	4.38
8	a	3.8051	1.6541	2.4046	2.6294	7.8638	2.98	0.84	2.28	2.82
	b						2.38	0.59	1.95	2.31
	c	—	—	—	1.5760	5.1120	1.85	0.53	1.52	4.03
9	a	0.1811	7.0755	0.6580	2.6212	7.9146	0.18	3.12	0.61	2.36
	b						0.34	2.86	0.47	2.07
	c	—	—	—	1.9401	5.1378	0.23	2.25	0.57	4.37
10	a	1.9986	0.3766	5.7171	2.5697	8.0923	1.44	0.16	4.90	2.48
	b						1.39	0.15	4.64	2.35
	c	—	—	—	1.8603	5.1981	1.00	0.10	3.48	4.45

^{a} m equals Σm_i for injections a, b, d, e and to weight of second part of sample for injection c.

TABLE II

QUANTITATIVE COMPOSITION OF 3-COMPONENT MIXTURES $[n = 3]$

Mixture no.	Component	Percentage concentration present x_{p1} or calculated x_{a1}					
		Present	CMN	CMS	CAFN $k_{14} = 1.36$ $k_{24} = 1.96$ $k_{34} = 1.10$	CAFS $k_{14} = 1.36$ $k_{24} = 1.96$ $k_{34} = 1.10$	LR (procedure 1) $k_{14} = 1.37$ $k_{24} = 1.97$ $k_{34} = 1.11$
1	1	32.2	32.1	32.4	31.0	31.7	31.1
	2	33.3	32.7	33.0	34.6	35.4	34.6
	3	34.5	35.2	35.6	34.4	35.1	34.3
2	1	89.6	88.3	83.2	85.8	78.0	85.8
	2	8.4	8.5	8.0	11.5	10.5	11.5
	3	2.0	3.2	3.0	2.7	2.5	2.7
3	1	2.1	2.3	2.5	3.0	3.2	3.0
	2	1.9	2.0	2.2	2.8	3.0	2.9
	3	96.0	95.7	104.0	94.2	100.0	94.1
4	1	19.6	19.2	18.5	18.3	17.8	18.4
	2	29.9	31.5	30.3	33.7	32.7	33.6
	3	50.5	49.3	47.5	48.0	46.6	48.0
5	1	69.3	67.6	71.1	71.1	78.3	71.2
	2	10.6	9.9	10.4	10.0	11.1	10.1
	3	20.1	22.5	23.7	18.9	20.8	18.7
6	1	25.2	25.2	23.3	26.5	25.5	26.5
	2	48.9	49.0	45.2	47.9	46.2	47.9
	3	25.9	25.8	23.9	25.6	24.7	25.6
7	1	10.0	8.9	8.5	9.7	9.2	9.7
	2	69.6	70.6	67.5	69.4	65.7	69.4
	3	20.4	20.5	19.6	20.9	19.8	20.9
8	1	48.4	48.0	49.7	49.3	48.2	49.5
	2	21.0	23.7	24.5	20.1	19.6	20.0
	3	30.6	28.3	29.3	30.6	29.8	30.5
9	1	2.3	1.1	1.1	3.5	3.4	3.5
	2	89.4	89.0	85.5	87.0	85.6	87.0
	3	8.3	9.9	9.5	9.5	9.4	9.5
10	1	24.7	24.4	24.3	25.6	25.0	25.6
	2	4.7	4.7	4.7	4.1	4.0	4.1
	3	70.6	70.9	70.6	70.3	68.8	70.3

Apparatus

A laboratory-constructed chromatograph with a flame ionisation detector and 0–2 mV recorder was employed. The column (2 m × 4 mm I.D.) was packed with 15% polyethylene glycol on Chromosorb W. Temperature of the column was 100° and of the injector 120°. Carrier gases were nitrogen (50 ml/min), hydrogen (40 ml/min) and air (1000 ml/min). The samples diluted with water (1:300) were injected in equal amounts (0.4 μl) with a Hamilton syringe. Peak areas were calculated as products of the height and width at half height.

Sample preparation

The samples (Table I) prepared by weighing the appropriate amounts of components were placed in stoppered conical flasks. The mixtures thus obtained were divided into two parts. The first part was treated once as an analysed mixture (injection a) and the second as a calibration mixture (injection b). Mixture 1 was

TABLE III

QUANTITATIVE COMPOSITION OF 4-COMPONENT MIXTURES $[n = 4]$

Mixture no.	Component	Percentage concentration present x_{pl} or calculated x_{al}			
		Present	CMN	CAFN $k_{14} = 1.36$ $k_{24} = 1.96$ $k_{34} = 1.10$	LR (procedure 2) $k_{14} = 1.37$ $k_{24} = 1.89$ $k_{34} = 1.20$
1	1	24.1	24.1	23.5	23.2
	2	25.0	24.5	25.8	24.8
	3	25.8	26.5	25.9	27.7
	4	25.1	24.9	24.8	24.3
2	1	66.4	64.2	61.9	62.1
	2	6.2	6.3	8.4	8.1
	3	1.5	2.4	1.9	2.2
	4	25.9	27.1	27.8	27.6
3	1	1.6	1.7	2.2	2.1
	2	1.4	1.6	2.2	2.1
	3	72.4	73.7	72.1	73.8
	4	24.6	23.0	23.5	22.0
4	1	14.7	14.3	13.8	13.5
	2	22.5	23.5	25.1	23.5
	3	38.0	36.8	35.8	38.3
	4	24.8	25.4	25.3	24.7
5	1	51.6	51.0	54.1	53.9
	2	7.9	7.5	7.8	7.3
	3	15.0	17.0	14.4	15.5
	4	25.5	24.5	23.7	23.3
6	1	21.5	21.3	22.5	22.5
	2	41.6	41.1	40.6	38.9
	3	22.1	21.8	21.7	23.5
	4	14.8	15.8	15.2	15.1
7	1	7.5	6.6	7.1	7.3
	2	52.2	52.4	51.4	49.7
	3	15.3	15.1	15.5	16.9
	4	25.0	25.9	26.0	26.1
8	1	36.3	36.2	36.8	36.4
	2	15.7	17.9	14.9	15.2
	3	22.9	21.4	22.7	24.3
	4	25.1	24.5	25.6	25.1
9	1	1.7	0.8	2.7	2.7
	2	67.2	66.3	65.1	63.8
	3	6.2	7.3	7.1	7.9
	4	24.9	25.6	25.1	25.6
10	1	18.7	18.5	19.3	18.5
	2	3.6	3.6	3.1	2.8
	3	53.6	53.8	53.1	55.3
	4	24.1	24.1	24.5	23.4

injected additionally twice for calculating CAF (injection d and e). The second part had been weighed again and a known amount of butanol was added (mixture c).

RESULTS

The data given in Table I were calculated as for a 3-component mixture composed of acetone, methanol and propanol and butanol as external standard (Table II) or as for a 4-component mixture of acetone, methanol, propanol and butanol (Table

TABLE IV

THE VARIANCES OF METHODS

No.	z	n = 3					n = 4		
		CMN	CMS	CAFN	CAFS	LR (procedure 1)	CMN	CAFN	LN (procedure 2)
1	10	1.12	2.60	1.60	3.31	1.61	0.94	1.31	1.58
2	9	1.13	2.44	1.20	2.62	1.42	0.88	1.05	1.53
3	9	1.13	2.44	1.41	2.46	1.54	0.88	0.95	0.96

III). The following expressions and equations were used for calculating values included in Tables II and III.

Present concentration

$$x_{pi} = \frac{m_{bi}}{\sum\limits_{i=1}^{n} m_{bi}} \cdot 100 \tag{1}$$

CMN

$$x_{ai} = \frac{m_{bi} \cdot \dfrac{P_{ai}}{P_{bi}}}{\sum\limits_{i=1}^{n} m_{bi} \cdot \dfrac{P_{ai}}{P_{bi}}} \cdot 100 \tag{2}$$

CMS

$$x_{ai} = \frac{m_{bi} \cdot m_{as} \cdot P_{bs} \cdot P_{ai}}{m_{bs} \cdot m_a \cdot P_{bi} \cdot P_{as}} \cdot 100 \tag{3}$$

CAFN

$$x_{ai} = \frac{k_{ij} \cdot P_{ai}}{\sum\limits_{i=1}^{n} k_{ij} \cdot P_{ai}} \cdot 100 \tag{4}$$

$$k_{ij} = \frac{m_{bi} \cdot P_{bj}}{m_{bj} \cdot P_{bi}} \tag{5}$$

CAFS

$$x_{ai} = \frac{k_{is} \cdot P_{ai}}{P_{as}} \cdot \frac{m_{as}}{m_a} \cdot 100 \tag{6}$$

$$k_{is} = \frac{m_{bi} \cdot P_{bs}}{m_{bs} \cdot P_{bi}} \tag{7}$$

k_{ij} and k_{is} were calculated for b = b, d, e injections of sample 1 and the mean value was taken for further calculations.

LR

The area factors were calculated according to procedure 1 (ref. 2) for a 3-component mixture:

$$\begin{cases} \sum_{i=1}^{3} k_{is} \cdot P_{ai} = \dfrac{m_a}{m_{as}} \cdot P_{as} \\[2mm] \sum_{i=1}^{3} k_{is} \cdot P_{bi} = \dfrac{m_b}{m_{bs}} \cdot P_{bs} \end{cases} \tag{8}$$

and according to procedure 2 (ref. 2) a for 4-component mixture:

$$\begin{cases} \sum_{i=1}^{3} k_{ij} \cdot P_{ai} = \dfrac{m_c}{m_{cj}} \cdot (P_{kj} - P_{aj}) - P_{aj} \\[2mm] \sum_{i=1}^{3} k_{ij} \cdot P_{bi} = \dfrac{m_c}{m_{cj}} \cdot (P_{kj} - P_{bj}) - P_{bj} \end{cases} \tag{9}$$

$$P_{kj} = \frac{\sum_{i=1}^{3} P_{bi}}{\sum_{i=1}^{3} P_{ci}} \cdot P_{cj} \quad \text{or} \quad P_{kj} = \frac{\sum_{i=1}^{3} P_{ai}}{\sum_{i=1}^{3} P_{ci}} \cdot P_{cj} \tag{10}$$

x_{ai} was calculated according to eqn. 4, taking $j = s = 4$, $k_{jj} = 1$ where

m_a, m_b, m_c are total weight of sample a, b, c;

m_{ai}, m_{bi}, m_{ci} are weights of component i in sample a, b, c;

x_{pi}, x_{ai} are actual and calculated concentrations of component i;

P_{ai}, P_{bi}, P_{ci} are peak areas of component i of a, b, c injection;

k_{is}, k_{ij} are area factors related to the external standard or j component of mixture.

From the results collected in Tables II and III, the variances of each method were calculated from equation

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n \cdot z} (x_{pi} - x_{ai})^2}{n \cdot z - 1}} \tag{11}$$

where

n is the number of components in the mixture;

z is the number of analysed mixtures.

DISCUSSION

For this work we chose to use a laboratory-made chromatograph whose performance is not perfect. We attempted to make all laboratory work routine but not sophisticated. For the mixtures, we used components which could be mixed together to give maximal differences in the area factor values. We hope that all this makes our results reliable, even for gas chromatographic laboratories, that are not well equipped.

As seen from the values in the first row of Table IV, the methods which yield concentrations related to the external standard are less accurate; the method of constant area factors and method of linear relationship are much more accurate. The most accurate seems to be the method of calibration mixtures. We believe that the method is slightly overrated because the calibration mixtures were identical with analysed ones.

The revision of data collected in Tables II and III reveals that mixture 2 exhibits the greatest deviation from the true value because it contained nearly pure acetone which had evaporated during the handling. This mixture was eliminated, the area factors for LR were recalculated and the new variances of all methods are given in the second row of Table IV. The variances were compared with the Fisher test and it was found that at the 95% level differences in variances are not significant between CMN, CAFN and LR (procedure 1) (for 3-component mixtures) but are significant between CMN and CAFN from one side and LR (procedure 2) from the second (for 4-component mixtures).

In the third row variances calculated according to the following equation are given.

$$\sigma = \sqrt{\frac{\sum\limits_{i=1}^{n \cdot z} (x_{ai} - x_{bi})^2}{n \cdot z - 1}}$$

where x_{ai}, x_{bi} are percentage concentration of component i calculated from a and b injections, which characterise the reliability of instrument recordings and area measurements. Comparison of the values in the second and third rows indicates that these last errors are the greatest part of the total errors of each method. This probably explains why LR (procedure 2) is less accurate if we notice that P_{ki} was calculated according to eqn. 10 and the left side of eqn. 9 are operations on the areas of peaks.

The method of linear relationship requires no components of the analysed mixture as chromatographically pure compounds. It is simple to carry out and its accuracy is as satisfactory as that of comparative methods.

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