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ARTICLES

Characterization of the Interlaboratory Reproducibility of Results in Quantitative Gas-Chromatographic Analysis Using the Internal Normalization Method

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Abstract—A comparison of the results of gas-chromatographic analysis performed for the same samples with the use of various instruments with flame-ionization detectors and different (packed and capillary) columns indicates statistically significant differences in the results of data processing by the internal normalization method. Such variations in relative peak areas were detected on the same instrument on a comparison between data obtained under isothermal conditions and with temperature programming. Conceivable reasons for the observed changes in relative peak areas and procedures for the evaluation of errors due to this effect in the analysis of various samples on particular instruments are considered.

A complete chromatographic analysis usually implies the identification and quantitative determination of the concentrations of all or only particular target components in test samples. To solve the latter problem, various quantitative methods of analysis are used; these differ in sample preparation and data processing techniques [1, 2]. The most accurate versions of determination imply the availability of certified reference materials, which are required for the preparation of calibration mixtures (absolute calibration and external standard techniques); the direct addition to test samples (standard addition); or the predetermination of the calibration coefficients $(f_i)_{expt}$ of the target components with reference to standard substances chosen (internal standard and internal normalization). In the absence of reference samples, quantitative analysis is usually restricted to the use of only external and internal standards or internal normalization on the condition that the chromatographic relative sensitivity coefficients $(f_i)_{calcd}$ for various compounds were theoretically precalculated. In the presentation of analytical results obtained for chemically similar substances by the internal normalization method with the use of flame-ionization detectors (FIDs), it is often assumed that $f_i \equiv \text{const}$. The same approach (the calculation of relative peak areas) is used in processing analytical results obtained by chromatography–mass spectrometry in multicomponent mixtures, although the ionization cross sections of various organic compounds are dramatically different [3].

Two objective causes are responsible for such a reduction in the requirements imposed on the results of the quantitative determination of the composition of complex samples. First is the problem of finding analyte reference samples, long considered as insignificant and completely irrelevant to quantitative analysis. However, the attitude to this problem has changed in recent years because the inappropriately great consumption of time at this stage or the high cost of these samples can make unreasonable the performance of the analysis in general [4–8]. Second, various procedures for the theoretical evaluation of relative detector sensitivity coefficients to various compounds based on the composition (or, more rarely, the structure) of analytes [1, vol. 2, p. 173; 7] give only estimated values of $(f_i)_{calcd}$, usually without estimated errors; in particular, they do not reflect the known effects of analytical conditions on the values of $(f_i)_{expt}$.

The effects of conditions (detector geometry, flame temperature, carrier gas, etc.) were characterized in the greatest detail for the absolute characteristics of FID sensitivity [1]. However, variations in the relative values $(f_i)_{expt}$ were usually considered to be comparatively small, and they were ascribed to the random component of determination errors. For this reason, specific features of data processing by the internal normalization method were not related to the temperature conditions of chromatographic separation, which were considered practically equivalent. Nevertheless, an important problem of gas chromatography consists in the determination of the sources of variations in quantitative data due to instrument factors and various analytical conditions; this is necessary for the evaluation of expected errors in the results.

In this work, we discuss the dependence of the results of quantitative gas-chromatographic analysis of the same samples by the internal normalization method

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on both the type of instruments and analytical conditions (isothermal or temperature-programming conditions) on the same instruments. The latter factor, which was not specially discussed in previous publications, is most important for the formation of concepts of the expected accuracy of the results of exploratory [9] quantitative analysis (in the absence of appropriate certified reference materials).

EXPERIMENTAL

The model mixtures of C_{11}, C_{13}, and C_{15} *n*-alkanes were prepared by weight (55–170 mg of each particular component) and analyzed as solutions (≈10 vol %) in heptane. The results discussed below belong to a sample with 50.2, 32.4, and 17.3% concentrations of these components, respectively. A sample of validol from ZAO Adaptogen Interregional Center was analyzed as a solution (≈10 vol %) in ethanol.

Gas-chromatographic analysis was performed on various instruments with FIDs and packed and capillary columns under various conditions (isothermal and with temperature programming), chosen so that the retention times of the highest boiling target components (*n*-pentadecane or isovaleric esters of menthol) were no longer than 15–20 min. Table 1 summarizes analytical conditions on each particular instrument (see below).

The flow rates of hydrogen (about 30 mL/min) and air (about 300 mL/min) considered optimum for all the instruments to be compared were adjusted on each particular instrument in the course of verification. They were not additionally controlled or optimized immediately before determinations; this is consistent with the common practice of analyzing real samples. Samples (0.4–2 μL) were injected with Gazokhrom-101 and MSh-10 microsyringes. In each regime, the reproducibility of analysis was characterized on the basis of the results of three or four determinations. A TR 2213 integrator, a Multikhrom computer system, or a Khromatek data processing system was used for measuring chromatographic peak parameters.

RESULTS AND DISCUSSION

The starting point for this study of the interlaboratory reproducibility of the results of quantitative analysis with the use of internal normalization and the dependence of these results on the temperature conditions of analysis on particular instruments was a comparison of the calculated FID relative sensitivity coefficients $(f_i)_{calcd}$ [1] with the experimental values $(f_i)_{expt}$ under various conditions, as well as the results of analysis of real samples with different compositions. It is most likely that the scatter of data observed in this case was due to a set of causes rather than a single cause; the effect of these causes is difficult to separate. Therefore, to exclude at least the uncontrolled effects due to the sorption of polar compounds in chromatographic systems, a combination of three nonpolar substances was chosen as a model mixture. These substances were C_nH_{2n+2} *n*-alkanes with $n = 11$, 13, and 15, whose boiling temperatures are significantly different (195.9, 235.4, and 270.6°C, respectively). The mixture of these components was analyzed on various instruments in at least one isothermal regime and one temperature-programmed regime followed by data processing by the internal normalization method without considering FID relative sensitivity coefficients to different alkanes. In this case, relative peak areas should be close to the relative concentrations of components in the mixture because the values of $(f_i)_{calcd}$ [1] are virtually no different from unity:

$$f(c_{13}/c_{11})_{calcd} \approx 0.998 \quad \text{and} \quad f(c_{15}/c_{11})_{calcd} \approx 0.997.$$

The degree of coincidence between the set of the average values of relative peak areas (S_i, %) and the specified model mixture composition (m_i, wt %) can be evaluated as the sum of the absolute values of corresponding differences D (%) (the summation is made over all sample components other than the solvent):

$$D = \Sigma|m_i - S_i|. \quad (1)$$

The degree of noncoincidence of relative peak areas under different temperature conditions of analysis on the same column and the same instrument (Δ, %) can be expressed using an analogous relationship:

$$\Delta = \Sigma|S_{i1} - S_{i2}|. \quad (2)$$

Finally, to evaluate the statistical significance of observed differences (Δ), they can be compared with the corresponding sum of standard deviations of relative peak areas (%) under both conditions under comparison. Differences can be considered beyond the limits of a random scatter of data if the following inequality is true:

$$\Delta > \Sigma s(S_{i1}) + \Sigma s(S_{i2}). \quad (3)$$

The absolute values of differences and standard deviations in (1)–(3) are given for simplicity and a more convenient illustration of further comparisons. More strictly speaking, the relationships should contain the squares of the corresponding values; however, such a rearrangement does not affect all the subsequent conclusions.

Table 1 generally summarizes the results of analysis of a model mixture of *n*-alkanes on instruments manufactured in different years under various analytical conditions. The principles of this comparison are analogous to, for example, a comparison of the results of analysis of carboxylic acid mixtures at different procedures used for the preparation of the methyl esters of these acids [10]. Consideration of these data demonstrated unsystematized variations in them, because of which the main parameters affecting the accuracy and the repeatability of the results cannot be revealed. Thus, for example, the best fit of relative peak areas to the specified model mixture composition (a minimum of

Table 1. Comparison of the results of analysis of a mixture of C_{11}, C_{13}, and C_{15} *n*-alkanes by the internal normalization method under various temperature conditions

Chromatograph model; column parameters; carrier gas; detector thermostat temperature; data processing system						
analytical regime no. 1	S_{rel}, %	D, %	analytical regime no. 2	S_{rel}, %	D, %	$\Delta <> [\Sigma s_{i1} + \Sigma s_{i2}]$, %
(1) Tsvet-102 (1972); packed column (3 m × 3 mm); 5% SE-30 on Chromaton N-AW; nitrogen, 30 mL/min; no detector thermostat; TR 2213 integrator						
Isothermal,	55.2 ± 0.8		Program,	52.3 ± 0.3		
140°C	31.4 ± 1.6		80 ⟶ 225°C,	32.6 ± 0.3		
	13.3 ± 0.8	10.0	12 K/min	15.1 ± 0.2	4.5	5.9 > 4.0
(2) Tsvet-500 (1995); packed column (1 m × 2 mm); 5% SE-30 on Chromaton N-AW HMDS; nitrogen, 10 mL/min; detector thermostat, 220°C; Multikhrom computer system						
Isothermal,	48.8 ± 0.8		Program,	49.7 ± 0.2		
100°C	33.8 ± 0.3		80 ⟶ 150°C,	32.8 ± 0.3		
	17.4 ± 0.5	2.9	12 K/min	16.5 ± 0.2	1.7	2.8 > 2.3
(3) Biokhrom-1 (1980); capillary column (25 m × 0.2 mm) with OV-101 (0.1 μm); nitrogen, 14 cm/s; split ratio, 1 : 25; detector makeup gas unknown; detector thermostat, 240°C; TR 2213 integrator						
Isothermal,	49.6 ± 0.2		Program,	45.8 ± 0.6		
150°C	32.9 ± 0.1		80 ⟶ 240°C,	33.0 ± 1.5		
	17.3 ± 0.1	1.1	8 K/min	21.2 ± 2.0	8.5	7.8 > 4.5
(4) Biokhrom-1 (the same conditions; detector heating turned off)						
Program,	49.8 ± 0.8		Program,	49.2 ± 0.4		
140 ⟶ 200°C,	32.8 ± 0.3		100 ⟶ 250°C,	32.8 ± 0.3		
2 K/min	17.3 ± 0.6	0.8	12 K/min	18.0 ± 0.6	2.7	1.3 < 3.0*
(5) Tsvet-800 chromatograph (1999); capillary column (25 m × 0.32 mm) with HP-1 polysiloxane; nitrogen, 1.0 mL/min; split ratio, 1 : 200; detector makeup gas, 30 mL/min; detector thermostat, 250°C; Khromatek version 1.2 data processing system						
Isothermal,	49.4 ± 0.2		Program,	49.9 ± 0.5		
150°C	33.8 ± 0.0		100 ⟶ 220°C,	33.6 ± 0.3		
	16.8 ± 0.2	2.7	10 K/min	16.5 ± 0.4	2.3	1.0 < 1.6*
Isothermal,	49.2 ± 0.2					
170°C	33.8 ± 0.1		Same	Same		
	17.0 ± 0.1	2.7			2.3	1.2 < 1.6*
(6) Kristall 2000M chromatograph (2001); capillary column (50 m × 0.32 mm) with CP Sil 5 CB polysiloxane (1.2 μm); nitrogen, 2.0 mL/min; split ratio, 1 : 50; no detector makeup gas; detector thermostat, 250°C; Khromatek version 1.2 data processing system						
Isothermal,	47.5 ± 0.3		Program, 100	48.5 ± 0.2		
200°C	34.2 ± 0.1		100 (1-min exposure) ⟶ 270°C,	33.8 ± 0.1		
	18.3 ± 0.2	5.5	10 K/min	17.7 ± 0.1	3.5	2.0 > 1.0

* Statistically insignificant differences between the results $\Delta < (\Sigma s_{i1} + \Sigma s_{i2})$.

D) was observed on a Biokhrom-1 chromatograph with a capillary column; in one case ($D = 0.8$), there was no heating of the detector thermostat. Thus, this instrument factor is not one of the main reasons for the observed effects. In general, the values of the parameter *D* varied from 1 to 10% (on the average, 3.2 ± 2.0) for various instruments and analytical regimes. With temperature programming, the values of *D* may be unpredictably higher or lower than the values of *D* under isothermal conditions.

Differences in the results of analysis of the model mixture under isothermal conditions and with the temperature programming (Δ parameters) for four of the seven versions of the analysis were higher than the sum of corresponding standard deviations of peak arrears in each of the regimes under consideration [$\Sigma s(S_{i1}) + \Sigma s(S_{i2})$] (see the last column in Table 1). One of these versions (no. 4) is a comparison between two different temperature-programming conditions, when minimal

differences should be expected. Note that the values of Δ were twofold higher than the sum $[\Sigma s_{i1} + \Sigma s_{i2}]$ even for a Kristall 2000M chromatograph, which is equipped with an electronic flow control system with a capillary column (but with no additional supply of a carrier gas to the detector). Statistically insignificant values of Δ were obtained only with a Tsvet-800 instrument with a capillary column and an additional supply of the carrier gas to the detector. In all the other versions of analysis, $\Delta > [\Sigma s_{i1} + \Sigma s_{i2}]$, but it was no higher than the doubled value of this sum, which corresponds approximately to the confidence probability of the significance of such differences at a level of 0.75–0.95 (t value) [11]. The data in Table 1 did not reveal noticeable systematic differences in the values of D and Δ for packed and capillary columns. Thus, it is believed that a further extension of such consolidated data will not radically change due to both instruments the general characteristics of the results and analytical conditions. If a statistical processing (randomization) of all interlaboratory and interinstrument data in Table 1 is performed, the results of analysis of the model mixture as compared with the specified composition take the following form:

Component	Specified concentration, wt %	Average relative peak area, %	Relative standard deviation $\delta(S)_i$, %
n-C_{11}	50.2	49.7 ± 2.5	5.0
n-C_{13}	32.4	33.0 ± 0.8	2.4
n-C_{15}	17.3	17.2 ± 2.1	12.2

Consequently, in spite of the observed scatter of data given in Table 1, the general average values of relative areas are consistent with the composition of samples. The value of D was equal to 1.2, much lower than the sum of the standard deviations of relative peak areas (5.4). However, the coefficient of variation $\delta(S_i)$ of the least volatile component of the mixture (n-pentadecane) was higher than 12%, and it is believed that the concentrations of mixtures containing higher boiling components estimated by the internal normalization method may be even more ambiguous. It is interesting to note an additional practically important feature of data in Table 1. For instruments of the last generation (manufactured after 1995), the values of Δ (1.5 ± 0.7%) were much lower than those for earlier models (6–8%). Consequently, in terms of this value, state-of-the-art instrumentation is preferred in order to achieve maximum accuracy in the results.

The most annoying feature in the revealed interlaboratory irreproducibility of relative peak areas in the internal normalization method consists in both the unpredictable underestimation and overestimation of the concentrations of particular components, as compared with the true concentrations in the samples. By analogy with the mass discrimination effect of signal intensities with high mass numbers in mass spectrometry [12], this chromatographic effect can be designated as the discrimination of relative peak areas. Thus, much smaller relative peak areas of n-C_{15} (version no. 1) could be explained by the absence of detector thermostatting and by errors in the on-line integration of peak areas (see discussion in [8]). However, this conclusion was not supported by analytical version no. 4 with the use of the same data acquisition system. The relative concentrations of the specified component determined with temperature programming were unpredictably found either lower (no. 2) or higher (nos. 1 and 3) than that found under isothermal conditions (in the other cases, they were comparable within the limits of determination errors). It is likely that there is no way to determine at least the sign of such systematic deviations in the analysis of mixtures with unknown compositions in each particular case.

The inconstancy of the flow rate of a carrier gas through the column seems the most important (but probably not the only) reason for observed variations in relative peak areas in the internal normalization method with temperature programming with reference to isothermal conditions (or vice versa). This can affect the geometry parameters of a flame in the FID; its temperature; the localization of the zone of predominant ionization of organic compounds with respect to detector electrodes; and, probably, the mechanism of ionization. These effects are aggravated by analyte sorption, which is difficult to take into account (particularly under isothermal conditions); the discrimination of components with different volatilities on split sample injection into capillary columns; and unavoidable errors in the integration of the areas of weak signals [8]. It is likely that the temperature conditions of the detector were changed in the course of temperature programming in spite of thermostatting. It is not only unreasonable but also impossible to discover and characterize individually all of the above factors, and the data in Table 1 should be considered as the result of their "integral" action. Data obtained on a Tsvet-800 chromatograph provide support for the appropriateness of revealing variations in the carrier-gas flow rate as the most important cause of discrepancy between the results obtained under different temperature conditions of analysis. The combination of a small (1 mL/min) carrier-gas flow rate through a capillary column with a much greater (30 mL/min) constant makeup-gas flow rate to the detector, which compensates for variations in the carrier-gas flow rate, is the most effective means of eliminating these errors. In the absence of a makeup gas, even electronic flow control does not eliminate completely these errors, although it does reduce the differences in the relative peak areas under various conditions (version no. 6).

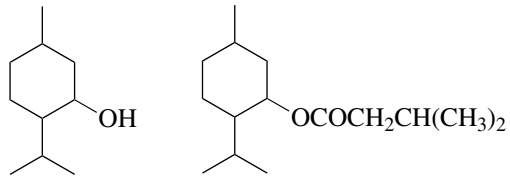
Serious analytical problems related to the effects observed can be illustrated by various examples; it is reasonable to consider only the most typical example. An officially approved procedure (FS 42-3006-98) for the gas-chromatographic analysis of validol [a solution of racemic menthol (**I**) in a mixture of menthyl isoval-

Table 2. Comparison of the results of gas-chromatographic analysis of a validol preparation under various conditions on different instruments (the true concentrations of menthol and its isovaleric esters are unknown)

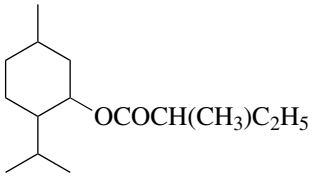
Chromatograph model; column parameters; carrier gas; detector thermostat temperature; data processing system	Temperature conditions of analysis (initial temperature ⟶ final temperature)	Ratio of the total peak area of esters to the peak area of menthol, S_{rel}
Tsvet-102; packed column (3 m × 3 mm) with 5% SE-30 on Chromaton N–AW; nitrogen, 30 mL/min; no detector thermostat; TR 2213 integrator	Program, 70 ⟶ 200°C, 8 K/min	2.83 ± 0.06
	Program, 100 ⟶ 200°C, 8 K/min	2.88 ± 0.04
	Program, 50 ⟶ 200°C, 12 K/min	2.82 ± 0.03
	Isothermal, 190°C	3.10 ± 0.06
Average value of S_{rel} over all data		2.9 ± 0.1
Tsvet-500 (three instruments); packed column (1 m × 2 mm) with 3% SE-30 on Chromaton N Super (first two regimes) or Inerton; nitrogen, 30 mL/min; detector thermostat, (a) without heating, (b) 250°C, and (c) 280°C; Multikhrom computer system	Program, 80 (0.5-min exposure) ⟶ 100°C, 25 K/min	2.64 ± 0.15
	Program, 70 (1.5-min exposure) ⟶ 200°C, 15 K/min	2.81 ± 0.08
	Isothermal, 170°C	2.77 ± 0.02
	Isothermal, 200°C	3.05 ± 0.03
	Isothermal, 220°C	3.18 ± 0.04
Average value of S_{rel} over all data		2.9 ± 0.2
Tsvet-800 chromatograph; capillary column (25 m × 0.32 mm) with HP-1; nitrogen, 1.0 mL/min; split ratio, 1 : 200; detector makeup gas, 30 mL/min; detector thermostat, 250°C; Khromatek version 1.2 data processing system	Isothermal, 170°C	2.95 ± 0.05*
	Program, 100 (1-min exposure) ⟶ 200°C, 10 K/min	2.97 ± 0.01*
Average value of S_{rel} over all data		2.96 ± 0.05

* The ratio of the total peak area of esters to the total peak areas of menthol and isomenthol, which are separated on the capillary column.

erates (**II**, **III**)] is based on the evaluation of component concentrations using the internal normalization method (the expected relative sensitivity coefficient of the esters with reference to menthol is $f_i = 1.03$ [1]). In this case, other methods of quantitative analysis are inapplicable in actual practice because only menthol, rather than its esters, is available as a reference sample.



(**I**) (**II**)



(**III**)

However, as in the case of the above model mixture of alkanes, the gas-chromatographic analysis of validol can also be associated with the irreproducibility of ester peak areas with reference to menthol under various conditions (Table 2). This was observed in analyses on Tsvet-102 and Tsvet-500 chromatographs with packed columns (in this case, the general average values of relative peak areas determined on different instruments were practically coincident). Because the signs of discrimination effects are unknown, the only opportunity is to average all the results to obtain a rough estimation of 2.9 ± 0.2. However, let us consider analytical regime no. 5 (Table 1), found from the results of analysis of a model mixture. This regime is characterized by minimal discrimination of relative peak areas (2.97 ± 0.01 and 2.95 ± 0.05 under isothermal conditions and with temperature programming, respectively), and the average value is 2.96 ± 0.05; this is consistent with the previous result (2.9 ± 0.2) but superior to it in accuracy.

Thus, the above allowed us to formulate a new assessment criterion for the reliability of results in gas-chromatographic analysis with the use of the internal standard method in the absence of analyte reference samples. Because the sign of the effect of discrimination of relative peak areas under particular analytical conditions is unknown, it is reasonable to recommend replicate determinations under different tempera-

ture conditions (for example, to compare isothermal conditions with the separation with temperature programming) rather than to restrict the analysis to an arbitrarily chosen regime. As a rule, the scatter of data observed in this case is greater than the estimated reproducibility of relative peak areas in each of these regimes, and it should be taken as the final evaluation of errors in the results. If test samples are complex (multicomponent) and cannot be analyzed under isothermal conditions for this reason, these estimations can be obtained for model mixtures. It is of considerable importance that, in this case, it is unnecessary to know the true composition of model mixtures, because the main comparison test for various regimes is expression (3): a comparison of the total differences of the relative peak areas of all of the sample components (Δ) with the corresponding sums of their standard deviations in both of the regimes.

The discrimination of relative peak areas under various temperature conditions of analysis should be considered in all versions of the quantitative determinations related to the absence of reference samples. For example, the use of relative sensitivity coefficients [13] (or relative signals of various detectors) for the identification of unknown compounds under arbitrary temperature conditions of chromatographic analysis is reasonable only when differences between them are greater than possible determination errors. On the other hand, the quantities in the experimental determination, of which all of the errors discussed in this paper are compensated for to a considerable extent regardless of the temperature conditions of analysis, can be exemplified by the distribution coefficients of analytes in the heterophase systems of organic solvents [14], because the successive analysis of each particular component of these systems is usually performed under identical conditions.

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