Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 985 (2003) 21–27
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Quantitative accuracy in the gas chromatographic analysis of solvent mixtures

Johan Pettersson, Johan Roeraade*
Royal Institute of Technology, Department of Analytical Chemistry, Teknikringen 36, SE-10044 Stockholm, Sweden

Abstract

Quantitative accuracy is of great importance in the analysis of bulk mixtures of solvents, particularly when the analysis is related to quality control of very large product volumes like in solvent recovery plants. Serious errors can be made if the effects of density differences between the pure solvents and volume contractions are not properly addressed. In earlier work, the use of an iterative process for correcting such errors has been suggested. However, in the case of volume contractions and mixtures of several solvents, this procedure is difficult to apply. In the present paper, we describe a simple procedure where calibration curves based on mass concentration are utilized. The densities of calibration mixtures of known compositions are determined with a density meter, in order to provide for correction factors caused by volume contractions. Model experiments with mixtures of water, ethanol, acetone and methanol showed a significant improvement in quantitative accuracy, when the suggested calibration strategy was applied.

Keywords: Accuracy; Calibration; External standards; Volume contraction; Molar excess volumes; Gas chromatography; Ethanol; Water; Methanol; Acetone

1. Introduction

Quantitative analysis of solvents and solvent mixtures is a routine application of gas chromatography (GC) in industry, e.g., in solvent recovery distillation plants, the paint industry, etc. In striving for good accuracy, internal standards are usually employed. However, this is not always feasible, for example in process analysis where a direct on-line sampling is performed from a production unit or a storage tank. In such instances calibrations based on external standards need to be carried out. Due to the volumetric precision and repeatability of modern automatic injectors excellent quantitative results can be obtained. Moreover, if a large number of different samples are to be analyzed the use of external standards saves time and simplifies the overall procedure, which can be important in an at-line or on-line setup in a production environment.

However, there is an important issue to be considered when analyzing bulk mixtures of solvents. Different solvents usually have different densities. In addition, changes in molar volumes can occur when certain solvents are mixed, thereby further affecting the density of the sample. This is caused by reduced or increased molecular interaction on mixing, and the degree of volume change is dependent on the relative concentrations of the compounds involved. A typical and well-known example is mixing of ethanol and water, which leads to a considerable volume reduc-

*Corresponding author. Tel.: +46-8-790-8214; fax: +46-8-108-425.
E-mail address: jroe@analyt.kth.se (J. Roeraade).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)01830-7

tion [1]. In applications where the sample is only one solvent, containing minor or trace amounts of other analytes, the variation in the density due to the sample composition is negligible. However, when analyzing mixtures of solvents, where each of the components are present in large proportions, overlooking variations in the density or using incorrect calibration procedures can result in severe quantitative errors.

Marsman et al. [2] have pointed out this problem and suggested a possible strategy. To deal with variations in the density, a term called ''specific response area'' was introduced.

For a given component, the term consists of the peak area (A_i) divided by the density (ρ_m) and the volume (V_I) of the injected sample. The term is a function of the mass fraction of the relevant component according to:

$$\frac{A_i}{\rho_m V_I} = k_i w_i \quad (1)$$

where, A_i = peak area for component i (arbitrary units); ρ_m = density of the mixture (kg m^{-3}) at temperature T and pressure p; V_I = injection volume (m^3); k_i = detector constant for the component i (arbitrary units); w_i = mass fraction of component i in the mixture [kg (i) kg (mixture)$^{-1}$].

Since the density of an analyzed sample is unknown, Eq. (1) cannot be applied directly. However, by using the relationship shown in Eq. (2), the results (expressed in mass fraction) can be determined by iteration:

$$\rho_m = \frac{1}{\sum_{i=1}^{n} \frac{w_i}{\rho_i}} \quad (2)$$

where ρ_i = density of component i (kg m^{-3}) at temperature T and pressure p.

Thus, from the peak area obtained for each compound, and starting with an estimated value for the sample density ρ_m in Eq. (1), a first estimate of the mixture composition is made. Using the obtained values, a new and more accurate density can be calculated using Eq. (2). Then the new estimate of ρ_m is utilized to calculate a new composition using Eq. (1). The procedure is repeated until the calculated density equals the estimated one.

With Marsman et al.'s approach, variations in density caused by sample composition are compensated for, but the peak areas of all the main compounds (except one, $n-1$) have to be measured and utilized to enable the subsequent iteration.

If changes in molar volume occur, Eq. (2) needs to be replaced with a more complicated relation that also includes these effects. Unfortunately molar volumes of components in solvent mixtures are often unknown. The data available (e.g., Refs. [1,3,4]) are usually only for binary systems. The methodology as described by Marsman et al. is therefore not suitable for all cases.

In this paper, we suggest a simple and more straightforward approach to deal with the described density variations. The procedure is based on performing injections of a given, constant sample volume, and the use of a calibration curve based on mass concentration (kg m^{-3}), where the actual mass concentration of the calibration samples are determined after their change in volume. We exemplify the severe quantitative errors that can be made, if the effects of density changes are disregarded. We also show the improvements obtained by applying our suggested calibration strategy.

2. Experimental

2.1. Apparatus

All GC separations were performed using a HP6890 gas chromatograph, equipped with a split/splitless injector, a flame ionization detection (FID) system (250 °C) and a thermal conductivity detection (TCD) system (200 °C) (Agilent Technologies, Palo Alto, CA, USA). The original injector was extended with a separately heated body, to hold an injector liner of a total length of 20 cm. The empty top part of the liner (8 cm) was kept at 180 °C. The bottom part of this liner (12 cm) (filled with Porapak-Q, 80–100 mesh) was kept at 160 °C. With this arrangement, a highly reproducible sample vaporization of the injected sample is accomplished [5,6]. The injection volume was 0.5 μl and a HP7673A liquid autosampler (Agilent Technologies) was used. The capillary column was a DB-624, 30 m × 0.32 mm I.D., 1.8 μm film thickness (Agilent Technologies).

The oven temperature was set to 45 °C (isothermal). The carrier gas was helium, 2.0 ml/min, and the split ratio was 1:60. Density measurements were performed with a density meter from Mettler-Toledo (DA-100M).

2.2. Sample preparation and calibration

All samples were prepared on a mass basis. Four replicate runs were performed on each sample. In the study concerning insignificant volume contraction two calibration sets were prepared. The first set consisted of 14 different mixtures of 1,2-dichloroethane (EDC) and ethanol evenly ranging between 100 and 6.7% (w/w) ethanol. The second set consisted of mixtures of ethanol and methanol evenly ranging between 100 and 9.8% (w/w) ethanol. In the study concerning significant volume contraction mixtures of four solvents (acetone, methanol, ethanol and water) were prepared and allowed to cool to room temperature before their density was measured. The uncorrected mass concentrations, measured densities and correction factors for volume contraction are listed in Table 1.

2.3. Chemicals

Methanol, acetone, 1,2-dichloroethane (analytical-

Table 1
Sample mixtures for calibration models

Uncorrected mass concentrations				Measured density (g/ml)	Volume contraction factor
Ethanol (g/ml)	Water (g/ml)	Methanol (g/ml)	Acetone (g/ml)		
Calibration samples					
0.039	0.450	0.160	0.235	0.920	1.0405
0.078	0.403	0.079	0.314	0.910	1.0407
0.197	–	0.398	0.196	0.793	1.0032
0.210	0.301	0.020	0.321	0.884	1.0364
0.299	0.401	0.154	0.020	0.907	1.0384
0.359	0.303	0.191	–	0.882	1.0340
0.527	–	–	0.262	0.791	1.0017
0.531	0.299	–	0.021	0.879	1.0320
0.727	0.051	–	0.022	0.808	1.0104
0.789	–	–	–	0.789	1.0000
Validation samples					
0.154	0.503	–	0.238	0.930	1.0392
0.277	0.051	0.232	0.240	0.811	1.0127
0.272	0.454	–	0.158	0.919	1.0391
0.288	0.529	0.083	–	0.933	1.0367
0.293	0.326	–	0.239	0.890	1.0373
0.310	0.152	0.360	–	0.842	1.0246
0.307	0.394	0.171	–	0.905	1.0379
0.355	0.503	–	0.036	0.927	1.0364
0.433	0.399	–	0.040	0.904	1.0359
0.471	0.376	–	0.021	0.898	1.0349
0.501	–	0.146	0.143	0.791	1.0016
0.540	–	0.250	–	0.790	1.0005
0.575	0.051	0.021	0.154	0.809	1.0112
0.594	–	0.195	–	0.795	1.0070
0.588	0.154	0.079	–	0.841	1.0237
0.614	–	0.175	–	0.790	1.0007
0.613	–	–	0.177	0.802	1.0159
0.635	0.102	–	0.074	0.825	1.0178
0.685	0.104	–	0.021	0.825	1.0174

reagent grade) and water (LiChrosolv) were obtained from Merck (Darmstadt, Germany). Ethanol (>99.5%, v/v) was obtained from Kemetyl (Sweden).

3. Results and discussion

In many industrial situations, very large volumes of solvent mixtures are handled, e.g., in solvent recovery plants. High precision in the determination of the individual components is very important, in view of the value of the large bulk volumes. Volume contractions are often minor and can hence be neglected. However, when water is present together with other polar solvents, volume changes can be considerable, e.g., acetone with water can generate a volume contraction of up to 4.5% [7].

3.1. Insignificant volume contractions

Let us consider the situation where the volume contraction is insignificant. In this case, the peak area obtained for a certain component A in a solvent mixture can be described by a rearranged form of Eq. (1). For a binary system a unique calibration curve always exists but no linear relationship would be obtained if the density of the components were dissimilar. Concerning multi-component mixtures with dissimilar densities, no unique calibration curve can be obtained since the density of the sample depends on its overall composition. A solution for this problem would be to use the algorithm developed by Marsman et al. [2]. However, an obvious approach is to utilize a calibration curve, based on mass concentration, according to:

$$A_i = k_i m_i = k_i V_I \gamma_i \quad (3)$$

where γ_i = mass concentration of component i in the mixture (kg m^{-3}) at temperature T and pressure p.

As can be seen, no internal correlations are present and consequently, linear calibration curves are obtained. For reporting the quantitative results in mass fraction (w/w), the density of the sample has to be known. To enable this, all bulk components (or at least $n-1$) have to be quantified and calibrated for (as w/v) or the density of the sample has to be determined separately.

As a model example, two sets of calibration samples of binary mixtures were prepared on mass basis. One set contained ethanol mixed with methanol whereas the other set was mixed with EDC, four replicates were analyzed on the GC system. The volume change on mixing these solvents can be considered as negligible (max +0.16% and min −0.05%) over the entire concentration span [4,8]. The diagram in Fig. 1 shows the two calibration curves obtained, based on mass fraction. While the calibration curve for the mixture of methanol and ethanol is close to linear reflecting the fact that the density of these solvents is very similar, the calibration curve for the EDC–ethanol mixtures is significantly non-linear. The maximum difference between the two calibration curves is theoretically ~56% at low concentration of ethanol (point 1 in Fig. 1), reflecting the full density difference between methanol and EDC. For ternary mixtures including these solvents, neither of these calibration curves is suitable. To illustrate this, a ternary calibration mixture of the three solvents methanol, ethanol and EDC was analyzed. The result is indicated by the

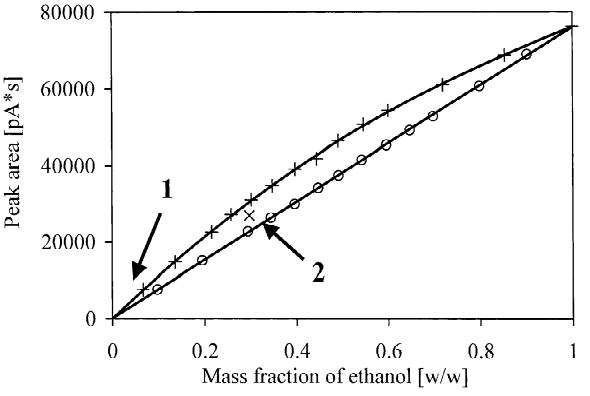

Fig. 1. Mean absolute peak area ($n=4$) of the two calibration sets vs. the mass fraction of ethanol ($\rho=0.789$ g cm^{-3}). The curved line (+) is a polynomial fit for samples containing 1,2-dichloroethane ($\rho=1.235$ g cm^{-3}, curve fit: β_0 (intercept) = 447.0, β_1 = 111 031, β_2 = −35 557 and correlation coefficient = 0.9996). The straight line (○) represents mixtures with methanol (negligible density difference, $\rho=0.791$ g cm^{-3}, curve fit: slope = 75 963.7, intercept = 275.0, standard error = 256.9, standard deviations of slope and intercept: 271.8 and 160.1, respectively). The mark (×) at point 2 represents a ternary calibration sample (not included in the regression calculations) and has a y-residual of −10.9% relative the curved line and +18.2% to the straight line. This sample contained 29.6% (w/w) methanol and 40.7% (w/w) EDC.

cross between the two drawn lines at point 2 in Fig. 1, which clearly shows a deviation. However, if mass concentration is used on the *x*-axis, both calibration sets fit well to a single straight calibration line. This calibration line will be valid not only for mixtures of the actual solvents but also for samples containing other solvents. A regression analysis based on all of the binary calibration samples in Fig. 1 yields a correlation coefficient of 0.9997 (slope = 96 755.4, intercept = 109.5, standard error = 353.5, SDs of slope and intercept: 336.1 and 156.8, respectively). The ternary calibration mixture fits well to the calibration curve (*y*-residual: 1.06%, $n = 4$).

The results obtained from the described experiments could perhaps be regarded as obvious, but we have encountered several cases in industry, where the effects of different densities were disregarded and where the resulting poor accuracy was incorrectly interpreted as due to instrumental systematic errors.

3.2. Significant volume contractions

As pointed out in the Introduction, volume changes on mixing of solvents can be significant, thereby affecting the quantitative accuracy of an analysis. Any volume contraction will alter the volume fraction of analytes in a complex manner while the mass fraction of the analytes will be unaffected. The mass concentration is obviously affected proportionally to the degree of volume contraction. In order to obtain accurate calibration values it is therefore necessary to know the true mass concentrations after mixing. If the density of the calibration samples after mixing is known then the true mass concentrations can be calculated.

One approach to obtain correct density values when preparing calibration samples is by polynomial interpolation from literature values or by the use of other empirical relationships that can be found in the literature (e.g., Refs. [7–9]). However, only binary systems and ternary systems have been reported. The most straightforward way is to prepare calibration samples on a mass basis while filling a container with a known total volume, e.g., a pycnometer and the actual densities of the calibration samples are obtained. However, this procedure is rather laborious. It is easier to utilize a commercial density meter for this purpose. An accuracy of ± 0.001 g/ml is readily obtained, which is fully adequate. The measured density of the calibration sample is divided by the calculated density value, where it is assumed that no volume contraction would have taken place. In this way, factors correcting for contraction are obtained. Once these correction factors have been obtained, they can be reused in forthcoming calibrations when using the same compositions.

To exemplify the effects of contraction in quantitative analysis, 28 different mixtures of the four components water, methanol, acetone and ethanol were prepared randomly in various proportions, but covering a wide range of the ethanol concentrations (Table 1). Of these samples, nine were randomly selected and used to calibrate the instrument; pure ethanol was also included as a calibration level. Four replicates of each of the samples were analyzed with respect to ethanol concentration. Two calibration models were created, one using mass concentration not corrected for any possible volume contraction and the other with corrected values. Volume contractions ranged between 0.0 and 4.1%. Conventional regression calculations were performed and the data are shown in Table 2. As can be seen, the uncorrected model yielded a higher standard error, probably due to the presence of systematic errors. The remaining 19 prepared samples were used to validate the two calibration models. The calculated mass concentration of ethanol based on the mass and

Table 2
Regression data of the two calibration models

	Model 1 (uncorrected γ)	Model 2 (corrected γ)
Slope	25 173.5	25 119.9
Intercept	289.2	153.2
Standard error	295.4	176.0
SD of the slope	378.5	224.9
SD of the intercept	170.1	102.3

Table 3
Regression data obtained when plotting predicted mass concentrations versus mass concentrations obtained through mass and density measurements

	Model (uncorrected γ)	Model (corrected γ)
Slope[a]	1.0091±0.018	1.0113±0.018
Intercept[a]	−0.0111±0.0088	0.0057±0.0088
Standard error	0.00587	0.00588
SD of the slope	0.00868	0.00870
SD of the intercept	0.00419	0.00419

[a] ± gives the 95% confidence limits.

density measurements (reference values) were subtracted from the predicted mass concentrations to yield the estimation errors. Evaluation of the results was performed by using the Rankit procedure [10]. The results from both models are shown in Fig. 2 where the rankits are plotted versus the estimation errors. The two good fits by the regression lines clearly show that both sets of estimation errors have a normal distribution. By visual inspection, the model using uncorrected mass concentrations appears to have systematic errors that lead to underestimations of the mass concentrations. Systematic errors were investigated by plotting the estimated values versus the reference values and the calculated regression data for each model are presented in Table 3. It can be concluded from Table 3 that the intercept parameter of the uncorrected model is significantly smaller than zero and consequently there is a constant negative systematic error in this model. This systematic error will cause a significant loss in accuracy. No systematic errors could be detected in the model using corrected mass concentrations.

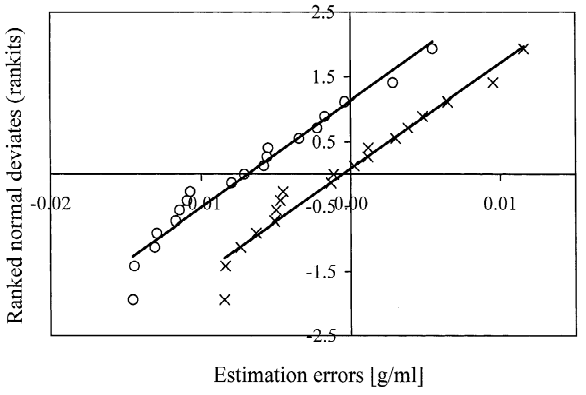

Fig. 2. Results of the Rankit method applied to the two sets of estimation errors. Individual estimation errors obtained using the calibration model based on uncorrected mass concentrations are shown by (○) and the other calibration model based on corrected values is represented by (×). Regression data of the two lines are (the values in parentheses are for the corrected model): slope = 164.8 (162.2), intercept = 1.14 (0.090), standard error = 0.223 (0.213), SD of slope = 8.94 (8.38), SD of intercept = 0.080 (0.049).

4. Conclusions

Our work shows that serious quantitative errors can occur in the analysis of bulk mixtures of solvents if differences in density and effects of volume contractions are not taken into account. By adopting a procedure based on mass calibration combined with a correction, based on the measurement of the density of the calibration samples, these errors can be avoided.

Acknowledgements

The Swedish Research Council is acknowledged for financial support.

References

[1] R.C. Weast, M.J. Astle, W.H. Beyer (Eds.), Handbook of Chemistry and Physics, 65th ed., CRC Press, Boca Raton, FL, 1984, p. D-231.
[2] J.H. Marsman, H.J. Panneman, A.A.C.M. Beenackers, J. Chromatogr. 483 (1989) 111.
[3] M. Iglesias, B. Orge, M.M. Piñeiro, B.E. de Cominges, G. Marino, J. Tojo, J. Chem. Eng. Data 43 (1998) 776.
[4] S.K. Chaudhari, S.S. Katti, J. Chem. Thermodynamics 21 (1989) 667.

[5] V.G. Berezkin, T.P. Popova, A.A. Korolev, V.E. Shiryaeva, L.S. Vasin, V.N. Lipavskii, J. High Resolut. Chromatogr., Chromatogr. Commun. 11 (1988) 42.
[6] A.L. German, E.C. Horning, Anal. Lett. 5 (1972) 619.
[7] E.W. Washburn (Ed.), International Critical Tables of Numerical Data, Physics, Chemistry and Technology, 1st ed., McGraw-Hill, New York, 1928.
[8] L. Albuquerque, C. Ventura, R. Gonçalves, J. Chem. Eng. Data 41 (1996) 685.
[9] B. Orge, M. Iglesias, J. Tojo, J.L. Legido, J. Chem. Thermodynamics 26 (1994) 121.
[10] B.G.M. Vandeginste, S.C. Rutan (Eds.), Handbook of Chemometrics and Qualimetrics: Part A, Elsevier, Amsterdam, 1997.