CROATICA CHEMICA ACTA CCACAA **72** (4) 819–825 (1999)

ISSN-0011-1643
CCA-2616

Original Scientific Paper

Correction Factors for Direct Gas Chromatographic Determination of Acrylic Acid in Aqueous Solutions Using Polyethylene Glycol Adipate as Stationary Phase

Olga M. Tsivileva

Laboratory of Structural Research Methods, Institute of Biochemistry and Physiology of Plants and Microorganisms of the Russian Academy of Sciences, 13 Entuziastov pr., Saratov 410015, RUSSIA

Recieved March 3, 1997; revised June 5, 1998; accepted June 17, 1999

The problem of »repeated peaks« associted with the direct gas chromatographic determinations of aqueous acrylic acid solutions with the concentration range of 0.05 – 10.00 g dm^{-3} has been discussed for the case of polyethylene glycol adipate as a stationary phase. Based on more than 700 injections of standard solutions on the packed column, a set of correction factors has been proposed. Simple relations between the »repeated peaks« heights and the reference solution concentrations were found. The reproducibility of the method was evaluated.

Key words: Acrylic acid; aqueous solutions; correction factors; gas chromatography; polyethylene glycol adipate

INTRODUCTION

Determination of carboxylic compounds by gas chromatography (GC) is well known to be rather complicated because of their pronounced adsorption and chemisorption in the chromatographic column, unsatisfactory peak symmetry and other related effects interfering with the analysis.[1] Considerable effort has been put in improvement of columns with appropriate coatings. Gas chromatographic determination of low levels of fatty acids in water solution was accomplished by using the polar Tween 80 stationary phase.[2,3] Hunter *et al.*[4] reported a method for preparing concentrated anhy-

drous extracts of organic acids that applies regeneration of carboxylic acids from their salts by use of dichloroacetic acid in acetone. The acids were analysed by GC on glycol adipate polymer stationary phase. However, the interfering peaks of dichloroacetic acid decomposition products appeared in the acetic-propionic acid region of the chromatogram. The application of polyethylene glycol adipate (PEGA) as a polyester stationary phase enables gas chromatographic determination of samples containing free organic acids. In earlier works,[5] PEGA was applied in GC analysis of some saturated acids in water.

Relevant literature describes rather complicated, time-consuming techniques necessary for high precision analysis of acrylic acid (AA).[6–10] AA extraction with tri-*n*-octylphosphine oxide dissolved in organic solvent and derivatization with pentafluorobenzyl bromide have been proposed for determination of AA in aqueous samples by GC/ECD.[6] The detection limit was near 450 femtograms. Other similar yet less precise procedures included the GC determination of AA esters extracted into the nonaqueous phase.[7–10] Our experience shows that the determination of AA in aqueous samples without derivatization on a packed PEG column is followed by the appearance of interfering »repeated« peaks resulting from adsorption of free acids in the stationary phase and its elution from the column on the subsequent sample injections. No similar effects have been reported earlier for the determination of saturated acids in water on the same stationary phase. In the present work, we have made efforts to overcome the drawbacks related to the aforesaid effect in the GC analysis of AA. The development and verification of a set of correction factors are described for the GC analysis of free AA aqueous samples on a PEGA stationary phase within a fairly wide range of concentrations.

EXPERIMENTAL

Gas chromatographic analysis was performed on a Chrom 5 gas chromatograph (Laboratorni Pristroje Praha) equipped with a splitless injector and flame ionization detector and linked to a CI 100 computing integrator. The glass, 350 × 0.3 cm i.d, column was packed with 5% PEGA on Inerton AW-DMCS (0.20–0.25 mm particle size). The injector, column, and detector temperatures were 180, 150 and 190 °C, respectively. Helium served as the carrier gas at 40 cm^3/min. Detector gas flow rates were 30 cm^3 H_2/min and 500 cm^3 air/min. Quantification was accomplished by measuring chromatographic peak heights along with electronic integration. AA aqueous solutions of concentrations ranging from 0.05 to 10.00 g/dm^3 were used as calibration standards for calculating response factors in day-to-day work. Reproducibility of peak areas was not worse than 10%. The overall analysis times were within 5 min. A freshly prepared column was conditioned for 24 hours and the analysis of AA aqueous solutions were preceded by at lest 120 subsequent injections of 10^{-3} cm^3 of water.

RESULTS AND DISCUSSION

As already mentioned in the introduction, the adsorption and chemisorption of analytes in the GC column and many interrelated phenomena affect detector response. Since the losses of acid depend on several factors (injected sample amount, column temperature, compound retention time), the determination of a response factor is difficult. The correction strategy selected in this work is almost purely empirical. A direct analysis of AA in aqueous solutions at concentrations as high as 10 g/dm^3, without dilution by so sensitive a technique as GC might be considered as somewhat unreasonable. However, we performed the studies in a rather wide AA concentration range by recognizing that the upper concentration is worth evaluating in order to get a complete picture of the applicability of the proposed correction factors.

A thorough investigation of the influence of polyester stationary phase quantity relative to a solid support mass upon the gas chromatographic analysis of AA aqueous samples was outside the scope of this work. We compared the AA peak shapes and checked the appearance of »repeated« peaks on three columns differing in the PEGA percentage. The broadened AA peaks and substantially enhanced effects of »repeated« peaks were observed by analysis on columns containing 0.5% and 15% of PEGA, respectively. An improvement was achieved with 5% of PEGA. Thus, the 5% PEGA column was used in further studies.

One of the primary requirements in the GC analysis of aqueous samples is to eliminate or to reduce the use of water-soluble agents in the column. Hence we avoided conventional additives such as phosphoric acid in our experiments despite their commonly recognized, though varying, capability to prevent acidic tailing.

The GC accessories, such as a syringe, column terminals, *etc.*, were clearly confirmed not to be the source of »repeated« peaks. Column temperature was sufficiently lower than the working upper limit for PEGA (220 °C),[11] along with rather short analysis times.

Figure 1 illustrates a quite perfect shape of AA peak in the chromatogram of AA aqueous solution on the 5% PEGA column.

The height of »repeated« AA peaks in the chromatograms of pure water injected several times after analysis of AA aqueous solutions decreased gradually under the chosen experimental conditions. A higher AA peak in AA sample was followed not only by a higher »repeated« peak, but also by the more rapid decrease of the »repeated« peak height absolute values. In other words, sufficiently small »repeated« peaks remained roughly unchanged in chromatograms produced by subsequent water injections.

To get an equation for calculating the overall AA concentration in an aqueous sample, it was necessary to take into consideration only the two »repeated« AA peaks obtained by water injections immediately before and after the injection of AA aqueous sample. Thus, the pattern of every AA determination should consist of three sequential injections: water – AA aqueous solution – water. One is to note that the time intervals between subsequent injections in this scheme should be maintained as equal as possible.

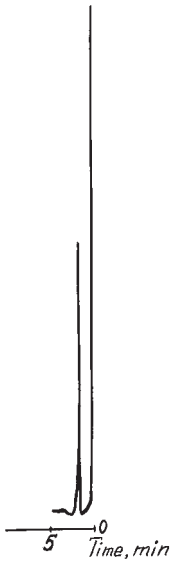

Figure 1. Gas chromatogram of AA aqueous solution analyzed on the column packed with 5% PEGA on Inerton AW-DMCS.

An initial schematic diagram with three straight-line segments corresponding to the GC peak heights was constructed showing the changes in the basic and two accompanying residual (»repeated«) peak heights with respect to each other.

The GC system calibration was performed within the wide range of concentrations using the external standard method and the AA standard solutions indicated above. Calibration coefficient K was calculated as a ratio of injected AA mass M and the sum S of AA peak areas in chromatograms of sample and pure water injected immediately before and after the sample. The evaluation of the experimental data obtained from more than 700 successive injections of aqueous AA standard solutions, containing either only AA or a mixture of AA and different amide and carboxylic compounds and

pure water resulted in the following expression for calculating the AA content in an aqueous sample:

$$M = K\,[S + k_w(h_a - 2h_b + 3\Delta h)]$$

where k_w is the ratio of »repeated« peak area and its height, h_a and h_b are heights of »repeated« peaks corresponding to pure water injections after and before injection of the sample and Δh is the decrease of h_b value on sequential injections of pure water. S, h_a and h_b are the parameters to be measured in every AA gas chromatographic determination, whereas Δh value is obtained from the plot showing the dependence of Δh on repeated peak heights determined experimentally by analysis of AA standard aqueous samples of different concentrations. Figure 2 gives an example of such dependence. In Table I, some statistical data are listed showing the adequate reproducibility of the AA determination in aqueous samples by the proposed procedure.

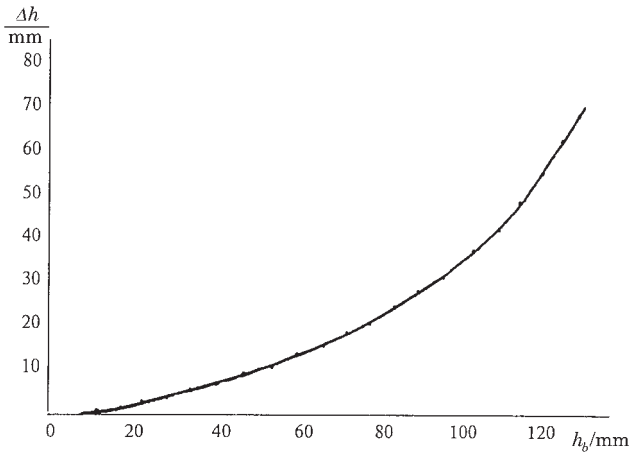

Figure 2. Dependence of the »repeated« peak height decrease, Δh, on the »repeated« peak heights.

CONCLUSION

The method enables a direct determination of AA in aqueous samples without previous acid derivatization and addition of any organic solvent. However, the sensitivity of direct AA acid determination is lower than the achieved with other GC methods used for analysis of AA in water. The proposed procedure might be a reasonable solution for an analysis of AA in aqueous samples when the complete elution of AA retained in the chroma-

TABLE I

Reproducibility data for GC determinations of AA aqueous solutions on the column packed with 5% PEGA on Inerton AW-DMCS, (n = 6, concentration in g/dm^3)

Mean	0.13	0.25	0.61	1.40	2.6	4.7
S.D.	0.015	0.020	0.041	0.083	0.12	0.16
C.V.%	12.0	8.4	7.1	6.2	4.8	3.6

tographic column and entire elimination of »repeated« peaks in subsequent injections are not possible. By using a few correction factors which are easy to obtain, apply, and verify, one could overcome this drawback. As the procedure becomes time-consuming when analysing very concentrated samples, the AA aqueous samples of concentrations higher than 5g/dm^3 should be diluted before the analysis.

The introduced correction factors are valid for the analysis of AA in aqueous samples on the PEGA stationary phase in described working conditions. However, we suppose that this simple approach is not limited to this particular GC system and that it might be applied to other systems in which the appearance of interfering »repeated« peaks complicate the GC analyses of a certain compound.

Acknowledgement. – The author is grateful to O. E. Makarov (IBPPM RAS) for technical assistance.

REFERENCES

1. G. Odham, L. Larsson, and P.-A. Mardh (Eds.), *Gas Chromatography/Mass Spectrometry Applications in Microbiology*, Plenum Press, New York, NY, 1984.
2. E. M. Emery and W. E. Koerner, *Anal. Chem.* **33** (1961) 146–147.
3. E. S. Erwin, G. J. Marco, and E. M. Emery, *J. Dairy Sci.* **44** (1961) 1768–1771.
4. I. R. Hunter, N. G. Hawkins, and J. W. Pence, *Anal. Chem.* **32** (1960) 1757–1759.
5. M. I. Goryaev and N. A. Evdakova, *Reference Book on Gas Liquid Chromatography of Organic Acids*, Nauka Press, Alma-Ata, KazSSR (FSU), 1977.
6. A. Vairayamurthy, M. O. Andrease, and J. M. Brooks, *Anal. Chem.* **58** (1986) 2684–*2687.*
7. S. Czerczak, *Chem. Anal. (Warsaw)* **28** (1983) 35–41.
8. A. Horna and J. Churacek, *J. Chromatogr.* **389** (1987) 293–298.
9. G. Stoev and M. Angelova, *J. High Resolut. Chromatogr. and Chromatogr. Commun.* **10** (1987) 25–26.
10. E. G. Pomerantseva and E. V. Lunicheva, *Methods of Acrylic Copolymers Investigations*, V. A. Kargin Sci. Res. Inst. Press, Moscow, 1990.
11. *Supelco Chromatography products Catalog.* Supelco, Inc., 1991.

SAŽETAK

Korekcijski faktori pri neposrednom plinskokromatografskom određivanju akrilne kiseline u vodenoj otopini uz primjenu polietilenglikol-adipata kao stacionarne faze

Olga M. Tsivileva

Razmatran je problem »ponovljenih vrhova« u plinskokromatografskoj analizi vodenih otopina akrilne kiseline masenih koncentracija od 0.05 do 10.00 g dm^{-3} na polietilenglikol-adipatu kao stacionarnoj fazi. Predložen je niz korekcijskih faktora utemeljenih na više od 700 injektiranja standardnih otopina na punjenu kolonu. Eksperimentalno su utvrđeni jednostavni odnosi između visine »ponovljenih vrhova« i koncentracije referentnih otopina. Procijenjena je reproducibilnost metode.