Journal of Chromatography, 457 (1988) 372–376
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 923

Note

Industrial applications of chromatography

I. Determination of methanol, *n*-butanol and toluene by direct aqueous injection gas chromatography

ALEŠ HORNA
Research Institute of Industrial Chemistry, East Bohemia Chemical Works Synthesia, 532 17 Pardubice-Semtín (Czechoslovakia)

(First received April 19th, 1988; revised manuscript received August 1st, 1988)

The processing of industrial waste waters is a very important operation in which chromatography is one of the most frequently used analytical methods.

Gas chromatographic (GC) methods for the determination of volatile compounds in aqueous liquids, reviewed in many recent papers[1,2], usually utilize headspace analysis[3] or organic solvent extraction[4]. On the other hand, only a small number of methods for the determination of organic compounds by direct injection GC have been reported[5–8], although this very simple method seems to be very advantageous. Moreover, because of possible errors associated with purging efficiency or the efficiency of extraction of volatile polar organic compounds, the direct aqueous injection of an aliquot of the effluent on to a GC column is considered to be the only realistic approach to the determination of polar organics[5]. In addition, using existing modern column and detector technology, this rapid and not labour-intensive technique can be used for the analysis of water-based samples for parts per 10^9 to low percentage levels of many organic compounds[5].

In this paper, direct aqueous injection GC employing a flame ionization detector and an Apiezon L packed column for the simultaneous determination of methanol, *n*-butanol and toluene in industrial waste waters is described, together with the effects of water on both the retention behaviour and detection.

EXPERIMENTAL

A Fractovap GV gas chromatograph (Carlo Erba, Milan, Italy) equipped with a flame ionization detector was used. The injector and detector temperatures were both 250°C; the nitrogen carrier gas flow-rate was, *ca.* 30 ml/ min and the chart speed 0.05 mm/s.

A glass column (2.5 m × 4 mm I.D.) containing 17.5% Apiezon L on acid-washed Chromosorb W (60–80 mesh) was operated at an oven temperature of 97°C. A glass column (2.5 m × 4 mm I.D.) packed with 120–150-mesh Porapak Q (Waters Assoc., Milford, MA, U.S.A.) was operated at 180°C. A 1-μl sample volume was injected into the instrument, and the methanol, *n*-butanol and toluene were eluted

0021-9673/88/$03.50

with attenuation producing peaks of reasonable size. The retention times and peak areas were measured with an Autolab System IV computing integrator (Spectra-Physics, Mountain View, CA, U.S.A.).

The amounts of the organic solvents were calculated from calibration graphs of the ratio of the amounts of the organic solvent and internal standard *versus* their peak-area ratio. The calibration was performed on Apiezon L using standard solution of methanol, *n*-butanol, toluene and *n*-propanol (internal standard) in distilled water at various mass ratios. A least-squares determination of the line of best fit of the points was performed with a TI 58 C calculator. With the exception of methanol (correlation coefficient 0.989), correlation coefficients of better than 0.999 were obtained, indicating good linearity of the calculated straight lines. Hence with toluene, *n*-butanol or isobutanol daily calibration was performed using only one standard concentration for each solvent.

For the determination of trace amounts of methanol in water, an absolute calibration graph on Porapak Q for methanol concentration in the range 0.005–0.250% in distilled water was established.

RESULTS AND DISCUSSION

For the analysis of water-based samples, the choice of the GC column is limited because water can cause chemical changes to the GC packing or interfere in the analysis. On the other hand, it is generally known that the flame ionization detector selectively detects low-molecular-organic compounds but hardly responds to water. Hence a glass column packed with Chromosorb W AW coated with Apiezon L and a flame ionization detector were selected for the simultaneous determination of methanol, *n*-butanol and toluene for monitoring industrial waste water processing.

On non-polar Apiezon L stationary phase water elutes at about the same time as methanol. Hence it can be expected that with a high flame ionization detector

Fig. 1. Chromatography of distilled water containing 0.01% of each alcohol on an Apiezon L glass column (2.5 m × 4 mm I.D.) at 97°C. Peaks: 1 = methanol; 2 = water; 3 = and *n*-butanol.

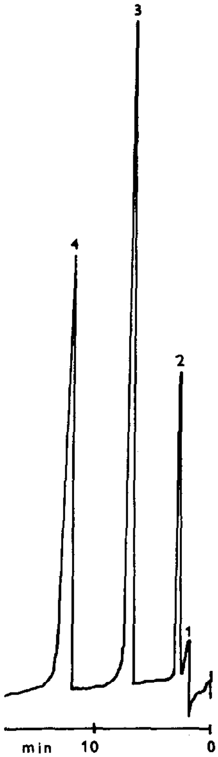

Fig. 2. Chromatography of distilled water containing 0.01% of each alcohol on a Porapak Q glass column (2.5 m × 4 mm I.D.) at 180°C. Peaks: 1 = "water"; 2 = methanol; 3 = *n*-propanol; 4 = *n*-butanol.

sensitivity, which is needed for trace analysis, the water response will be large enough to affect the methanol peak. According to our experiments, when the methanol concentration in water approached 0.01% the water response was large enough to distort the methanol peak (Fig. 1). For this reason, a Porapak Q packed column was employed for trace methanol determination to separate water effectively from the methanol peak (Fig. 2). For the routine analysis of industrial waste waters and with extraction- and/or distillation-isolated organics, an Apiezon L packed column was preferred owing to the short analysis time.

When methanol, *n*-butanol and toluene were determined in both water- and organic-based samples on an Apiezon L column a shift in the retentions of the organic solvents relative to one another was observed. To illustrate how the concentration of organic compounds affects the retention of methanol and *n*-butanol on Apiezon L, the relative retention times (internal standard *n*-propanol) were calculated and plotted against the total concentration of volatile organics in the injected sample. From Fig. 3, it can be seen that the relative retention time of methanol tends to increase with increasing proportion of volatile organic compounds in the sample. On the other hand (Fig. 4), the relative retention time of *n*-butanol tends to decrease with increasing proportion of organics in the sample.

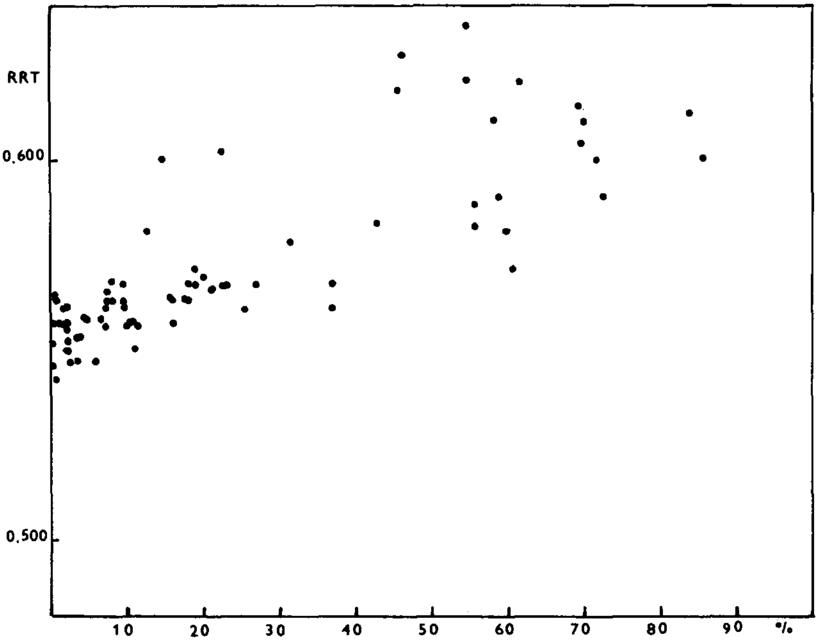

Fig. 3. Relationship between the relative retention time (RRT) of methanol and the total concentration of the determined solvents in water on Apiezon L Chromosorb W AW packed column. For *n*-propanol employed as the internal standard, RRT = 1.000.

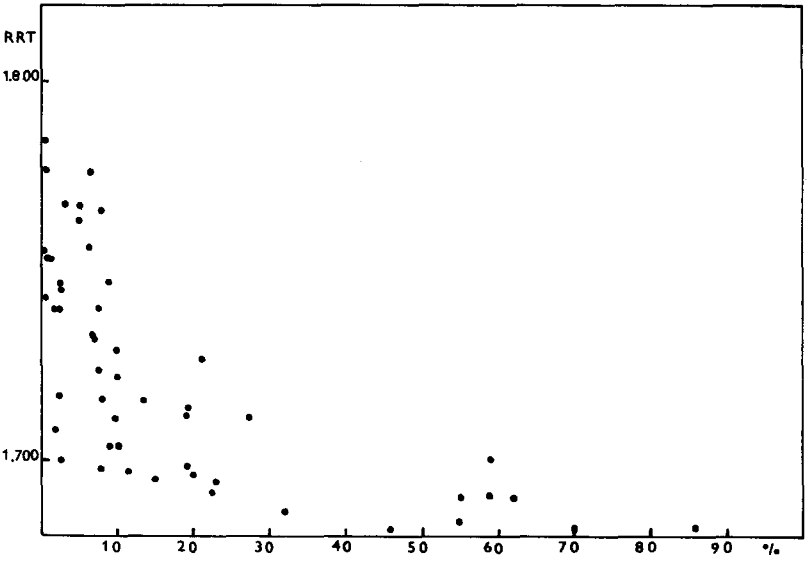

Fig. 4. Relationship between the relative retention time (RRT) of *n*-butanol and the total concentration of the determined solvents in water on Apiezon L Chromosorb W AW packed column. For *n*-propanol employed as the internal standard, RRT = 1.000.

TABLE I

RETENTION TIMES OF METHANOL, *n*-PROPANOL, *n*-BUTANOL AND TOLUENE ON APIEZON L AT THE DIFFERENT TOTAL CONCENTRATIONS OF THE ORGANIC SOLVENTS IN DISTILLED WATER

Five injections were performed for each concentration.

Total concentration (%, w/w)	*Retention time ± S.D.*			
	Methanol	*n-Propanol*	*n-Butanol*	*Toluene*
6.1	53.3 ± 0.6	94.8 ± 1.0	161.5 ± 0.6	407.5 ± 0.7
9.5	53.3 ± 0.6	94.7 ± 0.6	161.7 ± 0.6	406.3 ± 0.6
16.7	53.0 ± 0.1	94.0 ± 0.1	161.8 ± 0.5	407.8 ± 0.5
52.5	54.3 ± 1.0	95.0 ± 0.8	161.5 ± 0.6	408.0 ± 1.2
100	56.6 ± 0.6	95.4 ± 0.6	162.2 ± 0.5	408.8 ± 1.6

To confirm the above-mentioned observations in the analysis of real samples, model mixtures containing methanol, *n*-propanol, *n*-butanol and toluene (2:2:2:1, w/w) in distilled water with a total concentration from 6.1 to 52.5% (w/w) were prepared and 1-μl samples were injected. With decreasing content of water in the injected samples the retention times of the solvents began to shift slightly (Table I). However, when a dry organic solvent mixture was injected, maximum retention times for all solvents were obtained. Especially with methanol more a 3 s increase in the retention time was observed.

The reduction in the retention times of organic compounds injected together with a large volume of water is in agreement with earlier work[9,10] and can be explained by the carrier gas being temporarily saturated with water.

No significant changes in the efficiency or polarity of the Apiezon L column were observed after many hundred injections.

ACKNOWLEDGEMENT

The author is grateful to Mrs. Lenka Martínková for excellent technical assistance.

REFERENCES

1 J. R. Garbarino, T. R. Steinheimer and H. E. Taylor, *Anal. Chem.*, 57 (1985) 46R.

2 A. Cailleux, A. Turcant, P. Allain, D. Toussaint, J. Gaste and A. Roux, *J. Chromatogr.*, 391 (1987) 280; and references cited therein.

3 B. V. Ioffe and A. G. Vitenberg, *Headspace Analysis and Related Methods in Gas Chromatography*, Wiley, New York, 1984.

4 J. Curvers, T. Noij, C. Cramers and J. Rijks, *Chromatographia*, 19 (1984) 225.

5 B. S. Middleditch, N.-J. Sung, A. Zlatkis and G. Settembre, *Chromatographia*, 23 (1987) 273.

6 S.-T. Cheung and W.-N. Lin, *J. Chromatogr.*, 414 (1987) 248.

7 *GC Bull., No. 816*, Supelco, Bellefonte, PA, 1984.

8 *Supelco Reporter, Vol. 4, No. 2*, Supelco, Bellefonte, PA, 1985, p. 4.

9 G. Urbach, *J. Chromatogr.*, 404 (1987) 163.

10 J. Janák, J. Růžičková and J. Novák, *J. Chromatogr.*, 99 (1974) 689.