

Sampling and analysis of 1,3-butadiene in air by gas chromatography on a porous-layer open-tubular fused-silica column

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Abstract

The preparation of standards for 1,3-butadiene analysis is complicated, because butadiene is a gas at room temperature. The method to prepare stock solutions developed in this study is reliably, as confirmed by a standard plot from these independent stock solutions. The qualitative and quantitative analysis was carried out using high-resolution gas chromatography with flame ionization detection (FID) and a fused-silica porous-layer open-tubular (PLOT) column. The use of acetonitrile as a desorption solvent gave a good recovery from charcoal and no interfering impurities were present. Active and passive sampling were tested in the laboratory and in petrochemical plants. These two methods had a very good correlation when tested in the field.

1. Introduction

1,3-Butadiene (BD) is a colourless flammable gas used mainly in the production of synthetic rubbers and it is one of the top 50 chemicals manufactured in the USA [1]. The National Institute for Occupational Safety and Health (NIOSH) estimated that 9500 workers in the USA are potentially exposed to BD, and the worldwide exposure to this chemical has been estimated to involve ca. 50 000 workers [2].

Also the US Environmental Protection Agency (EPA) expressed concern that this compound may be potentially carcinogenic, and more recently the California Air Resources Board has estimated that BD is the second

important toxic compound, after benzene, in the emission from motor vehicles [3].

The conventional methods of sampling gaseous impurities require the use of pumps to draw a known volume of air through tubes packed with adsorbent. In recent years an alternative sampling system has been developed in the form of the "passive" or more correctly "diffusive" sampler. These devices sample, by gaseous diffusion of the analyte, onto a collecting medium. Their advantages are lower costs and greater user acceptability, as they do not require bulky, expensive pumps that are subject to regular checking and an inherent error in flow-rate.

For the analysis, a chromatographic method capable of resolving BD from other light hydrocarbons present in petroleum refineries is desired. Such separations reported in the literature used high-resolution gas chromatography mainly with KCl-deactivated aluminium oxide porous-

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layer open-tubular (PLOT) columns, or with a methyl silicone fused-silica column with a thick film using subambient temperature [3–6].

The detection has been carried out mainly with flame ionization detection (FID) which gives a satisfactory detection limit, but which may not be sufficiently selective [4–6]. It has also been shown that photoionization detection (PID) offers a high selectivity and sensitivity for unsaturated hydrocarbons [7].

2. Materials and methods

Butadiene used in this study was a kind gift from a Finnish petrochemical company. Before use the purity was tested in our laboratory using gas chromatography (GC), and it was observed to be higher than 99%. Pentadiene, hexadiene, heptadiene, octadiene, nonadiene, dodecadiene, dodecan and undecan were all from Aldrich (Germany). Acetonitrile was HPLC grade from Rathburn (Walkerburn, UK).

Charcoal tubes, type 226-01, having front and rear sections of 100 and 50 mg, respectively, were from SKC (Wimborne, UK), and type 3520 passive monitors, also having a backup section, were from 3M (St. Paul, MN, USA). The flow-rate in active sampling was set at 50 ml/min, which was confirmed before and after sample collection. A diffusion rate of 42.8 ml/min was used in calculations and the amounts of BD were lower than 0.4 mg in all analyses.

Standard atmospheres with varying concentrations of BD were generated in a stainless-steel dynamic 1 m³ exposure chamber. The desired air concentration was kept constant by an automatically controlled feedback mechanism. The valve which controlled the gas flow of BD was regulated by a power integrated derivative controller (Eurotherm 70, Eurotherm, Sussex, UK) based on the feedback circuit signal from an infrared analyser (Miran 1A, Wilks Scientific Corp., USA), which was used for continuous monitoring of BD concentrations in the chamber air. The chamber air exchange rate was 6 times/h, and short-term deviations from nominal concentrations were less than 5%.

The standards were made in 10-ml bottles (in each batch five separate stock solutions were made), which were weighted and cooled in dry ice (10 min). Butadiene was liquefied into the bottle (ca. 100–200 μ l) and 5 ml of acetonitrile was added. The bottles were allowed to warm to room temperature and weighted, the amount of butadiene in the bottle calculated, after which they were filled to the reference point (10 ml). The concentrations of BD in these stock solutions were determined and one of the bottles which lay in the calibration line of stock solutions was selected as stock solution to prepare a calibration curve suitable for actual air samples.

The desorption efficiencies were tested in autosampler vials at +6°C in 1 ml of desorption solvent. Before the solvent was slowly added, the vials were cooled in an ice bath (ca. 0°C).

The samples were analysed with a gas chromatograph equipped with a FID detector (HP 5890, Hewlett-Packard, CA, USA). The detector and injector temperatures were 280°C and 200°C, respectively. Air and hydrogen flow-rates were set at 280 ml/min and 30 ml/min, respectively. The helium make-up gas flow-rate was 30 ml/min. The samples (1 μ l) were introduced using splittless injection (splittless time 0.5 min) and both autosampler and manual injections were used.

A PLOT AL₂O₃/KCl (50 m \times 0.32 mm I.D.) fused-silica column was used (Chrompack, Netherlands). The carrier gas flow-rate was set at 1 ml/min and the following temperature program was used. The injection temperature of 40°C was kept for 1 min after which the temperature was raised to 190°C with 5°C/min. The final temperature was maintained for 12 min.

3. Results and discussion

The gas chromatographic profiles of the five terminal dienes from 1,3-butadiene to 1,7-octadiene using linear temperature programming are shown in Fig. 1. The carrier gas did not have a great influence on the retention behaviour and, as expected, helium (Fig. 1A) gave longer retention times than hydrogen (Fig. 1B). When

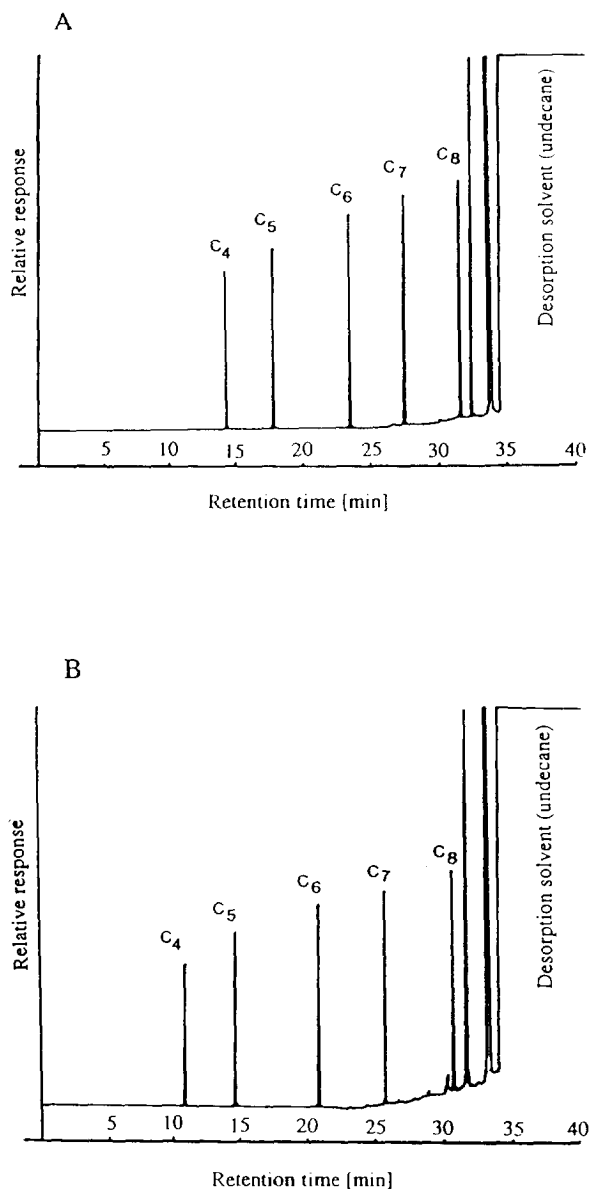


Fig. 1. Gas chromatographic profiles containing a homologous series of terminal dienes (from 1,3-butadiene to the 1,7-octadiene). Helium (A) and hydrogen (B) were used as carrier gases. C_4 , C_5 , C_6 , C_7 and C_8 refer to the number of carbons in the dienes.

retention times are plotted as a function of the carbon number, it can be seen that the total retention times t_R or the retention temperatures are not linearly proportional to the number of

carbon atoms of the homologues when using linear temperature programming. A non-linear increment in retention time was observed between C_5 and C_6 dienes. The type of carrier gas had no effect on these nonlinear increments in retention time. Dienes in a PLOT-type column also behave differently when the half height of the peaks is compared to the half height of the peaks traditionally obtained with capillary columns. BD has the highest half height in this series and the other dienes have a half height of approximately the same size. This phenomenon is shown in Fig. 2 where the half height of the dienes is plotted as a function of carbon number. The results of the studies on the chromatographic behavior indicate that the use of the diene homologue series may not be applicable to the

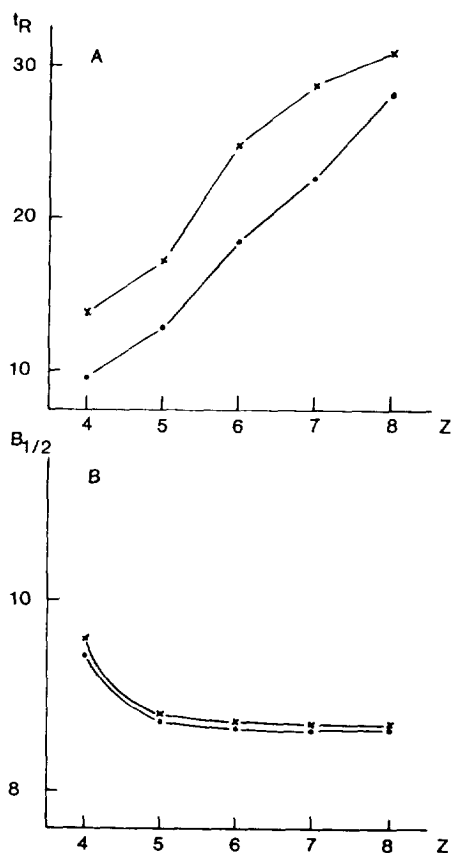


Fig. 2. The total retention times t_R (A) and the peak widths at half height ($B_{1/2}$) as a function of the number of carbons in the dienes: (x) helium, (●) hydrogen.

determination of the BD concentration in samples.

In the quantitative analysis of BD one of the most critical steps is the preparation of stock solutions. To overcome this problem various techniques have been described in the literature, but none of them worked satisfactorily in our hands [4,5,8]. Therefore we had to develop our own method for the preparation of standards. The method we are currently using is a user-friendly method which reveals possible problems at an early stage in the analysis. The reliability of the stock solutions is confirmed by performing a standard plot of stock solutions ($n = 5$, $r = 0.9999$). These stock solutions cannot be stored for more than 12 h in a refrigerator due to the high concentration of BD in the solution. The loss of BD from stock solutions is mainly caused by dimerization of BD to vinylcyclohexene and a loss of BD through evaporation. However, once the stock solutions have been diluted, the standards can be stored for up to 2 weeks in a refrigerator without any loss of BD (data not shown).

Dichloromethane, carbon disulphide, dodecan, undecan and acetonitrile were tested as possible desorption solvents for butadiene. Several gas chromatographic conditions were tested, but BD could not be separated from dichloromethane or carbon disulphide. Therefore, the solvents which were further tested were dodecan, undecan and acetonitrile and the desorption efficiency for the selected dienes is presented in Table 1. Because the desorption efficiency of BD was low when hydrocarbons were used, acetonitrile was selected.

The standard deviation of injection was tested for 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene using autosampler and manual injections and acetonitrile as a solvent. The concentration of dienes in the samples was 11 $\mu\text{g}/\text{ml}$ and 12 injections were made. The standard deviations for injections made with the autosampler were 6.2, 6.7 and 6.4% for each diene. Better results were obtained when manual injections were performed with the "hot needle technique" [9]. The standard deviations for manual injection were 2.6, 2.8 and 1.9% for each diene.

Table 1
Desorption efficiencies of butadiene into dodecane, undecane and acetonitrile ($n = 3$)

Concentration ($\mu\text{g}/\text{ml}$)	Desorption efficiency (%)	S.D. (%)
<i>Dodecane</i>		
13	13.2	12.1
27	15.8	11.1
<i>Undecane</i>		
13	11.3	13.1
27	21.5	10.1
<i>Acetonitrile</i>		
2.5	53.9	4.4
5.4	58.2	3.3
8.8	60.0	3.2
12.9	64.2	3.5
26.3	64.1	3.0

The detection limit of the passive sampling method was 400 ng/ml, which corresponds to 0.01 ppm for an 8-h sample using a diffusion rate of 42.8 ml/min. About the same sensitivity was achieved using SKC charcoal tubes with a flow-rate of 50 ml/min. A typical chromatogram of a sample collected from a petrochemical plant is shown in Fig. 3.

In order to compare the two different sampling methods, they were first tested in the

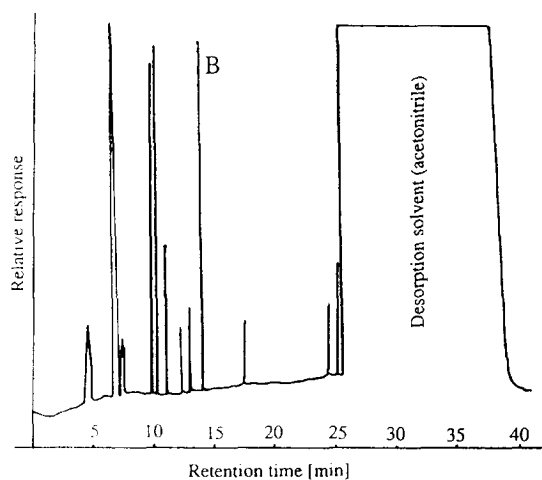


Fig. 3. A typical chromatogram of an air sample collected from a petrochemical plant worker (B = butadiene).

laboratory in a dynamic exposure chamber. The relative humidity was monitored (R.H. 82%) but not altered during the measurements. The sampling efficiency and possible breakthrough were tested for two different BD concentrations. The first experiment was carried out at 8.8 ppm and the sampling time was 3 h. Nine active and passive samples were taken, each of them having a backup section to detect possible breakthrough. No breakthrough could be observed in either sampling method. The samples based on passive diffusion showed values somewhat lower than the set value. The mean value of the dosimeters was 8.6 ppm, S.D. ± 0.5 ppm, S.E.M. ± 0.1 ppm, and the range was from 7.9 to 9.4 ppm. The samples taken with active air sampling showed values somewhat higher than the set value. The mean value of the charcoal tubes was 9.8 ppm, S.D. ± 0.5 ppm, S.E.M. ± 0.3 ppm, and the range was from 9.2 to 10.6 ppm. With a higher concentration of BD (16 ppm), also no breakthrough could be detected. The mean value of the passive dosimeter was 13.7 ppm, S.D. ± 1.1 ppm, S.E.M. ± 0.3 ppm, and the range was from 12.2 to 15.3 ppm. For the charcoal tubes the mean value was 18.7 ppm, S.D. ± 1.0 ppm, S.E.M. ± 0.4 ppm, and the range was from 17.5 to 20.3 ppm.

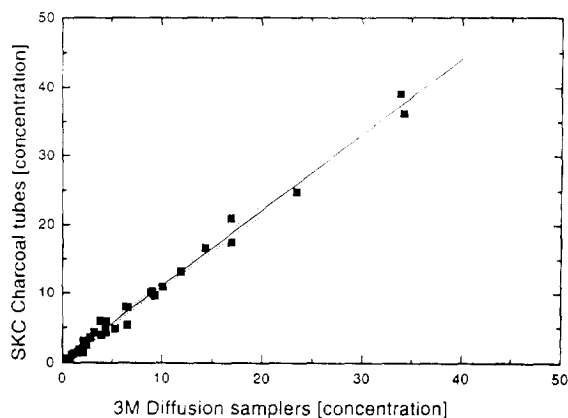


Fig. 4. The correlation of active and passive sampling. The samples were collected from three different petrochemical plants during winter, summer and autumn ($n = 35$, $r = 0.9956$).

The methods were also tested in a field study in three different petrochemical plants, where the work is mainly performed outdoors. All samples were personal samples, the sampling device being placed on the right shoulder of a worker during the full shift (6–8 h). The samples were collected during the winter when the temperature range was from -4 to -13°C , during summer with a temperature range from 15 to 25°C , and during autumn with a temperature range from 3 to 10°C . The two methods showed a good correlation ($r = 0.9956$) when field-tested (Fig. 4).

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