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# Determination of acetic acid in aqueous samples, by water-phase derivatisation, solid-phase microextraction and gas chromatography

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**Abstract**

The direct derivatisation of acetic acid with *n*-hexyl chloroformate and with benzyl bromide in water was evaluated. With *n*-hexyl chloroformate, acetic acid did not give the *n*-hexyl acetate derivative, but the reaction of acetic acid with benzyl bromide in aqueous solution resulted in the formation of benzyl acetate. The derivatisation of acetic acid with benzyl bromide and the headspace solid-phase microextraction (SPME) of benzyl acetate were optimised. Under optimum conditions, the limit of detection for acetic acid was 260 n*M*, and the relative standard deviation of the overall procedure at $1\cdot10^{-4}$ *M* acetic acid was 15.6% ($n=10$). A linear response was obtained in the $1\cdot10^{-4}$ to $5\cdot10^{-6}$ *M* concentration range ($R^2=0.993$, $n=6$). Although Carbowax–divinylbenzene (CW–DVB)-coated fibres exhibited a higher extraction capacity for benzyl acetate, polyacrylate (PA) was selected, because its mechanical stability was better than that of CW–DVB fibres. Moreover, the relative standard deviation of the SPME was better with PA (1.5%, $n=10$ at $1\cdot10^{-5}$ *M*) than with CW–DVB-coated fibres (8.0%, $n=10$ at $1\cdot10^{-5}$ *M*). Thus, a new analytical method for the quantitative determination of micromolar concentrations of acetic acid in the aqueous phase was developed. This method is based on water-phase derivatisation with benzyl bromide, headspace SPME with PA fibres and GC–FID. It was observed experimentally that benzyl alcohol formed by hydrolysis of the reagent affected the fibre–gas phase partitioning of benzyl acetate. 

*Keywords:* Derivatization, GC; Acetic acid

## 1. Introduction

The direct analysis of low-molecular-mass carboxylic acids by gas chromatography (GC) is difficult because of the poor GC separation and detectability of these compounds [1]. These characteristics can be improved by chemical derivatisation [2–4]. The derivatives (in most cases esters) display much better GC behaviour and their detection is more sensitive than that of the parent compounds. The reagents used for derivatisation are usually sensitive to water. Separation of the acids from the sample matrix prior to derivatisation is therefore necessary. In most cases, this involves liquid–liquid or liquid–solid extraction, but because of their hydrophilic nature it is difficult and causes analyte loss and poor reproducibility [5].

Papers were recently published on the derivatisa-

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tion of carboxylic acids directly in water [3,4,6,8,9]. In this approach too, the derivative has to be separated from water prior to GC analysis. This can be achieved effectively by means of solid-phase microextraction (SPME) [10]. The commercially available SPME fibre coatings are apolar or moderately polar and SPME can thus be used effectively for the extraction of apolar compounds from water [11]. Examples of analytical methods involving the application of direct, water-phase derivatisation and SPME, have recently been reported [6,7]. Different combinations of derivatisation and SPME as sample preparation for GC–mass spectrometry (MS) were applied to the analysis of phenoxy acid herbicides. The most successful combination was aqueous-phase derivatisation with benzyl bromide and headspace SPME of the derivative [6]. Pentafluorobenzyl bromide (PFBBr) and pentafluorophenyldiazoethane (PFPDE) were used for the derivatisation of butyric and valeric acids in water, and the derivatives were extracted with SPME. The derivatisation prior to SPME enhanced the limit of detection (LOD) by 1–4-orders of magnitude as compared to the direct SPME of the underivatised acids. Acetic and propionic acids were analysed with PFPDE only, since interfering peaks disturbed the GC–electron-capture detection (ECD) analysis of the PFBBr derivatives [7].

It has been reported that *n*-hexyl chloroformate reacts with carboxylic acids to give *n*-hexyl esters via the mixed anhydride [4,8,9,14]. The derivatives were isolated via either liquid–liquid extraction or SPME [12] and were subsequently analysed by GC.

The aim of the present work was to investigate the direct derivatisation of low-molecular-mass carboxylic acids in order to develop an analytical method based on derivatisation in water, SPME and GC–flame ionisation detection (FID).

## 2. Experimental

### *2.1. Materials*

Acetic acid, benzyl bromide, benzyl acetate, *n*-hexyl chloroformate, 1,3-dicyclohexylcarbodiimide and pyridine were purchased from Aldrich. They were used without further purification. Standard acetic acid solutions were prepared from a 0.05 *M* solution by dilution. A 0.1 *M* benzyl acetate stock solution was prepared by dissolving a known amount of analyte in acetone. The solution was stored at 4°C. Further dilutions were prepared daily from the stock solution. All solvents used in this study were of analytical-reagent grade. Deionised water was used in all aqueous sample preparations. Buffer solutions were made from phosphate and borate salts according to the literature [13].

Poly(dimethylsiloxane) (PDMS), polyacrylate (PA) and Carbowax–divinylbenzene (CW–DVB)-coated SPME fibres with coating thicknesses of 100, 85 and 65 μm, respectively, and manual fibre holders were obtained from Supelco (Bellefonte, PA, USA). Prior to use, they were conditioned at 250°C for 5 min under a helium flow.

For derivatisation and SPME, 5.5-ml screw-capped vials with PTFE–silicone septa (Supelco) and with 10 mm×3 mm PTFE-coated stirring bars were used. The extraction was performed either directly from the 3.0-ml liquid samples or from the headspace.

### *2.2. Derivatisation*

#### *2.2.1. Derivatisation with n-hexyl chloroformate [8,9]*

A 300-μl volume of $5 \cdot 10^{-4}$ *M* acetic acid solution, 30 μl of 400 g $l^{-1}$ dicyclohexylcarbodiimide in pyridine and 33 μl of *n*-hexyl chloroformate were placed in a 5.5-ml vial. During the addition, the solution was sonicated in an ultrasound bath (Branson 2200) at 30°C. After 60 s, the mixture was extracted with 300 μl of hexane. From the hexane phase, 1 μl was injected into a gas chromatograph.

#### *2.2.2. Derivatisation with benzyl bromide*

The standard procedure for derivatisation was as follows: 2 ml of an aqueous acetic acid solution sample was transferred into the reaction vial, followed by 1 ml of buffer and 5–20 μl of benzyl bromide. The sample was stirred at 50°C for a defined time (210 min). After derivatisation, the vial was cooled in an ice-water bath, and the solution was saturated with 990 mg of NaCl. Subsequently, it was thermostated at 30°C and the analyte was extracted either directly or by headspace SPME.

### 2.3. Instrumental parameters

#### 2.3.1. Gas chromatography–flame ionisation detection

A Varian 3700 gas chromatograph and flame ionisation detector were used. A capillary column (30 m×0.25 mm I.D.) coated with 1.5 μm of 5% phenyl, 95% methyl polysiloxane stationary phase (J&W, DB5) was used. The GC conditions were as follows. The initial oven temperature was 40°C for 5 min. The temperature was then programmed to 250°C at a rate of 7°C $min^{-1}$, with a final hold time of 1 min. The FID system and the injector were held at 250°C. The fibre desorption time was 5 min. The carrier gas was helium and the flow-rate was 3.3 ml $min^{-1}$. The response of the detection system used was determined by injecting a known amount (1 μl) of stock solution and determining the corresponding peak area.

#### 2.3.2. Gas chromatography–mass spectrometry

A Varian 2700 gas chromatograph with a DB-1 column [30 m×0.53 mm I.D. with 5 μm 100% dimethyl polysiloxane stationary phase (J&W)] coupled to an MAT 112 mass spectrometer was used. The initial temperature was 40°C for 5 min. The temperature was then raised to 250°C at a rate of 4°C $min^{-1}$. The temperature of the transfer line was 250°C and the mass spectrometer was operated in the electron impact mode (70 eV).

## 3. Results and discussion

### 3.1. Derivatisation of acetic acid with n-hexyl chloroformate and benzyl bromide

It has been reported that *n*-hexyl chloroformate reacts with carboxylic acids to give *n*-hexyl esters via the mixed anhydride [8,9,14]. The procedure was developed to analyse very polar organic compounds (hydroxycarboxylic acids, dicarboxylic acids, glycols, etc.) [8,9]. The derivatisation reaction between *n*-hexyl chloroformate and acetic acid was therefore carried out by using the parameters described in the literature. After the reaction, the solution was extracted with hexane, and the extract was analysed by means of GC–MS. The reaction products were identified on the basis of their retention times and mass spectra. In this experiment, the derivative *n*-hexyl acetate could not be detected. Only the hydrolysis products of the reagent (dihexyl carbonate and hexyl formate) were obtained. It was concluded that the *n*-hexyl chloroformate derivatising agent did not work for acetic acid under the reaction conditions used. This may be due to the specific reaction procedure employed in this study. Indeed, the derivatisation is strongly dependent on the shaking degree and the rate of addition of the derivatising agent [8]. Due to these reaction factors which are not specifically described in quantitative figures, it was decided to investigate another derivatising agent, facilitating better reproducibility conditions.

Next, benzyl bromide and acetic acid were reacted in water (pH 6.0, 50°C, 3 ml of $1 \cdot 10^{-4}$ *M* acetic acid, 10 μl of benzyl bromide, 12 h) and the solution was immediately subjected to SPME (headspace extraction, salt-saturated solution, 30°C, 20 min) and analysed by GC–MS. Benzyl alcohol resulting from the hydrolysis of benzyl bromide was the main reaction product (~99%). Other components, such as benzyl acetate and dibenzyl ether, were present in low, but measurable concentrations. It was decided to investigate the derivatisation reaction of acetic acid with benzyl bromide in further detail. As the extraction capacity of the coatings is very low for the ionic form of carboxylic acids [11] and because in the derivatisation reaction this is the reactive species, the ''in fiber'' reaction with benzyl bromide was not considered.

### 3.2. Optimisation of the SPME of benzyl acetate

For the aqueous-phase extraction of benzyl acetate with PDMS, PA and CW–DVB-coated fibres, no liquid-phase modifier was used, because the presence of high salt concentrations can cause accelerated coating deterioration [15]. With an extraction time of 60 min, the amounts of benzyl acetate extracted from 3 ml of $1 \cdot 10^{-5}$ *M* benzyl acetate solution varied from $5.3 \cdot 10^{-11}$ mole for PDMS to $1.9 \cdot 10^{-10}$ mole for PA and to $5.7 \cdot 10^{-10}$ mole for CW–DVB. Extracted amounts versus time curves were recorded. These results are presented in Fig. 1. The data were fitted to the asymptotic equation

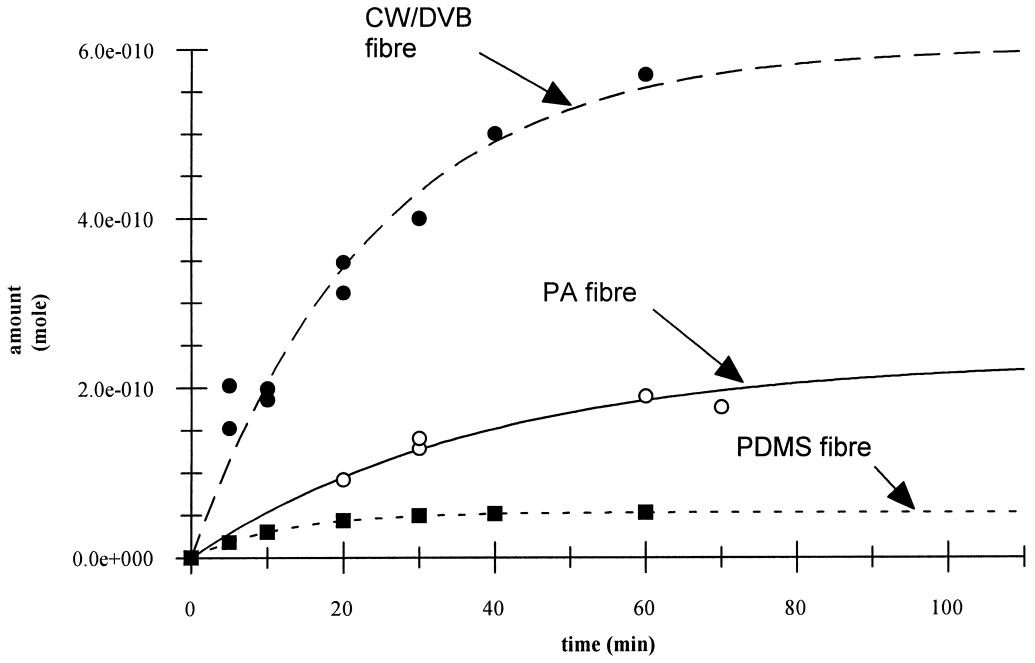


Fig. 1. Amount of benzyl acetate extracted during various time intervals (water-phase extraction, 3.0 ml $1 \cdot 10^{-5}$ *M* solution, 30°C).

$$f_t = 1 - \exp(kt) \quad (1)$$

in which $f_t = m_t / m_{eq}$; this is the fraction of the amount ($m_t$) of benzyl acetate extracted after time $t$ (min) and the amount ($m_{eq}$) extracted when equilibrium is reached, and $k$ ($min^{-1}$) is a fitting parameter [16]. Calculations showed that, for the extraction with PA, for example, about 70% of the maximum amount was extracted after 60 min ($k = -0.022$), so that it would take about 105 min to reach near-equilibrium conditions ($f_t > 0.9$). Since mass transfer in the aqueous phase is generally limiting the equilibration time in water-phase SPME, headspace SPME was tested. However, since the uptake of benzyl acetate by PDMS was more than 10-times less than that extracted with CW–DVB, and since the ratio of the fibre–water partitioning coefficient and the fibre–gas partitioning coefficient is given by Henry's law coefficient, which is independent of the type of fibre, PDMS was not used further. Furthermore, it turned out that working with CW–DVB fibres under the given conditions was troublesome due to mechanical problems (fibre deterioration) as a result of swelling of the fibre coating material. Therefore, only PA fibres were used in the further work.

With a similar approach to that described above, it was shown that near-equilibrium conditions were reached within an extraction time of 30 min ($k = -0.075$, see Eq. (1)) with headspace SPME. Accordingly the extraction time of 30 min was used during the further experiments. Working under these conditions also improved the reproducibility, e.g., the relative standard deviation decreased from 3.3% ($n = 10$) to 1.5% ($n = 10$) when the extraction time was increased from 20 min to 30 min. With the use of $1 \cdot 10^{-5}$ *M* benzyl acetate solutions, headspace SPME extraction was compared for aqueous and salt-saturated solutions. The results are presented in Table 1. From the experimental results, partitioning coefficients, which have a more fundamental meaning than extracted amounts, can be calculated. These calculations additionally allow a quantitative interpretation of the salt effect on SPME. When equilibrium is

Table 1
Amount of benzyl acetate extracted by SPME of a 3 ml of $1\cdot10^{-5}$ *M* aqueous benzyl acetate solution under salt-free and salt-saturated conditions, and calculated partition coefficients[a]

| | Amount extracted (mole) | Henry's law coefficient (dimensionless) | Fibre–gas coefficient (dimensionless) | Fibre–water coefficient (dimensionless) |
|---|---|---|---|---|
| Salt-free | $7.09\cdot10^{-11}$ | $4.62\cdot10^{-4}$[b] | 29 600 | 13.7 |
| Salt-saturated | $6.12\cdot10^{-10}$ | $4.48\cdot10^{-3}$ | 29 600 | 132 |

[a] Extraction conditions: 30°C, 30 min, from 2.2 ml headspace of 3.3 ml of $1\cdot10^{-5}M$ solution.
[b] Value taken from Ref. [17].

reached during sampling, the mass of benzyl acetate present in the vial (*M*, in mole) is partitioned over the three phases:

$$M = M_g + M_w + M_f = C_g V_g + C_w V_w + C_f V_f \quad (2)$$

where $C_g$, $C_w$ and $C_f$ are the concentrations of benzyl acetate in the gas, water and fibre phases (mole $l^{-1}$), respectively, and $V_g$, $V_w$ and $V_f$ are the volumes of gas, water and fibre (2), respectively. The organic fibre–gas phase partitioning coefficient can be calculated as

$$K_{FG} = \frac{C_f}{C_g} \quad (3)$$

and the Henry's law coefficient as

$$H = \frac{C_g}{C_w} \quad (4)$$

Through a combination of Eqs. (2), (3) and (4), $C_g$ and $C_w$ can be eliminated, which results in

$$K_{FG} = \frac{V_g + \frac{V_w}{H}}{\frac{M}{C_f} - V_f} \quad (5)$$

From known data [$H = 4.62\cdot10^{-4}$ for deionized water [17], $V_f$ for PA = 0.520 μl (data supplied by Supelco), $V_g = 2.5$ ml and $V_w = 3.0$ ml] and via Eq. (5), $K_{FG}$ can be calculated. From the $K_{FG}$ values, the fibre–water equilibrium partitioning coefficient $K_{FW}$ for the salt-free closed system can be calculated via Eq. (6):

$$K_{FW} = \frac{C_f}{C_w} = K_{FG} H \quad (6)$$

For the salt-containing system, the Henry's law coefficient value of $4.62\cdot10^{-4}$ is no longer valid because of the salt effect, which results in changed gas–water equilibrium partitioning. Although the total mass in the system remains the same, concentrations $C_f$, $C_g$ and $C_w$ will become concentrations $C'_f$, $C'_g$ and $C'_w$, respectively. Through similar mass balances as that for the salt-free system, it can be shown that $H'$, the salt-saturated solution partitioning coefficient, can be calculated from

$$H' = \frac{\frac{V_w}{K_{FG}}}{\frac{M}{C'_f} - V_f - \frac{V_g}{K_{FG}}} \quad (7)$$

In Eq. (7), all data required to calculate $H'$ are known. Indeed, the fibre–gas equilibrium partitioning coefficient $K_{FG}$ is not affected by the presence of salt in the system and $C'_f$ is determined experimentally. Subsequently, the fibre–salt water equilibrium partitioning coefficient, $K'_{FW}$, can be calculated via Eq. (6), but with $H$ replaced by $H'$. All data are given in Table 1, from which it is clear that the salt effect increases the partitioning by a factor of about 10. In the literature, no other partitioning coefficient was found for benzyl acetate on PA fibres. The effect of salt saturation could be evaluated indirectly in the following way. Dewulf et al. [18] earlier determined the dependence of $H$ on temperature and salinity for a number of organic compounds. From the ex-

perimental data in Table 1, and by using Eq. (11) in Ref. [18], the dependence of the Henry's law coefficient on salinity can be estimated. The value of the calculated regression coefficient for benzyl acetate is 0.00688 l $g^{-1}$, which is nicely within the range from 0.00473 and 0.01196 mentioned by Dewulf et al. [18]. In order to increase the sensitivity of the method, salt-saturated solutions were used in all further experiments.

### *3.3. Optimisation of the derivatisation reaction*

#### *3.3.1. Effects of pH*

The overall effect of pH on the formation of benzyl acetate in the system is difficult to predict because different reactions can occur simultaneously. First there is the derivatisation reaction, but the hydrolysis of benzyl bromide and benzyl acetate are also pH-dependent.

The mechanism of the reaction of benzyl bromide and acetic acid involves a nucleophilic substitution, in which the nucleophile is the acetate ion. The concentration of acetate increases with the pH ($pK_a = 4.7$) and thus the formation of benzyl acetate will be favoured by higher pH values. The extents of hydrolysis of both benzyl bromide (predominantly $S_{N2}$ [19]) and benzyl acetate (irreversible hydrolysis under basic conditions) will increase as the pH increases, and will decrease the amount of benzyl acetate formed. An optimum pH for the formation of benzyl acetate is therefore expected. This optimum has to be determined experimentally.

Pan and Pawliszyn [7] reported that the pH optima for the derivatisations of butyric ($pK_a = 4.81$) and valeric ($pK_a = 4.82$) acids with PFBBr are both 5.5. Nilsson et al. [6] reported an optimal pH of 7.4 for the derivatizations of phenoxy acid herbicides ($pK_a = 3.17$) with benzyl bromide.

In order to establish the optimum conditions for the reaction of benzyl bromide with acetic acid, the amounts of benzyl acetate extracted from the reaction mixture were determined as a function of reaction time at pH 3.0, 5.0, 6.0, 7.0, 8.0 and 10.0. The results are shown in Fig. 2. At pH 3.0, and 10.0, the amounts of benzyl acetate extracted are lower than $10^{-11}$ mole. At pH 3.0, the concentration of the acetate ion is apparently too low for an efficient derivatisation reaction. At pH 10.0, the concentration of the hydroxide ion is so high that the hydrolysis of benzyl bromide and/or benzyl acetate is fast, which results in lower amounts of benzyl acetate extracted. At pH 6.0, 7.0 and 8.0, the amounts of benzyl acetate formed increase during the first 120–150 min of the reaction and then level off to about $10^{-10}$ mole. This does not change significantly (standard deviation of about $1.5 \cdot 10^{-11}$ mole, $n = 10$) over the next 100 min. At pH 5, the results were better than those at pH 3 and 10, but worse than those at pH 6–8. On the basis of these results, pH 7 and a reaction time of 210 min were chosen as optimum reaction parameters.

#### *3.3.2. Effects of excess benzyl bromide*

The excess of the derivatising reagent is considered to be an important parameter in derivatisation reactions. Pan and Pawliszyn [7] found that, when the excess of PFBBr was increased by a factor of 10 to 94, the amounts of the butyric and valeric acid derivatives increased by a factor of 10. When a 142-fold excess was used, the yield did not change, but it resulted in a significantly increased background noise, due to a large tailing reagent peak. Nilsson et al. [6] investigated the effects of the amount of benzyl bromide on the yields of the derivatisation reactions of phenoxy acid herbicides. They found that increase of the excess reagent from 1400- to 7000-fold did not result in a significantly increased derivatisation yield, but that more by-products were formed.

The effects of an excess of benzyl bromide on the yield of benzyl acetate were investigated. The derivatisation reaction was performed with 3 ml of $6.7 \cdot 10^{-5}$ *M* acetic acid and 5, 10, 15 or 20 μl of benzyl bromide (a 247-, 495-, 741- or 988-fold molar excess) and the amount of benzyl acetate was determined by headspace SPME–GC–FID. The results are illustrated in Fig. 3. It can be seen that, with 5, 10 and 15 μl of benzyl bromide, the amount of benzyl acetate formed increased from $1.4 \cdot 10^{-10}$ to $3.5 \cdot 10^{-10}$ mole. When 20 μl of benzyl bromide was used, the amount of benzyl acetate detected dropped to $1.9 \cdot 10^{-10}$ mole.

In a search for an explanation, the effects of the presence of benzyl alcohol on the headspace SPME of benzyl acetate were investigated. During the derivatisation reaction, the reagent was almost exclusively converted to benzyl alcohol. This resulted in

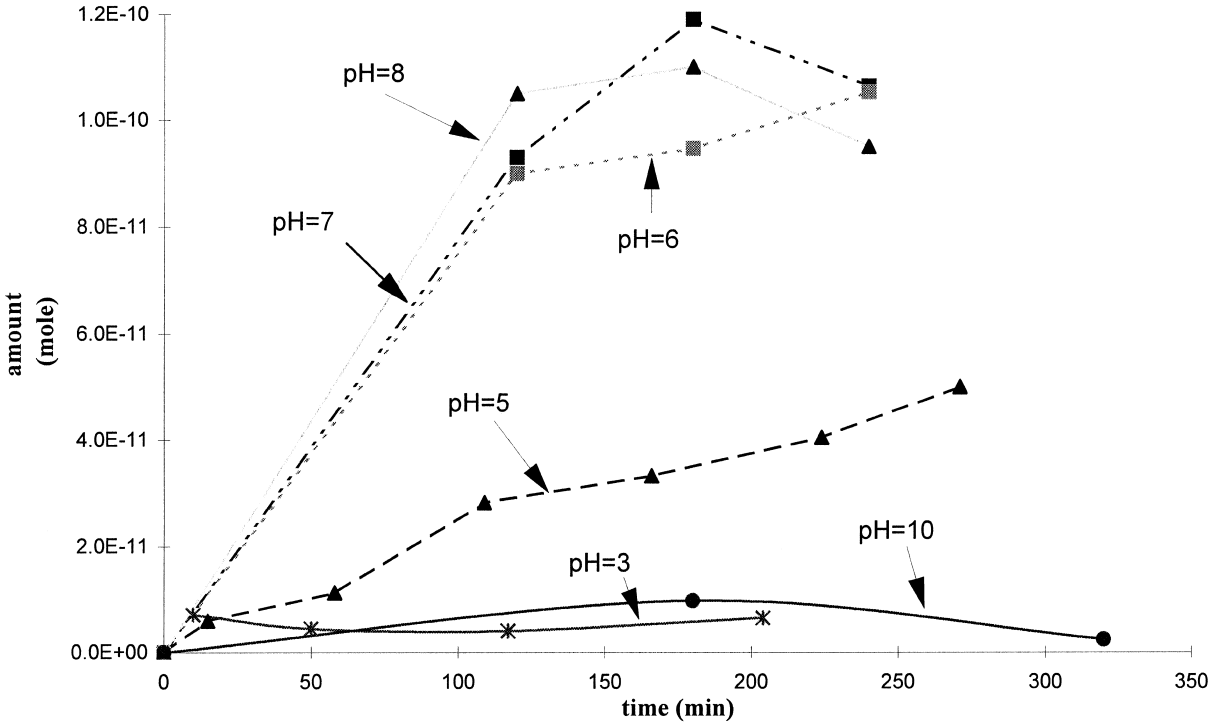


Fig. 2. Amounts of benzyl acetate detected at various pH values as a function of reaction time. Derivatisation: 3 ml of $6.7 \cdot 10^{-5}$ *M* acetic acid, 10 μl of benzyl bromide, 50°C. Every point was determined from a single experiment. Extraction: PA-coated fibre, 30 min, 30°C, headspace of salt-saturated solution.

the expected concentrations of 0.014, 0.028, 0.042 or 0.056 *M* of benzyl alcohol when 5, 10, 15 or 20 μl of benzyl bromide was used, respectively. An experiment was therefore set up in which the amount of benzyl acetate extracted from a $1 \cdot 10^{-5}$ *M* benzyl acetate solution (salt-saturated) containing 0, 0.014, 0.028, 0.042 or 0.056 *M* benzyl alcohol was determined. The amounts extracted as a function of the benzyl alcohol concentration are shown in Fig. 4. Up to a benzyl alcohol concentration of 0.028 *M*, the amount of benzyl acetate extracted increases by about 40% as compared to a solution without benzyl alcohol. If the benzyl alcohol concentration is increased further the amount of benzyl acetate extracted decreases from $8.5 \cdot 10^{-10}$ mole at 0.028 *M* to $3.0 \cdot 10^{-10}$ mole at 0.056 *M*. Moreover it was observed during the experiments that the alcohol did not dissolve entirely in the salt-saturated solution to which 15 or 20 μl of benzyl bromide had been added, and separated as a second liquid phase.

When the solution was not oversaturated in benzyl alcohol, two effects may influence the uptake of benzyl acetate into the fibre. (a) Increasing concentrations of benzyl alcohol may change the polarity of the liquid phase and hence might affect the gas–liquid partitioning of benzyl acetate. If this occurs, it is expected that the Henry's law coefficient will decrease, since benzyl alcohol will increase the solubility of benzyl acetate. Therefore, less benzyl acetate is expected to be extracted by the fibre. (b) Increasing benzyl alcohol concentrations will also result in increasing benzyl alcohol concentrations in the fibre. Similarly as in the water phase, the solubility of benzyl acetate in the fibre can be increased by the presence of benzyl alcohol. In order to see which of the effects dominates, the amount of benzyl acetate extracted from a salt-saturated 0.028 *M* benzyl alcohol solution was investigated as a function of its concentration, in comparison with that from a salt-saturated solution without benzyl alcohol. The results are shown in Fig. 5. As compared to the alcohol-free solution, the slope of the curve is higher

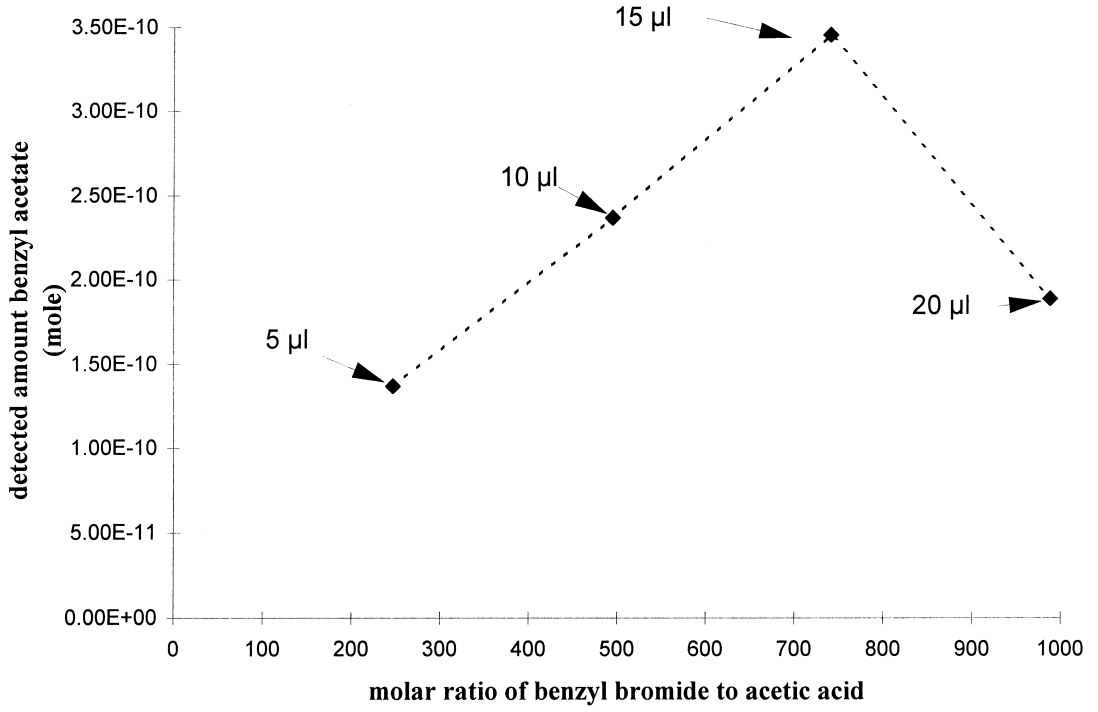


Fig. 3. Amounts of benzyl acetate detected as a function of reagent excess. Derivatisation: 3 ml of $1.7 \cdot 10^{-4}$ *M* acetic acid, pH 7, 50°C, 16 h. Extraction: 30°C, 30 min, headspace extraction of salt-saturated solution.

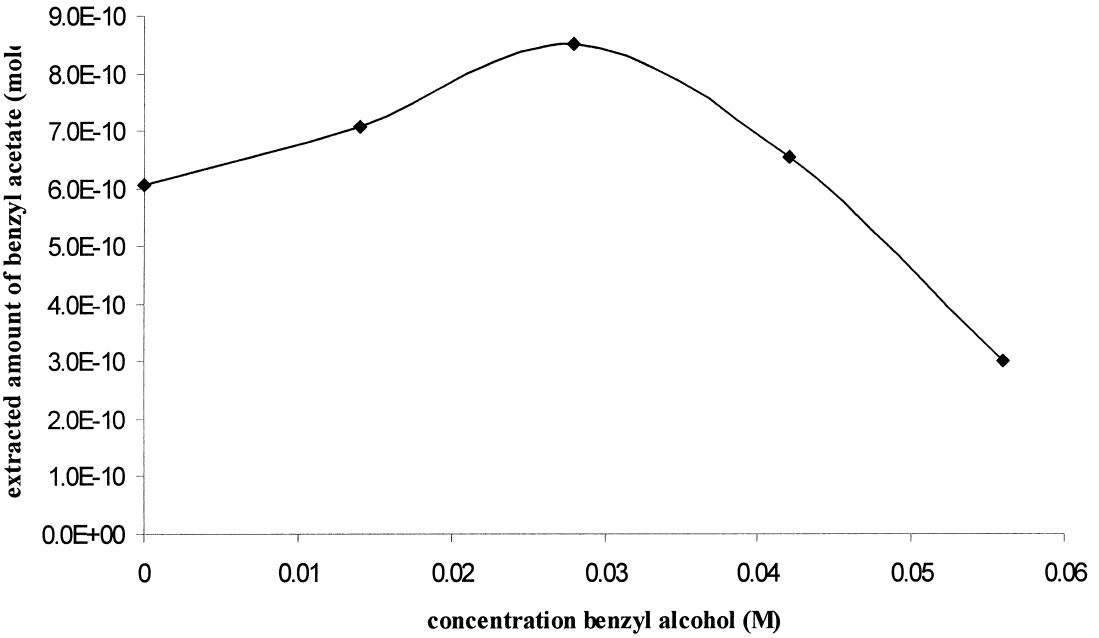


Fig. 4. Amount of benzyl acetate extracted from $1 \cdot 10^{-5}$ *M* solutions containing various amounts of benzyl alcohol. Extraction: PA-coated fibre, 30°C, 30 min, headspace of salt-saturated solution.

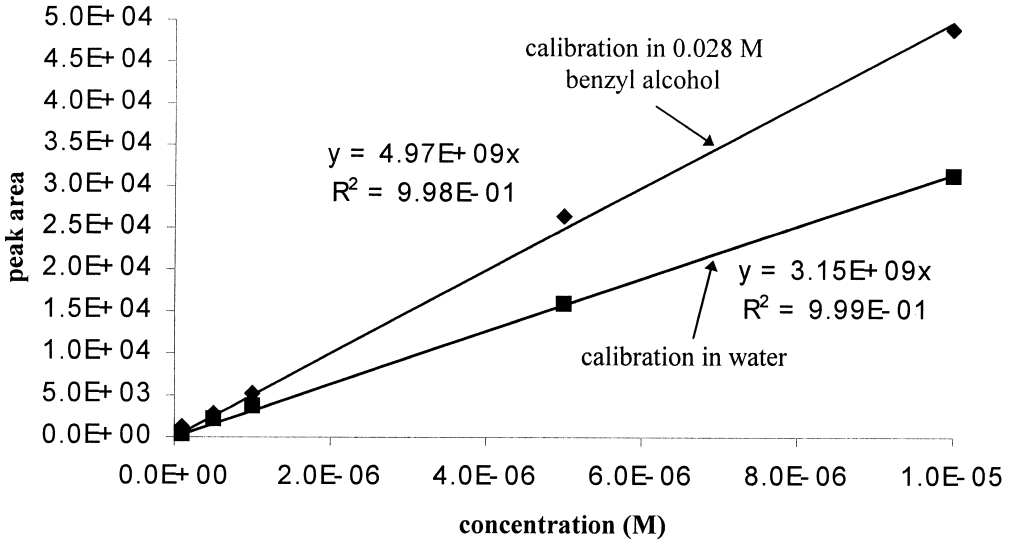


Fig. 5. Calibration curves of benzyl acetate in water and in 0.028 *M* benzyl alcohol. Extraction: PA-coated fibre, 30°C, 30 min, headspace of salt-saturated solution.

by a factor of 1.58 when 0.028 *M* benzyl alcohol is present. This clearly illustrates that the sorption of benzyl acetate by the fibre is increased by the presence of benzyl alcohol in the gas phase. When the liquid phase becomes saturated in benzyl alcohol, the concentration of benzyl alcohol in the gas phase becomes constant (corresponding to the saturated vapour pressure of 13.6 Pa at 25°C [20]). The amount of benzyl alcohol sorbed by the fibre will then not increase further. A second effect, however, is that some of the benzyl acetate can now dissolve in the benzyl alcohol present as a separate liquid phase. This will again lower the concentration of benzyl acetate in the fibre. Although there is no direct evidence, this explanation at least allows a qualitative understanding of the results presented in Fig. 4.

In accordance with the results for the analysis of the 3 ml sample, 10 μl of benzyl bromide reagent was used as an optimum quantity. With the application of the chosen parameters of the SPME and derivatisation (pH 7, 210 min, 50°C and 10 μl of benzyl bromide, headspace extraction during 30 min, salt saturation and PA coating) a relative standard deviation of 15.6% ($n=10$) was determined for the overall procedure at an acetic acid concentration of $6.7\cdot10^{-5}$ *M*. The linearity of the method was checked in the $1\cdot10^{-4}$ to $5\cdot10^{-6}$ *M* concentration range ($R^2=0.996$, $n=6$). The LOD, determined as a signal-to-noise ratio of 3, was 260 n*M* acetic acid. This LOD value is larger than those measured by Pan and Pawliszyn [7] for butyric and valeric acids with the use of PFBBr as derivatisation agent and GC–ECD. With this method, however, acetic and propionic acids could not be determined because of interfering background peaks. As compared to the direct SPME, the benzyl bromide headspace SPME method presented here is about 50-times more sensitive. The advantages of using benzyl bromide instead of PFPDE are that the latter has to be prepared and that it has to be handled as potentially hazardous.

From the results, the yield of the derivatisation could also be calculated and was found to be about 4%. This value might seem to be low, but it is of the same order as the yield reported for phenoxy acid herbicide derivatisation, which was about 1% [6].

## 4. Conclusions

An analytical method has been developed for the determination of acetic acid, based on water-phase derivatisation with benzyl bromide, SPME and GC.

The SPME of benzyl acetate and the derivatisation reaction have been optimised. The optimum parameters of derivatisation were found to be pH 7, 50°C, 210 min and the addition of 10 μl of benzyl bromide for a 3 ml sample. Headspace SPME with PA fibres, salt-saturated solutions and an extraction time of 30 min at 25°C, proved to give the best results. When these conditions were applied a relative standard deviation of 15.6% ($n=10$, $1\cdot10^{-4}$ $M$) was found for the overall method; a linear response was obtained in the $1\cdot10^{-4}$–$5\cdot10^{-6}$ $M$ ($R^2=0.996$, $n=6$) concentration range and the LOD was 260 n$M$. The derivatisation yield was about 4%.

During the experiments, it was also observed that benzyl alcohol, when present in millimolar concentrations, affects the sorption of benzyl acetate into the PA fibre. It is proposed that the uptake of benzyl alcohol into the fibre changes the polarity and the extraction characteristics of the coating. To the best of our knowledge, this is the first report of this phenomenon in SPME analysis. This point needs to be further investigated.

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