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The determination of trace quantities of isoamyl chloride in aqueous isoamyl alcohol solutions

For the determination of traces of isoamyl chloride in aqueous solutions, it is necessary to prepare calibration standards at concentration levels of 10–100 p.p.m. In preparing these standards, it was found that the resulting calibration curves were neither linear nor reproducible. The cause was finally traced to an adsorption effect; the isoamyl chloride appeared to be adsorbed by the walls of the glass container. This adsorption effect could be markedly reduced by the use of 30% aqueous aceto-nitrile as the solvent for preparing the standards. However, even under these con-ditions, adsorption of isoamyl chloride on the glass walls of the container did not appear to be completely eliminated.

Discussion

The solutions to be analysed were aqueous and contained organic materials in low concentrations, the major of these being isoamyl alcohol. The material of interest, isoamyl chloride, was present in the concentration range 10–100 p.p.m. As all the other organics were of a higher boiling point and more polar than isoamyl chloride, a column of β,β'-oxydipropionitrile proved suitable, as it eluted isoamyl chloride prior to the other organics. The use of a flame ionisation detector provided the neces-sary sensitivity.

In order to calibrate the instrument, a series of standard solutions were pre-pared by suitably diluting a stock solution of 100 p.p.m. isoamyl chloride, prepared by dissolving 10 μl in 100 ml distilled water. The resulting plot of concentration *versus* peak height was not linear (curve I, Fig. 1).

The possibility that this curvature was the result of a solubility limit of isoamyl
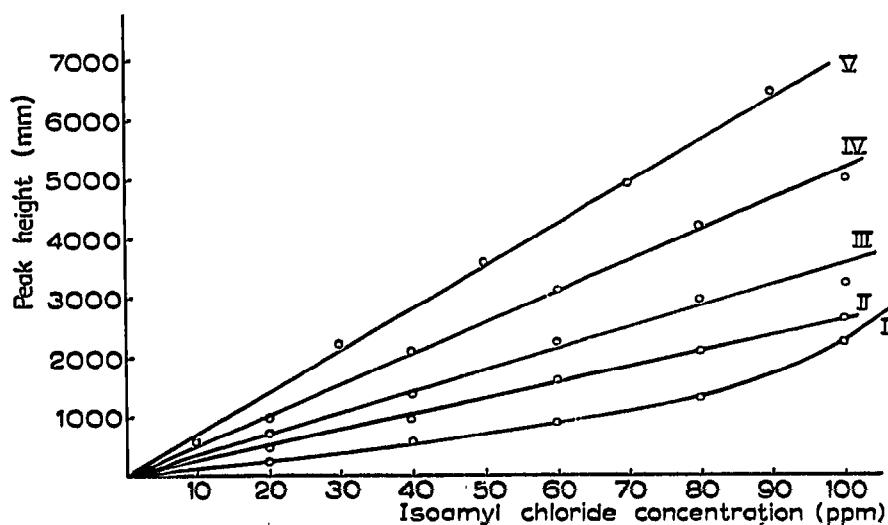

Fig. 1. Adsorbence of standard isoamyl chloride solutions. I = Aqueous solutions prepared in glass by dilution of a 100 p.p.m. solution; II = aqueous solutions prepared individually in glass; III = aqueous solutions prepared individually in polypropylene; IV = Solutions in 30% aqueous acetonitrile prepared individually in glass; V = as IV but vessel rinsed twice with same solution.

chloride in water below 100 p.p.m. suggested itself. A series of standard solutions was therefore prepared, not by diluting a stock solution but by preparing each standard separately. The resulting curve (II) was linear but the peak heights of the directly prepared standards were almost twice as high as those of the standards of equivalent concentration prepared by dilution (except the stock solution which was, of course, not diluted), which indicated that the non-linearity of curve I was not due to a solubility effect.

This suggested that the lower response for solutions produced by dilution was due to adsorption of the isoamyl chloride on the glass of the flasks in which the solutions were prepared. The possibility of adsorption by glass of trace organics in water has received little attention in the literature. The only mention of this effect that we could find was in the work of HOFFMAN AND ANACKER[1]. In determining the solubilities of tetradecanol and hexadecanol in water, they looked for but did not find any adsorption of these alcohols by glass.

In order to determine whether glass adsorbs isoamyl chloride, a series of standard solutions was prepared in polypropylene (Nalgene) measuring cylinders. The peak heights of these standards was higher than for those prepared in glass (curve III). However, the peak heights dropped continuously over a period of several hours, indicating absorption of the isoamyl chloride by the polypropylene.

Further evidence for adsorption of isoamyl chloride on glass was obtained when 1 g of glass wool (Pyrex) was added to 50 ml of a solution of 50 p.p.m. isoamyl chloride in water. The isoamyl chloride peak height dropped to 50% of its initial value.

An attempt to deactivate the glass by saturation with isoamyl chloride by prior rinsing with the same solution proved unsuccessful. After the first rinse, a peak height increase of 50% was observed and a further 10% increase after the second rinse; this, however, was still not as high as that obtained with the same concentration of solution prepared in polypropylene.

The fact that rinsing the glass twice with the standard solution gave a response for isoamyl chloride lower than that for the solutions prepared in polypropylene indicates that head space volatilisation losses are not the major cause of the lowered response for isoamyl chloride. Such losses have been found for traces of hydrocarbons in water[2]. DUNTON[2] used a detergent to increase the solubility of hydrocarbons in water for the preparation of standard solutions but found the use of ethanol as solvent gave better results. We have found that the use of 30% aqueous acetonitrile as solvent gave a larger response for isoamyl chloride than either water or acetonitrile alone.

A series of standard solutions was prepared in 30% solutions of acetonitrile (Matheson, Coleman and Bell) in water, by dissolving the isoamyl chloride in the acetonitrile and then adding the water. These solutions gave responses for isoamyl chloride almost twice those obtained in water alone and higher than those for solutions prepared in polypropylene (curve IV). Very similar results were obtained with a 50% acetonitrile solution. However, although the adsorption of isoamyl chloride on glass was reduced by acetonitrile, it was not completely eliminated as shown by the fact that rinsing the glass with the same solution caused a still further increase in peak height. As a second rinse (curve V) gave results almost identical to the first rinse, it appears that, under these conditions, the glass was saturated and no further isoamyl chloride was adsorbed from the solution.

If the isoamyl chloride was dissolved first in the water and acetonitrile then added, the responss were lower than with the reverse procedure but higher than for solutions containing no acetonitrile. A possible explanation for this is that whereas acetonitrile can displace isoamyl chloride adsorbed on some sites, it cannot do so on more active sites. However, if acetonitrile is adsorbed first on these sites, isoamyl chloride will not displace it.

When the isoamyl chloride was dissolved in pure acetonitrile, the response was lower than for the same concentration of isoamyl chloride in 30% aqueous aceto- nitrile. A 100 p.p.m. solution of isoamyl chloride in pure acetonitrile gave a peak height of 3700 mm as compared to 5000 mm for 100 p.p.m. in 30% aqueous aceto- nitrile. It would appear from this that the presence of water reduces the adsorption of isoamyl chloride on the glass.

Not only is isoamyl chloride adsorbed by glass, it also appears to be adsorbed by the column. Initially, both pure acetonitrile and 30% aqueous acetonitrile were injected and the resultant chromatogram showed that the acetonitrile contained no materials with the same retention time as isoamyl chloride. However, after the column had been in use for some time, if pure acetonitrile and a 30% aqueous solution of aqueous acetonitrile are then injected the pure acetonitrile behaved as initially, but the 30% aqueous solution of acetonitrile showed a fairly large peak with the retention time of isoamyl chloride.

2 μl of de-ionised distilled water gave a chromatogram almost identical to that of the 30% aqueous acetonitrile (2 μl). This did not change on repeated injection of water and conditioning at 60°.

The fact that the size of the isoamyl chloride peak was found to be independent of the amount of water injected indicated that this peak is not due to an impurity in the water. It therefore appears that isoamyl chloride is adsorbed on the column and then displaced by the water but not by the acetonitrile. In the determination of petrol in water, JELTES AND VELDINK[3] also found that the injection of water gave rise to spurious peaks.

It appears unlikely that isoamyl chloride–water represents a unique system and the possibility of adsorption effects should, therefore, be considered when pre- paring standard solutions for trace analysis.

Experimental

Column. 2 m, 0.125 in. diameter packed with 5% β,β'-oxydipropionitrile on acid washed Chromosorb G 60–80 mesh.

Operating conditions. Detector 170°, injection block 200°, column 40° for 1 min (until the isoamyl chloride had eluted), then programmed at 20° per minute to 60° and held at this temperature for 4 min until the acetonitrile had completely eluted (at this temperature there was a marked base line drift due to bleeding); carrier gas flow (nitrogen) 40 ml per min, hydrogen 50 ml per min, air 400 ml per min, detector make-up gas (helium) 40 ml per min.

Sample size. 2 μl. The electrometer was operated at a range setting of one (maximum sensitivity).

Standard solutions were prepared by adding the isoamyl chloride with a Hamilton microsyringe to 100 ml distilled water or to 30 ml acetonitrile and diluting with water to 100 ml. The solutions were prepared in 250 ml graduated flasks, which

permitted thorough mixing on vigorous shaking. The solutions were shaken vigorously intermittently over a period of 30 min.

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1 C. S. HOFFMAN AND E. W. ANACKER, *J. Chromatog.*, 30 (1967) 390.
2 M. L. DUNTON, *141st Am. Chem.-Soc. Meeting, March 1962.*
3 R. JELTES AND R. VELDINK, *J. Chromatog.*, 27 (1967) 242.

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Tetracyanoethylated pentaerythritol: an efficient polar liquid phase for analysis of trimethylsilyl derivatives of sugars and sugar alcohols

In recent years application of gas–liquid chromatography (GLC) for analysis of carbohydrates and other polyhydroxy compounds has been accomplished by preparing their volatile derivatives. Trimethylsilyl (TMS) ethers are some of the most suitable derivatives for routine determination of these compounds. Identification of closely related compounds by GLC generally requires that analysis be made on both polar and nonpolar liquid phases. If only one phase is used, resolution may be incomplete. The nonpolar phases such as silicone gums SE-52[1], SE-30[5], and XE-60[1] have been used to separate TMS derivatives. By linear temperature programming these nonpolar phases can be used for separating a mixture of compounds with a wide range of boiling points. Polar phases are usually more selective than nonpolar liquid phases. Polar phases which have been used with partial success for analyses of TMS derivatives include polyethylene glycolsuccinate (EGS)[1], Carbowax 1540* (ref. 1) and Carbowax 20M[2,3].

This report describes the use of dimethylsilicone gum OV-1 as a nonpolar phase and tetracyanoethylated pentaerythritol (TCEPE) as a polar phase for the separation of TMS derivatives of various sugars and sugar alcohols.

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* Use of trade names is for identification only and does not constitute endorsement by the Public Health Service or by the U.S. Department of Health, Education, and Welfare.