

CHROM. 8839

GAS CHROMATOGRAPHIC DETERMINATION AT THE PARTS PER MILLION LEVEL OF METHANOL AND ETHANOL IN AQUEOUS SOLUTIONS

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(Received September 23rd, 1975)

SUMMARY

A method for determining small amounts of methanol and ethanol in aqueous solutions based on a combination of stripping and gas chromatographic techniques, has been developed. By the reaction with alkali nitrite the alcohols are quantitatively converted into the corresponding volatile alkyl nitrites which are transferred to a liquid nitrogen sampling loop and after a instantaneous evaporation analysed by gas chromatography. Amounts of approximately 1 μg of the individual alcohols can be estimated in sample volumes of about 5 ml.

INTRODUCTION

One of the methods for the determination of small amounts of aliphatic or cycloaliphatic alcohols in aqueous solutions is based on the reaction of the alcohols with alkali nitrite in acidic medium. Extraction of the alkyl nitrites with *n*-heptane or similar light aliphatic hydrocarbon is followed by measurement of the typical UV absorption spectra¹. This method, originally proposed for the simultaneous determination of individual butyl alcohols in aqueous solutions, proved to be useful also for other aliphatic alcohols and some glycols, the nitrites of which possess sufficiently high boiling points²⁻⁴. Compared with the technique of direct gas chromatography (GC) the principal advantage can be seen in the possibility of analysing extremely dilute alcohol solutions. Both the formation and the subsequent extraction of the nitrous acid esters proceeds with suitable velocity¹ and with quantitative yields. However, this method is not sufficiently reliable for methanol and ethanol due to the high volatility of the corresponding nitrites (b.p. -12° and 17° , respectively). The losses are caused particularly by evaporation from the spectrometer cell.

In this communication the method for the determination of small amounts of methanol and ethanol in aqueous solutions is described. Alkyl nitrites and other volatile reaction products formed by the reaction of alcohols with alkali nitrite in a stripping vessel are transferred by a hydrogen carrier gas stream into a liquid nitrogen sam-

pling loop. They are then flushed out and introduced into a GC column. The procedure is convenient for the determination of microgram amounts of methanol and ethanol in 5-ml sample volumes.

EXPERIMENTAL

Materials

Methanol and ethanol (reagent grade, Lachema, Brno, Czechoslovakia) were purified by distillation from sodium. Their purity was checked by GC. The aqueous stock solutions contained 1–50 $\mu\text{g/ml}$. Sodium nitrite was recrystallized from water.

Apparatus

The apparatus consisted of the stripping line, shown in Fig. 1, and a gas chromatograph. Hydrogen used as the stripping gas was purified by passing it through a liquid nitrogen trap (2) into a 10- or 100-ml stripping flask (4) fitted with a condenser and a vessel containing hydrochloric acid. The gas leaving the flask was dried over magnesium perchlorate (6) and introduced through a six-way sampling valve (7) into a sampling loop (8) cooled by liquid nitrogen. The flow-rate of hydrogen was measured by a bubble flow meter (11).

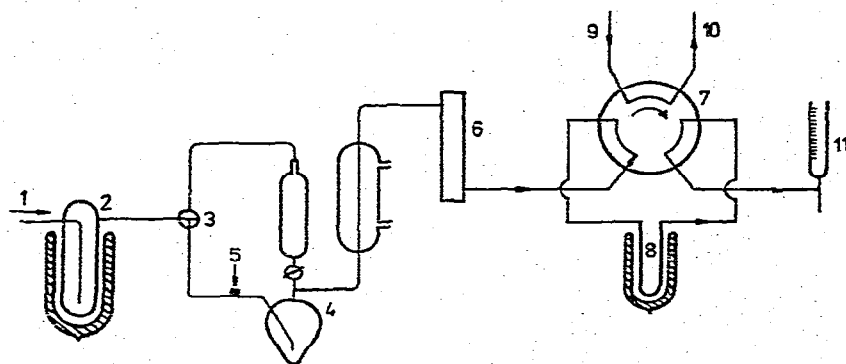


Fig. 1. Flow diagram of the stripping line. 1 = Gas inlet; 2 = liquid nitrogen trap; 3 = three-way stop cock; 4 = stripping flask; 5 = injection port; 6 = dryer; 7 = six-way sampling valve; 8 = sampling loop; 9 = carrier gas inlet; 10 = to gas chromatograph; 11 = bubble flow meter.

A modified Pye heated dual flame ionisation programmed chromatograph, Model 64 (Series 104), was used. It was equipped with a 0–1 mV recorder (Honeywell, Model Elektronik 194). The column employed was a 170×0.4 cm I.D. glass tube operating at 104° . Nitrogen was used as the carrier gas at a flow-rate of approximately 30 ml/min.

Column packing

Chromosorb 102, 80–100 mesh (Becker, Delft, The Netherlands) served as the stationary phase. The packed column was conditioned for 12 h at 230° with the carrier gas flowing.

Procedure

About 4 ml of a freshly prepared 2.5% solution of sodium nitrite were transferred to the stripping flask. Hydrogen was passed through with a flow-rate of 30 ml/min. The volume of the gas used was approximately seven times the dead volume of the line. After the air was swept out from the apparatus the sampling loop was immersed into liquid nitrogen, the sample of the aqueous solution of alcohol was injected into the stripping flask and 1 ml of 19% hydrochloric acid solution was added. A period of 10 min was necessary to strip all of the alkyl nitrites originating from the alcohols during the reaction. The sampling loop was then connected with the gas chromatograph by turning the six-way valve. Sampling of the trapped mixture was carried out by rapidly heating the loop with a water-bath, *ca.* 55–60°. The separation of methyl and ethyl nitrites is shown in Fig. 2. The shape of the retention curves of both components in question permitted quantitative evaluation.

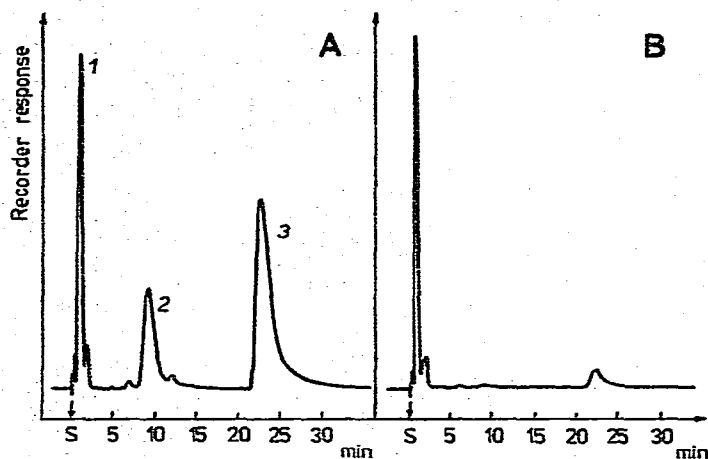


Fig. 2. Chromatogram of methyl and ethyl nitrites. Column, 170 \times 0.4 cm I.D., Chromosorb 102 80–100 mesh; carrier gas (nitrogen) flow-rate, 30 ml/min; column temperature, 104°. 1 = Nitrogen oxides; 2 = methyl nitrite; 3 = ethyl nitrite. A, Analysis of a methanol-ethanol mixture; B, blank.

RESULTS

The results of the present work showed that the rapid and quantitative formation of alkyl esters of nitrous acid is capable of providing reliable results in determining small amounts of methanol and ethanol in very dilute aqueous solutions of various origins. Because of the volatility of methyl and ethyl nitrite the original procedure¹, based on the characteristic UV spectrum in *n*-heptane extracts was replaced by a combination of stripping, freezing out and GC techniques. Contrary to the original procedure^{1–4} we have not succeeded in removing the by-products formed by the reaction of alkali nitrite with the mineral acid from the main products of interaction of aliphatic alcohols with nitrous acid, *i.e.* methyl and ethyl nitrite. The chromatogram of the mixture flushed from the sampling loop shows various peaks which correspond neither to methyl nor to ethyl nitrite (compare Fig. 2A and B). These peaks are very likely caused by various nitrogen oxides originating from alkali nitrite and

the acid and no difference is observed when hydrochloric or sulfuric acid is used. On carrying out both blank experiments and analyses of the alcohols we observed, in the freezing loop, at least two zones differing in colour and physical state. A ring of dark blue liquid condensed just above the liquid nitrogen level and white crystals formed on the bottom of the loop. Because of a relatively slow evaporation when heated in a water-bath (ca. 55–60°) the blue liquid can be considered more likely to be nitrogen trioxide (b.p. 3.5°) than nitric oxide (b.p. —152°). Attempts at analysing the white crystalline condensate were not successful. Fortunately, the correct evaluation of the methyl and ethyl nitrite peaks is not affected by the reaction by-products if the recommended column packing is used. The effects of the stripping flask volume and of the degree of the sample dilution on the results were not sufficiently investigated in the present paper. If a standard volume of the stripping flask and a standard dead volume of the line are maintained constant, reproducible results for methanol and ethanol are obtained. Amounts of 1–100 μg in 5-ml samples were determined without difficulty. However, the stripping time is proportional to the sample volume taken for analysis. The results were less satisfactory with more dilute samples. It is conceivable that a suitable modification of the experimental conditions can ameliorate the situation. The identification and elimination of reaction byproducts and extension of the method to higher aliphatic and cycloaliphatic alcohols is in progress.

ACKNOWLEDGEMENT

The authors thank Mrs. J. Kubešová and Mrs. P. Valentová for experimental assistance.

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