FULL PAPER
THE ANALYST
www.rsc.org/analyst

Headspace gas chromatographic determination of 2-alkyl-5,5-dimethyl-1,3-dioxane derivatives in wastewaters of a polyester resin plant

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Received 11th December 2000, Accepted 1st February 2001
First published as an Advance Article on the web 5th March 2001

The static headspace gas chromatographic technique can be conveniently employed to check the presence and amount of the odorous side-products, 2-R-1,3-dioxanes (R = H, CH_3, C_2H_5, *i*-C_3H_7, *n*-C_3H_7), directly from the wastewaters flowing from the reactors during the synthesis of polyester resins. By the optimisation of a simple and direct analytical method, the amounts of these compounds may be continuously monitored and controlled. This method is characterized by good repeatability (3–4%) and does not seem to suffer from matrix effects. The detection limits for the determination of the five dioxanes fall in the range 400–700 μg dm^{-3} ($\alpha = \beta = 0.05$).

Introduction

2-R-5,5-dimethyl-1,3-dioxane derivatives (R = H, CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7) are side-products of the acid-catalyzed poly-esterification processes based on the use of neopentyl glycol, (2,2-dimethylpropane-1,3-diol). Their formation is due to the processes of degradation of the glycol[1–5] that occur at high temperatures. These compounds are liquids at room temperature and have high volatility. Their presence in the environment is noticed at about the 50 μg m^{-3} level in air[6] owing to their sweetish taste and malodorous smell. Therefore, the environmental impact of these substances in urban areas near to polymer industries is very important. A paper dealing with the analysis and detection of these dioxanes present in the atmosphere of an industrial area was first published in 1991.[7]

These compounds are soluble in water and exhibit high stability in this medium, whereas in the ground they show a very low level of absorption. This behaviour, associated with their very low biodegradability,[8] implies that they easily reach the aquifers, causing odour problems in river and ground waters.[9,10] The determination of trace amounts of 1,3-dioxanes in surface and ground waters is usually performed by purge and trap GC-MS analysis,[10] which provides detection limits close to the threshold odour values (5–10 ng dm^{-3}) determined for these compounds.[11]

Even though detailed toxicological studies have not been reported in the literature,[12] the 1,3-dioxane derivatives could be considered potential etiological agents of cancers to the respiratory system and the skin, similarly to 1,4-dioxane derivatives,[13–17] a class of compounds more extensively studied.

A reduction in the amount of side-produced dioxanes formed in a polyesterification process may be achieved by varying the temperature of the reactor. Thus, in order to check the formation of these environmental pollutants in the reactors and to optimise the plant conditions, rapid and accurate analytical procedures must be developed.

In this paper, we report the use of the static headspace gas chromatographic technique for the qualitative and quantitative determination of mixtures of the above dioxanes directly from the wastewaters arising from the reactor of industrial poly-esterification processes. In this connection, the application of a known synthetic procedure for the preparation of 1,3-dioxanes, to be utilised for the preparation of accurate standard solutions for instrumental calibration, is proposed.

Experimental

Materials

All chemicals were of analytical-reagent grade; aldehydes, neopentyl glycol and butyltin trichloride were obtained from Aldrich (Steinheim, Germany) and were used as received. Methanol and HYDRANAL used for the determination of the water content were obtained from Riedel-de Haën (Hannover, Germany).

Preparation of 2-R-5,5-dimethyl-1,3-dioxane (R = H, CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7)

2-R-5,5-dimethyl-1,3-dioxanes (R = H, CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7) of high purity were prepared by mixing in an ice-bath equimolar amounts (0.3–0.5 mol) of the appropriate aldehyde, RCHO, and neopentyl glycol, $(CH_3)_2C(CH_2OH)_2$, in the presence of butyltin trichloride, $BuSnCl_3$, as catalytic precursor, following a procedure already reported.[18] Reactions were completed in 24 h at room temperature and during this time formation of water was observed. After separation from the water, the organic liquid residues were dried overnight on magnesium sulfate and then distilled at atmospheric pressure to give dioxanes in 60–70% yield. Redistillation of the dioxanes on a Perkin-Elmer Model 251 auto annular still gave compounds with a degree of purity >99%.

Instrumentation

The synthesised dioxanes were fully characterized by IR, ^{13}C NMR, conventional GC and GC-MS techniques; the water content (always between 0.01 and 0.07%) was determined by the Karl Fischer method. Measurements of density were also carried out.

IR spectra were recorded as a liquid film on a Perkin-Elmer IR Model 599B spectrophotometer using KBr optics. ^{13}C NMR spectra of the pure liquid compounds were measured on a Jeol FX90Q Fourier transform spectrometer operating at 90 MHz in 5 mm od tubes. The chemical shifts were measured relative to tetramethylsilane (TMS) as internal standard and off-resonance and insensitive nuclei enhanced polarization transfer techniques were employed to assign the carbon signals.[19]

GC analyses were carried out on a Perkin-Elmer Model 8310 gas chromatograph equipped with a flame ionisation detector and with an Alltech EC-WAX capillary column (30 m × 0.25 mm od, 0.25 μm film thickness). The following conditions were employed: $T_{detector}$ = 300 °C, $T_{injector}$ = 200 °C, T_{column} = isothermal at 50 °C for 2 min then increased from 50 to 250 °C at 10 °C min^{-1}, nitrogen as carrier gas at 2 cm^3 min^{-1} and splitting ratio 1 : 30.

GC-MS analyses were performed on a CE Instruments Model 600 HRGC gas chromatograph equipped with an electron ionization source (70 eV), a Fisons Instruments Model 800 quadrupolar analyser and an Alltech EC-Wax capillary column (30 m × 0.25 mm od, 0.25 μm film thickness). The temperature programme was the same as employed for GC, helium was used as the carrier gas at l cm^{3}min^{-1} and a splitting ratio of 1 : 50 was used.

The content of water was determined by Karl Fischer titration (Metrohm Model 684 KF coulometer) by dissolving 0.2 cm^3 of the prepared dioxane in 3 cm^3 of anhydrous acetonitrile.

The density (d) of the dioxanes was determined at 25.02 ± 0.01 °C on a capillary vibration densimeter (Paar Model DMA 60, measuring cell Model DMA 602 HT).

Analytical procedure for the determination of 2-R-5,5-dimethyl-1,3-dioxanes in wastewater samples

A 5 cm^3 volume of a wastewater sample, containing an estimated amount of each dioxane in the range 20–120 mg dm^{-3}, was added to 1 cm^3 of the internal standard (IS) solution (500 mg dm^{-3} of propan-1-ol) and diluted with distilled water to a total volume of 10 cm^3 in a calibrated round-bottomed flask. A 2 cm^3 volume of this solution was transferred into a 20 cm^3 headspace vial and held for 2 h at 75 °C in a Haacke F3 thermostated bath. After this time, 1 cm^3 of the vapour phase was injected into the gas chromatograph by means of a gas-tight syringe. Three independent chromatographic measurements were carried out for each sample solution and the amount of the appropriate dioxane was determined by the internal standard method [$t_{r(IS)}$ = 5.1 min] after the instrumental calibration, performed daily with three standard solutions in the 0–60 mg dm^{-3} concentration range of each analyte.

Chemical and physical data for the prepared dioxanes

5,5-Dimethyl-1,3-dioxane. Bp, 120 °C; d^{25}, 0.9486 g cm^{-3}; water, 0.07% w/w; GC retention time (t_r), 6.00 min; ^{13}C NMR, δ = 22.5 [(CH$_3$)$_2$C]), 30.8 [C(CH$_3$)$_2$]), 77.0 [(CH$_2$O)$_2$C], 93.9 [CH$_2$(OC)$_2$] ppm; GC-MS, m/z 115 [M − H]$^+$.

2-Methyl-5,5-dimethyl-1,3-dioxane. Bp, 131 °C; d^{25}, 0.9099 g cm^{-3}; water, 0.04% w/w; t_r, 5.46 min; ^{13}C NMR, δ = 21.0 (CH$_3$CH), 21.9 [(CH$_3$)C], 23.2 [(CH$_3$)C], 29.9 [C(CH$_3$)$_2$], 77.0 [(CH$_2$O]$_2$C), 99.2 [CH(OC)$_2$] ppm; GC-MS, m/z 129 [M − H]$^+$, 115 [M − CH$_3$]$^+$.

2-Ethyl-5,5-dimethyl-1,3-dioxane. Bp, 152 °C; d^{25}, 0.9039 g cm^{-1}; water, 0.03% w/w; t_r, 6.69 min; ^{13}C NMR, δ = 8.2 (CH$_3$CH$_2$), 21.9 [(CH$_3$)C], 23.2 [(CH$_3$)C], 28.1 (CH$_2$CH$_3$), 30.1 [C(CH$_3$)$_2$)], 77.0 [(CH$_2$O)$_2$C], 103.0 (CH(OC)$_2$] ppm; GC-MS, m/z 143 [M − H]$^+$, 115 [M − C$_2$H$_5$]$^+$.

2-*n*-Propyl-5,5-dimethyl-1,3-dioxane. Bp, 173 °C; d^{25}, 0.9062 g cm^{-3}; water, 0.06% w/w; t_r, 8.28 min; ^{13}C NMR, δ = 14.1 (CH$_3$CH$_2$CH$_2$), 17.3 (CH$_3$$CH_2CH_2$), 21.9 [($CH_3$)C], 23.2 [($CH_3$)C], 30.1 [$C$(CH$_3$)$_2$], 37.2 ($CH_2CH_2CH_3$), 77.1 [($CH_2$O)$_2$C], 102.1 [$C$H(OC)$_2$] ppm; GC-MS, m/z 157 [M − H]$^+$, 115 [M − C$_3$H$_7$]$^+$.

2-Isopropyl-5,5-dimethyl-1,3-dioxane. Bp, 165 °C; d^{25}, 0.8960 g cm^{-3}; water, 0.01% w/w; t_r, 7.01 min; ^{13}C NMR, δ = 17.0 [(CH$_3$)CH], 21.9 [(CH$_3$)C], 23.1 [(CH$_3$)C], 30.1 [C(CH$_3$)$_2$], 32.8 [(CH(CH$_3$)$_2$], 77.1 [(CH$_2$O)$_2$C], 105.5 [CH(OC)$_2$] ppm; GC-MS, m/z 157 [M − H]$^+$, 115 [M − C$_3$H$_7$]$^+$.

Results and discussion

The synthetic procedure adopted for the preparation of the 1,3-dioxanes of interest resulted in products of sufficient purity to be utilisable for analytical purposes. This allowed the preparation of standard solutions for instrumental calibration and the consequent development of an analytical methodology for the accurate determination of 2-R-1,3-dioxanes (R = H, CH$_3$, C$_2$H$_5$, n-C$_3$H$_5$, i-C$_3$H$_7$) in industrial wastewaters arising from polyesterification processes.

In view of the pronounced volatility of these compounds, a procedure based on static headspace GC was optimised with the aim of obtaining well resolved gas chromatograms for real sample analysis and with a relatively short time of analysis. The best instrumental conditions were chosen by the study of the relevant aspects of the analytical procedure: (i) the volume of sample to be introduced into the 20 cm^3 headspace vials, (ii) the temperature and the time of heating of the vials containing the samples together with the amount of vapour to be injected into the gas chromatograph and (iii) the choice of an appropriate internal standard.

Adopting the optimised GC conditions (see Experimental), the chromatogram in Fig. 1 was obtained for the direct analysis of a wastewater sample collected from the reactor in the treatment plant of a polyester factory. All analytes gave well resolved peaks free from possible chromatographic interferences, with an analysis time of about 15 min. The absence of chromatographic interferences was also assessed by GC-MS

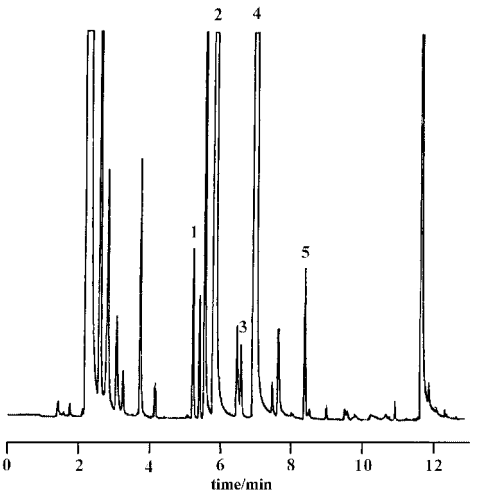

Fig. 1 Gas chromatogram of a real sample without addition of the internal standard (propan-1-ol, t_r = 5.1 min). Peaks 1–5 refer to the 2-R-5,5-dimethyl-1,3-dioxanes with R = CH$_3$, H, C$_2$H$_5$, i-C$_3$H$_7$ and n-C$_3$H$_7$, respectively. Conditions: $T_{detector}$ = 300 °C, $T_{injector}$ = 200 °C, T_{column} = isothermal at 50 °C for 2 min then increased to 250 °C at 10 °C min^{-1}, nitrogen as carrier gas at 2 cm^{3}min^{-1}, splitting ratio 1 : 30.

Table 1 Determination of 2-R-5,5-dimethyl-1,3-dioxanes in a real sample of wastewater from a polyester factory, using two instrumental calibration procedures[a]

Calibration procedure	Concentration of 2-R-5,5-dimethyl-1,3-dioxane/mg dm^{-3}[b]				
	R = H	R = CH_3	R = C_2H_5	R = n-C_3H_7	R = i-C_3H_7
Standard addition method	1519 ± 87	10.3 ± 0.4	3.0 ± 0.2	2.1 ± 0.2	665 ± 15
Internal standard method	1519 ± 14	10.1 ± 0.3	3.1 ± 0.1	2.9 ± 0.1	647 ± 8
t_{exp}[c]	0.0	0.69	0.77	6.19	1.83

[a] For details of calibration procedures, see Results and discussion. [b] Uncertainty is expressed as standard deviation (n = 3). [c] Critical value $t_{0.05/2,4}$ = 2.78.

analysis of real samples performed under the same experimental conditions.

A wide linear response range (up to 200 mg dm^{-3}) was observed, so that a daily calibration by three standard solutions in the 0–60 mg dm^{-3} concentration range was adopted.

The absence of matrix effects was assessed by the standard additions procedure (four additions of 5–30 mg dm^{-3} for each dioxane) on five different real samples, suitably diluted in order to obtain the concentration of the examined dioxane in the calibration range; a t-test (α = 0.05/2) evidenced no significant differences between the slopes of the experimental calibration functions determined for each analyte and those obtained by the standard additions procedure within the same analytical session. Moreover, the concentration values obtained by the application of the two calibration procedures were not statistically distinguishable, as shown in the example in Table 1, with a few exceptions for analytes present at very low concentrations in the real samples. These important results suggest the possible absence of bias for the proposed analytical method.

The uncertainty of the method, expressed as repeatability,[20] was estimated by repeated analyses (n = 3) of independent real samples (n = 4). In the 10–60 mg dm^{-3} concentration range an average repeatability of around 3–4% was evaluated for each analyte. In view of these excellent results, good precision together with the probable absence of bias, the proposed analytical procedure can be considered accurate.[20]

Adopting the IUPAC procedure[20,21] and analysing experimental calibration functions obtained at low concentrations (1–10 mg dm^{-3}) of each analyte, detection limits of 0.6, 0.5, 0.4, 0.6 and 0.7 mg dm^{-3} (α = β = 0.05) were determined for the 2-R-5,5-dimethyl-1,3-dioxanes (with R = H, CH_3, C_2H_5, n-C_3H_7 and i-C_3H_7, respectively. It is important to point out that these values are significantly higher than the detection limits reported in the literature for this class of water contaminants when instrumental procedures for ultra-trace analysis were adopted.[10] As a consequence, static headspace GC procedures cannot be utilised for the analysis of drinking or surface waters containing very low concentrations of dioxanes; for example, the odour threshold concentration of 2-ethyl-1,3-dioxane has been evaluated to be in the 5–10 ng dm^{-3} range by flavour profile analysis.[11] However, in view of the simple instrumentation required and the reduced time of analysis, the proposed analytical method appears to be more easily applicable for both direct analysis of industrial wastes and the control of reactor conditions in polyester production plants, where high levels of 1,3-dioxanes are normally present.

Acknowledgements

The authors thank the Ministero dell'Università e Ricerca Tecnologica (MURST, Rome) for financial support and Professor G. Tagliavini for helpful assistance.

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