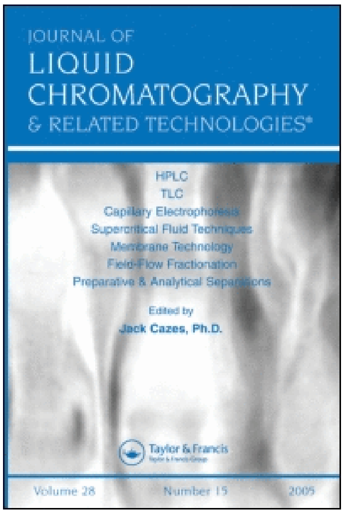

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DETERMINATION OF PHTHALIC ANHYDRIDE IN WORKPLACE AIR USING REVERSE PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

A reverse phase high performance liquid chromatographic procedure is described for the analysis of phthalic anhydride in workplace air. A glass fibre filter was used to collect the airborne phthalic anhydride and the analyte was then desorbed and hydrolyzed with dilute aqueous sodium hydroxide. Subsequent acidification of this solution with the mobile phase enabled the phthalic anhydride to be determined as phthalic acid using UV detection.

INTRODUCTION

Phthalic anhydride is a widely used organic chemical and is an important reactant in the surface coating and plasticizer industries. Its handling in the factory workplace often leads to unacceptable levels of phthalic anhydride dust in the

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breathing zone of the exposed operator. Phthalic anhydride is a sensitizer of the skin and an irritant of the respiratory tract (1). The National Health and Medical Research Council of Australia has adopted a threshold limit value of 6 mg/m^3 for an 8 hour day and a 40 hour week (2).

High performance liquid chromatography (HPLC) is recommended for the analysis of airborne phthalic anhydride by NIOSH (3). This procedure requires collection of the analyte on a cellulose membrane filter followed by desorption and hydrolysis of the phthalic anhydride with dilute aqueous ammonia. Subsequent acidification of this solution enables the analyte to be determined as phthalic acid using normal phase HPLC with UV detection.

Nelson et al (4) have suggested the use of reverse phase HPLC. Samples are collected on glass fibre filters and are desorbed with isopropanol. After allowing sufficient time for esterification the analyte is determined as the isopropyl ester using UV detection.

The procedure recommended in this paper uses a glass fibre filter to collect the airborne phthalic anhydride. Desorption and hydrolysis is carried out using dilute aqueous sodium hydroxide and subsequent acidification is followed by reverse phase HPLC with UV detection of phthalic acid. Dilute aqueous ammonia is not recommended as the desorption/hydrolysis solution due to the formation of two hydrolysis products : phthalic acid and phthalic acid monoamide (phthalamic or phthalamidic acid).

EXPERIMENTAL

Equipment

The liquid chromatograph used consisted of a Waters Model 6000A Solvent Delivery System, a Waters Model 440 UV-absorbance detector equipped with a 254 nm filter, a Waters Model U6K Universal Injector and a Waters Model 730 Data Module.

A reverse phase μ Bondapak™ C_{18} stainless steel column was used (150 x 3.9 mm I.D.) with a flow rate of 1.0 mL/min.

The filter used was a 25 mm GF/A glass fibre filter (Whatman) in a 25 mm cassette filter holder with a backing pad connected via plastic tubing to a personal sampling pump.

Chemicals

The methanol used was Waters HPLC grade and the water was glass, single distilled. All other solvents and chemicals used were of analytical grade.

Mobile Phase ; Water, methanol and glacial acetic acid (780 : 200 : 20).

0.2M sodium hydroxide ; 8.0 g of sodium hydroxide was dissolved in distilled water and made up to 1 L.

0.2M ammonia ; 14.0 mL of concentrated ammonia (15M) was diluted with distilled water and made up to 1 L.

Phthalic anhydride (BDH Chemicals) stock solution (10 mg/mL) ; 1.0000 g of phthalic anhydride was dissolved in ethyl acetate (dried over anhydrous sodium sulphate) and made up to 100 mL in a volumetric flask.

Phthalic Acid (BDH Chemicals) stock solution (11.2 mg/mL) ; 1.1217 g of phthalic acid was dissolved in methanol and made up to 100 mL in a volumetric flask.

Phthalic acid monoamide (Tokyo Kasei) ; 1.0 g of phthalic acid monoamide was dissolved in methanol and made up to 100 mL.

Preparation of standard solutions

Three working standards were prepared from the phthalic anhydride stock solution by transferring 10, 30 and 50 µL aliquots into three 10 mL volumetric flasks. A 1.0 mL aliquot of 0.2M sodium hydroxide was added to each flask and these were allowed to stand for 1 hour with occasional agitation. After hydrolysis was completed the contents were made up to volume with the mobile phase. A 20 µL aliquot was injected into the HPLC. The three standards corresponded to concentrations of 0.1, 0.3 and 0.5 mg phthalic anhydride per 10 mL of solution.

Procedure

After sampling, the glass fibre filter was placed in a 50 mL glass beaker to which was added 5.0 mL of 0.2M sodium hydroxide. The beaker was covered with a piece of Parafilm® and left to stand for 1 hour with occasional agitation. After desorption and hydrolysis was completed, a 1.0 mL aliquot of the extract was transferred into a 10 mL volumetric flask and made up to volume with the mobile phase. This solution was filtered through a Millex® - HV, 0.45 µm filter unit (Millipore) and 20 µL was injected into the HPLC system. Phthalic acid had a retention time of 5.5 min. Quantitation was performed using the external standard method.

RESULTS AND DISCUSSION

Initial work in our laboratory involved adapting the NIOSH procedure so that it could be used with a reverse phase HPLC column. However, a problem arose when it was observed that the hydrolysis of phthalic anhydride, using 0.2M aqueous ammonia followed by acidification, yielded two peaks on the chromatogram (Fig. 1). The minor peak corresponded to phthalic acid in retention time (5.5 min) and the major peak corresponded to phthalamic acid (2.8 min) (phthalic acid monoamide). The conversion of phthalic anhydride to ammonium phthalamate with aqueous ammonia has been documented in the past (5). When 0.2M aqueous sodium hydroxide was substituted for the dilute ammonia solution the chromatogram produced a single peak corresponding to phthalic acid in retention time.

Table 1 shows the results obtained when equal amounts of phthalic anhydride were hydrolyzed with either 0.2M ammonia or 0.2M sodium hydroxide solutions according to the above procedure. Conversions were calculated by comparing the peak areas of the phthalic acid formed with appropriate molar equivalent phthalic acid standards which were also put through the above procedure.

The results show that 0.2M sodium hydroxide quantitatively converts phthalic anhydride to phthalic acid.

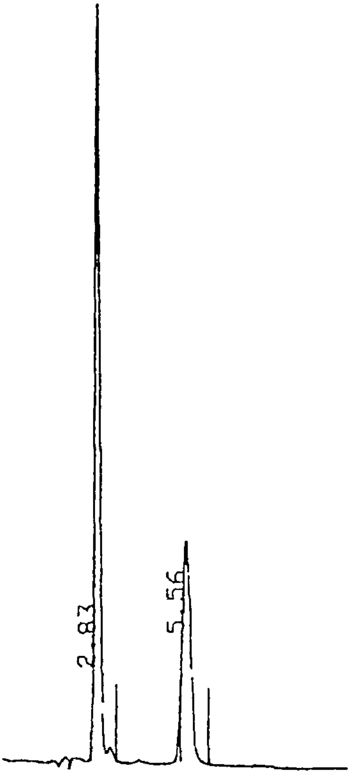

FIGURE 1. HPLC chromatogram showing phthalic acid monoamide (R_T 2.83 min) and phthalic acid (R_T 5.56 min). Desorption/ hydrolysis solution : 0.2M ammonia. Conditions : UV detection at 254 nm. Reverse phase μ Bondapak C_{18} column. Mobile Phase : water, methanol, glacial acetic acid (780 : 200 : 20). Flow rate : 1.0 mL/min. AUFS setting : 0.02. Injection volume : 20 μL.

TABLE 1

Conversion of phthalic anhydride to phthalic acid using ammonia and sodium hydroxide solutions

mg	% conversion to phthalic acid	
phthalic anhydride	0.2M NH_3	0.2M NaOH
0.1	12	95
0.3	12	95
0.5	12	97

TABLE 2

Recovery of phthalic anhydride from glass fibre filters

mg phthalic anhydride added	Recovery mean % ± RSD (n = 6)
0.5	99.9 ± 2.3
1.5	98.8 ± 2.4
2.5	95.8 ± 1.3

Glass fibre filters were investigated for recovery of phthalic anhydride. The filters were spiked at three levels, 0.5, 1.5 and 2.5 mg, with appropriate aliquots of the standard stock solution of phthalic anhydride in ethyl acetate. The filters were allowed to air-dry and were analyzed according to the above procedure. The results are shown in Table 2.

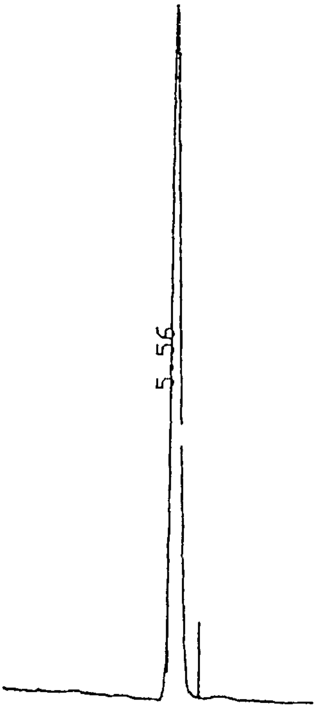

FIGURE 2. HPLC chromatogram of an air sample taken in the breathing zone of an operator in a paint factory. The phthalic acid peak represents approximately 0.5 µg of phthalic anhydride. Desorption/hydrolysis solution : 0.2M sodium hydroxide. The HPLC conditions are the same as described in Fig. 1.

The recovery figures were calculated by comparison with phthalic anhydride standard solutions.

Figure 2 shows a chromatogram of an air sample taken in the breathing zone of an operator handling bags of phthalic anhydride in a paint factory. The minimum quantifiable amount on a detector setting of 0.02 was 0.01 mg/10 mL standard solution. This corresponds to 0.05 mg on a filter sample or 0.5 mg/m^3 using a 100 L air sample. The linearity of phthalic anhydride, measured as phthalic acid, was confirmed in the range 0.1-1.0 mg/10 mL standard solution.

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