Journal of Chromatography, 368 (1986) 456–458
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 960

Note

Determination of maleic anhydride in workplace air by reversed-phase high-performance liquid chromatography

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(First received May 29th, 1986; revised manuscript received July 24th, 1986)

Maleic anhydride is a widely used chemical intermediate in the resin industry. It is also used in the manufacture of agricultural chemicals, dyes and pharmaceuticals. It is the principal raw material for the production of maleic and fumaric acids[1].

Maleic anhydride is an irritant and a sensitizer of the skin and respiratory tract. It is a severe irritant of the eyes[2]. The National Health and Medical Research Council of Australia has adopted a threshold limit value of 1 mg/m^3 for an 8-h day and a 40-h week exposure–time weighted average[3].

The current NIOSH high-performance liquid chromatography (HPLC) procedure[4] for analyzing airborne maleic anhydride is under review[5]. The method involves drawing an air samle through an impinger containing distilled water which hydrolyzes the maleic anhydride to maleic acid. An ion-pair chromatographic system (methanol, water, dicyclohexylamine and formic acid) with a reversed-phase column and UV detection is used to chromatograph the maleic acid.

The procedure described here also use reversed-phase HPLC but with a simpler mobile phase, 0.1% phosphoric acid in distilled water. This mobile phase is also used as the absorbing solution to collect the airborne maleic anhydride.

EXPERIMENTAL

Equipment

The Waters liquid chromatograph consisted of a Model 6000A solvent delivery system, a Model 440 UV absorbance detector equipped with a 254 nm filter, a Model U6K universal injector, and a Model 730 data module. A reversed-phase Nova-Pak^{TM}, 5 μm, C_{18} stainless-steel column was used (150 × 3.9 mm I.D.) and the flow-rate was 0.7 ml/min. The sampling equipment used was a midget impinger with 5-ml graduation marks, connected via plastic tubing to a personal sampling pump adjusted to a flow-rate of 1 l/min.

Chemicals

The mobile phase consisted of 0.1% orthophosphoric acid (93%, w/w, analytical reagent grade, May and Baker, Australia) in distilled water, pH 2.2.

The maleic anhydride standard solution (100 mg/l) was prepared by accurately weighing 100 mg of maleic anhydride (99.0%; Ajax Chemicals, Sydney, Australia)

0021-9673/86/$03.50

and dissolving it in a small volume of mobile phase. The solution was made up to 1 l with the mobile phase.

For preparation of the maleic acid solution 118.4 mg of maleic acid (99.0%; Ajax Chemicals) were accurately weighed and dissolved in a small volume of mobile phase. The solution was made up to 1 l with the mobile phase.

Preparation of working standard solutions

Three working standards were prepared from the maleic anhydride standard solution by transferring 0.5-, 1.0- and 2.0-ml aliquots into three 25-ml glass-stoppered test tubes. The standards were made up to 15 ml by adding 14.5, 14.0 and 13.0 ml of mobile phase, respectively. After mixing a 25-μl aliquot was injected into the chromatograph. The three standards corresponded to 0.05, 0.10 and 0.20 mg of maleic anhydride per 15 ml of solution, respectively.

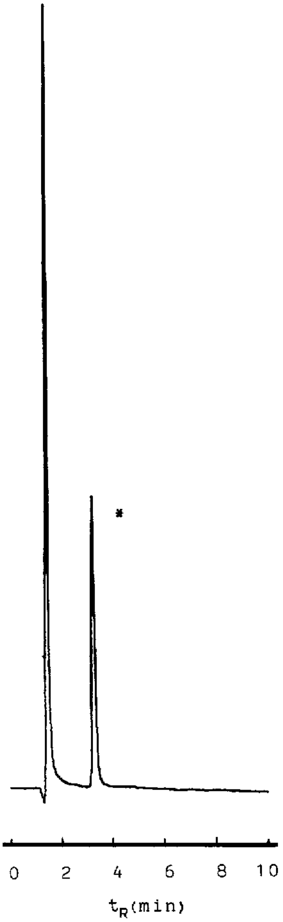

Fig. 1. HPLC chromatogram of an air sample taken while an operator in a paint factory was adding maleic anhydride to a polyester resin kettle. The maleic acid peak (*, t_R 3.2 min) represents approximately 0.08 mg of maleic anhydride. Conditions: UV detection at 254 nm at 0.02 a.u.f.s.; reversed-phase Nova-Pak, 5 μm, C_{18} column; mobile phase, 0.1% phosphoric acid in distilled water; flow-rate, 0.7 ml/min; injection volume, 25 μl.

Sample analysis

After sampling the absorbing solution was inspected for any possible evaporation and was appropriately made back up to 15 ml with distilled water if necessary. A 25-μl aliquot was injected into the chromatograph.

RESULTS AND DISCUSSION

The use of aqueous 0.1% phosphoric acid as the mobile phase (pH 2.2) has suppressed the ionization of maleic acid (pK_{a_1} 1.9, pK_{a_2} 6.2) sufficiently for the carboxylic acid to have adequate retention on the reversed-phase column. At a flow-rate of 0.7 ml/min maleic acid had a retention time of 3.2 min and was baseline separated from its structural isomer, fumaric acid, which had a retention time of 4.7 min. An approximate run time for the analysis was 5 min compared with over 8 min for the current NIOSH HPLC procedure[4].

The conversion of maleic anhydride to maleic acid in aqueous 0.1% phosphoric acid was checked and was found to be quantitative at the 0.05-, 0.10- and 0.20-mg levels. Conversions were calculated by comparing peak areas of the maleic acid formed with appropriate molar equivalent maleic acid standards which were prepared from the maleic acid solution (118.4 mg/l). The relative standard deviation for injection of the 0.05, 0.10 and 0.20 mg/15 ml maleic anhydride standards was found to be 3.3, 1.5 and 1.9%, respectively.

Fig. 1 shows a chromatogram of an air sample taken while an operator in a paint factory was adding maleic anhydride to a polyester resin kettle.

The minimum quantifiable amount with a detector setting of 0.02 a.u.f.s. was 0.01 mg/15 ml absorbing solution or 0.1 mg/m^3 using a 100-l air sample. The linearity of the detector response for maleic anhydride, measured as maleic acid, was confirmed in the range 0.05–0.20 mg/15 ml standard solution.

ACKNOWLEDGEMENTS

We would like to thank the Director of the Division of Occupational Health, Dr. B. M. Nolan, and the Coordinator of Occupational Health, Safety and Rehabilitation of the N.S.W. Dept. of Industrial Relations, Dr. H. Gwynne, for permission to publish this paper. The authors would also like to thank Roy Day and Dr. Jeff Kibby of Millipore Waters Associates Division for helpful suggestions made during the course of this work.

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