

Determination of maleic anhydride in occupational atmospheres

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Abstract

Maleic anhydride has many uses in industry, but workers' exposure to it is poorly known. Our new method allows airborne maleic anhydride to be determined with a limit of quantification of $1 \mu\text{g}/\text{m}^3$ per 12 l of air, i.e., the concentration of about 0.01 times the occupational exposure standard ($0.4 \text{ mg}/\text{m}^3$). Air samples are collected in Tenax tubes containing sodium sulfate as a drying agent. Maleic anhydride is eluted with methyl *tert*-butyl ether containing 5% acetonitrile and 0.1% acetic anhydride, and determined by capillary gas chromatography with electron-capture detection without interference from generic anhydrides. The tested method suits both long-term and short-term measurements.

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1. Introduction

Maleic anhydride (MA, furandione [108-31-6]) has many uses in industry [1,2], but the exposure of workers to this irritating and allergenic substance is poorly known [3]. In 1998 [4], $150 \cdot 10^6$ kg of MA were produced in Europe. About 50% of the production [1,2] is used for unsaturated polyester resins. In addition to ready esterification, the reactive double bond gives MA other important properties for industrial use.

The current methods for the determination of MA in the air are based on high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection. Midget-impingers [5,6] and *p*-anisidine-treated Amberlite XAD-2 tubes [7] are used for air

sampling. In the NIOSH method [5] and the Geyer and Saunders method [6], MA is hydrolysed to maleic acid (MAc). Because UV detection has low sensitivity for MAc, the methods require large volumes of air to be sampled to obtain sufficient concentrations of MA for the determinations. The two methods are, therefore, suitable only for relatively long-term sampling, hardly enabling short-term concentrations to be measured. Sampling based on liquid absorption also presents practical difficulties when personal samples are required. The detection limit of the OSHA method [7] is lower, and the *p*-anisidine derivative of MA is claimed to be specific, but we could not find any data on applications of this method.

Our present method has sufficient sensitivity not only for long-term determinations but also for moderately short-term sampling. The method is specific to MA and unaffected by generic anhydrides. The sampling device is small and easy to wear as a

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personal sampler, and it can also be used for stationary area sampling. As applications, the results of the measurements in two industrial workplaces are presented.

2. Experimental

2.1. Apparatus

The determination of MA was carried out by a HP 5890A series gas chromatography–electron-capture detection (GC–ECD) system (Hewlett-Packard, Palo Alto, CA, USA). The apparatus was equipped with a splitless injection mode, a fused-silica capillary column (HP-5, 30 m×0.32 mm I.D., phase thickness 0.25 μm) and a Hewlett-Packard auto-sampler with a 10 μl Hamilton syringe. The injected sample volume was 1 μl . The carrier flow in the column was 1.5 ml/min and the flow of the detector gas was 50 ml/min. The column temperature program was as follows: 7 min at 50 °C, then 2 °C/min to 70 °C and 25 °C/min to 250 °C. The injector was maintained at 230 °C and the detector at 320 °C. An SC-Chromatography Workstation Version 4.12.00 NT Data System (Sunicom, Espoo, Finland) was used for peak integration.

MA in field samples was verified by mass spectrometry (MS, Micromass, Quatro II, Manchester, UK; electron impact, EI, at 70 eV, connected to a HP 6890 Series II gas chromatograph with a HP5MS capillary column from Hewlett-Packard). The GC conditions were as described above.

To test the accuracy of the new GC–ECD method, MA solutions were also measured with a high-performance liquid chromatography (HPLC) method [6]. The apparatus was a Varian 5000 liquid chromatograph (Varian, Walnut Creek, CA, USA) equipped with a UV–Vis detector (at 254 nm, Model SPD-6AV, Shimadzu, Kyoto, Japan). The chromatographic data was processed by Dionex Peak Net Software, Version 4.3 (Dionex, Sunnyvale, CA, USA). A reversed-phase stainless steel C₁₈ column (150×4.6 mm, phase 5 μm , from Supelco, Bellefonte, PA, USA) was used for operation at room temperature. The injection loop was 20 μl .

An SKC “Personal air sampler” (SKC Model

222-3) obtained from SKC, Eighty Four, PA, USA was used for the collection of air samples.

2.2. Chemicals

MA as briquettes, 99%, (obtained from Aldrich, Steinheim, Germany) was resublimed for calibration standards. Tenax polymer tubes (No. 226-35, 35/15 mg) for sampling were obtained from SKC. Anhydrous sodium sulfate (Na₂SO₄) for drying purposes was from Merck (Darmstadt, Germany, min. 99%, pH 5.2–8.0). A filter holder with a PTFE filter (type FALP 01300, diameter 1 cm, pore 1 μm , Millipore, Watford, UK) was used for plausible particle collection. The eluent was a solvent mixture composed of methyl *tert.*-butyl ether (MTBE, HPLC grade, Rathburn, Walkerburn, UK), 5% acetonitrile (ACN, far UV grade, 99.9%, LabScan Analytical Sciences, Dublin, Ireland) and 0.1% acetic anhydride (AA, 99%; Sigma–Aldrich, Steinheim, Germany). This solvent mixture was allowed to equilibrate at room temperature for 2 days before use. Silica gel (redried at 200 °C) for drying pouches was from Merck. Gases for the GC–ECD determinations were helium as a carrier gas (99.996%, Messer Griesshem, Düsseldorf, Germany) and argon as an additive gas for the detector (99.998%, Aga, Espoo, Finland), with 5% methane (99.95% Aga).

The mobile phase for HPLC was 0.1% orthophosphoric acid (92%, w/w, analytical grade, Merck) in distilled water (pH 2). For HPLC standards, MA was diluted in the mobile phase and allowed to equilibrate overnight.

2.3. Sampling device and sampling

Air samples for the MA assay were collected in sampling sets composed of a PTFE filter and a Tenax polymer tube. The front capillary end of the Tenax tube was broken and 100 mg of anhydrous Na₂SO₄ was placed in the tube in front of the sampling layer. A small tuft of glass wool was inserted into the tube to keep the drying salt in place. Both Na₂SO₄ and glass wool were first moistened with equilibrated elution solvent (see above) and then allowed to evaporate at 50 °C. The tube was closed with a polyethylene cap and stored in a tightly covered

plastic case of polyethylene. The inside of the case was kept dry with two small polyester pouches containing 2 g of dried silica gel. Before field sampling, a filter holder with a PTFE filter was assembled in front of the Tenax tube. The sampling was maintained by an SKC “Personal air sampler”. The pump-related variation in the flow-rate was measured with the sampling set mounted on, and it averaged $\pm 5\%$. The flow-rates were 0.05 or 0.2 l/min. The sampling periods ranged from 15-min to 8-h shifts and the volumes were from 3 to 24 l (12 l for 4 h). After sampling, the devices were stored in the covered plastic case (with drying pouches) at $-20\text{ }^{\circ}\text{C}$ until assayed. Two unused capped sampling tubes were kept in the same case and checked as blanks.

To test the stability of MA in the sampling medium, and the recovery from the sampling tubes, different amounts of MA (0.05 to 5.0 μg , $n=12$) in the eluate were applied to the glass wool in the Tenax tubes. Laboratory air [12 l, relative humidity (RH) 25–60%; 28 $^{\circ}\text{C}$] was drawn through the spiked tubes.

2.4. Analysis

After sampling to desorb the collected MA from Tenax, the contents of the sampling tubes (front and back up sections separately) were emptied into test tubes containing 1 ml of the eluent. Calibration with external standards was by a phase balance method with Tenax added to standard solutions (Tenax standard, Tsdt). The contents of the Tenax tubes of the same batch and the same amount as used for the samples were added to 1 ml of the liquid standard solutions (Liquid standard, Lsdt). Both the samples and the standards were allowed to stabilise overnight at 6 $^{\circ}\text{C}$ before GC–ECD. The filters were assayed in the same way. Samples with high concentration were determined by desorbing them in 2 to 5 ml of the eluent. This may be necessary when determining short-term exposures during processes such as batch charging in polyester synthesis (Table 1). MA in field samples was verified by GC–MS. For accuracy determination of the GC–ECD assay, the MA standards were also determined by the HPLC method [6].

Table 1
Maleic anhydride concentration in the air during synthesis of polyester resin

Points of time and place	<i>n</i>	Sampling time (min)	Sample volume (l)	Concentration (mg/m^3)
Autumn 1995 ^a				
Charging	1	44	1.89	10.3
Charging	1	44	1.98	23.5
Area ^b	1	44	2.07	8.1
Autumn 2000 ^c				
Charging	1	145	9	1.2
Charging	1	45	9	1.2
Area ^b	1	45	9	1.3

n=Number of samples.

^a Charging glycol and solid anhydrides from large sacks to an open reactor.

^b Stationary sampling point about 5 m from the reactor in the general space to move.

^c After process renovation.

3. Results and discussion

3.1. Sampling

The sampling material, Tenax polymer (2,6-diphenyl-*p*-phenylene oxide), is not supposed to absorb water [8]. It is, however, polar [9] and may condense some moisture, as also the polar glass wall of the tube and the glass wool that is a stopper for the adsorbent. MA hydrolyses in direct contact with water (half-life 0.35 min) [10,11], although it is found to be stable in the vapour phase even at very high air humidity [11]. The recovery of MA from the spiked tubes with the drying agent was $94.4\pm 6.3\%$ (relative standard deviation, RSD, $n=12$), but it was only $66.3\pm 7.1\%$ ($n=8$) without drying.

According to Brown and Purnell [12], the retention volume of MA per 1 g of Tenax GC was up to 440 l. This volume equals 22 l of air drawn through the commercial tubes containing 50 mg of Tenax. Our result of the sampling volume with spiked samples corresponded well with this value (or even better). For the field samples, it was possible to extend the sampling period to 8 h (24 l) when the MA concentration was assumed to be comparatively low, and no other significant impurities (e.g., other anhydrides) were expected to appear in the air (Table 2). In the sampling sets of the field samples (24.4 l, $n=4$), the total amount of MA retained was divided

Table 2
Maleic anhydride concentrations in the air during polymerising thermoplastics

Point of time	Number	Sampling mean (h)	Sample volume mean \pm SD (l)	Concentration in the air, $\mu\text{g}/\text{m}^3$		Range, $\mu\text{g}/\text{m}^3$
				Mean \pm SD	Gmean; GSD	
Winter 1992	7+1 ^a	6.9	20.7 \pm 3.8	219.5 \pm 156.9	128; 4.0	5.8–470.7
Winter 1993	8	10.6	31.8 \pm 3.5	44.0 \pm 49.0	19.7; 4.0	2.0–129.3
Spring 1994	7	7.0	21.0 \pm 2.8	5.4 \pm 1.5	5.2; 1.4	3.0–7.6
Autumn 1996	5	4.2	12.8 \pm 1.5	17.3 \pm 8.5	20.2; 1.2	<2.6–25.5
Spring 1997	8	7.2	21.6 \pm 0.1	5.1 \pm 6.3	3.2; 2.3	<1.8–21.3
Spring 2002	6	6.6	19.7 \pm 6.6	5.8 \pm 8.3	3.4; 9.5	<0.4–24.0

Mean=Arithmetic mean, Gmean=geometric mean, SD and GSD=arithmetic and geometric standard deviations.

^a Result of one occasional short-term measurement (898 $\mu\text{g}/\text{m}^3/0.9$ l, 18 min) is not included in the mean.

as follows: 1.2% ($\pm 0.5\%$ RSD) on the filter, 92.3% ($\pm 8.1\%$) in the front section and 6.6% ($\pm 8.1\%$) in the back-up section of the Tenax tube. Because the work circumstances may, however, be variable, the sampling volume of up to 12 l collected during 4 h was recommended.

Excepting a too large retention volume, the saturation of the tube capacity at high MA concentrations might cause breakthrough from the tube. For instance, when 47 μg of MA was retained in a set of two sampling tubes connected in series (2 l; 44 min; 24 mg/m^3), 94% of the total amount retained was found in the first tube and 6.0% in the front section of the second tube. Nothing was detectable in the backup section of the second tube. Thus, this 6.0% value may indicate the saturation of the first tube capacity and start of breakthrough.

3.2. Analysis

Because MA hydrolyses, the eluent for desorption of sampling tubes and preparation of the calibration standards had to be non-aqueous. AA served as a drying agent and also ensured optimal acidic (<pH 5.5) conditions for the MA stability against the slightly basic glass wool, Na_2SO_4 and plausible basic impurities collected from air. The highly polar ACN accomplished a good desorption of the polar MA from the sampling tube and prevented a “memory effect” in GC.

MA was stable in the dry eluent. The storing of the standards without Tenax at 6 °C showed no loss of MA during 2 weeks. In the calibration standards

with Tenax (Tstd) and the sample eluates, the mean loss of MA was 2.7% during 2 weeks.

Desorption of MA from Tenax caused a loss of 15.1% (RSD 5.9%, $n=12$) in comparison with Lstds. To remove this loss, the samples were compared with Tstds by the phase-balance calibration method.

In chromatography, the retention time of the underivatised MA was 7.3 min (Fig. 1). Generic anhydrides did not interfere with MA determination.

The least-squares regression of the GC–ECD assay [13] gave the following results when compared the integrated area counts on the y -axis with the weighed standards (ng/ml, volumetric dilutions) on the x -axis. This regression line was linear ($r=0.9999$) for the samples in the practical concentration range of 0.010 to 5 $\mu\text{g}/\text{ml}$ of MA in the eluates that corresponded to 0.001 to 0.4 mg/m^3 of MA in 12 l of air samples. The slope (b) of this line was 380 ± 1.4 SD (standard deviation, $n=6$) or ± 4.0 at the 95% confidence limits (CLs) and the intercept (a) 275 ± 135 SD or ± 375 at the 95% CLs. The random error (SD of the blank) was ± 222 on the y -axis direction calculated from the $\pm y$ -residuals of the fitted individual y -points on the regression line. The limit of quantification (LOQ), corresponding to 10 times this SD of the blank divided by the slope value, was 6 ng/ml in the eluate. That corresponded to 1 $\mu\text{g}/\text{m}^3$ in an air sample of 12 l and 2 $\mu\text{g}/\text{m}^3$ in an air sample of 3 l. The SD of individual samples in the eluate was ± 2 ng/ml.

According to GC–MS, the identity of MA was confirmed in field samples with the molecular ion at m/z 98 and an abundant fragment ion at m/z 54 that corresponded to the loss of CO_2 from the molecule.

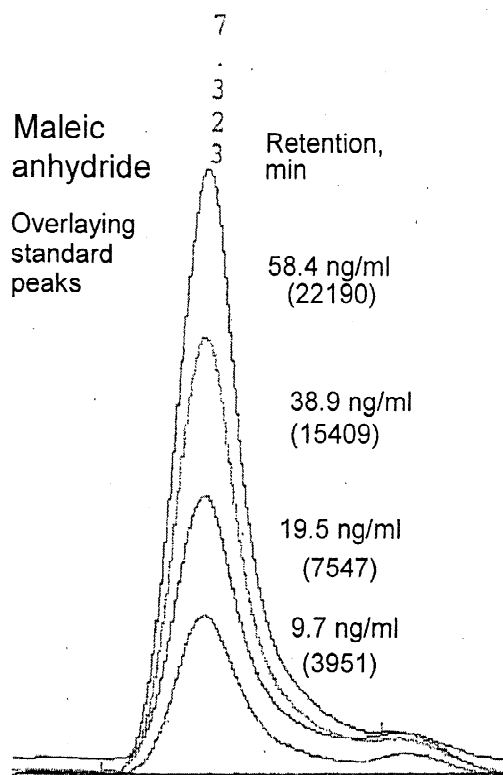


Fig. 1. Four overlaying GC peaks for Tenax phase balance standards, Tsd, of MA (1 μ l injection). The counts of the integrated peak areas are in parentheses.

Additional verification was carried out with calibration standards prepared from the commercial chemical.

The LOQ (1 μ g/m³ in 12 l of air) of the present GC–ECD method was lower than that of the HPLC method [6], which in our assay corresponded to 188 μ g/m³ in 100 l of air. Thus, the data points of the methods did not cover the concentration range of the interest even in a roughly uniform fashion. The accurate bias of the new method could not, therefore, be determined because of the lack of suitable methods for comparison.

The worst combined precision of the assay could, however, be considered to be less than 9.4%, including the precision related to the air pumping (5%), sampling and recovery from Tenax tube (6.3%), GC procedure (2%), storage (<2.7%), and sample handling in laboratory (3.5%, including distribution be-

tween two persons). The repeatability of the measurements at the thermoplastics process (Table 2) proved also good precision (± 3.0 standard error, SE) when calculated from the results of the four last occasions of the measurements.

3.3. Measurements at two industrial plants

In a plant that synthesised polyester resins, the MA concentrations were measured during batch charging for the polyester synthesis (Table 1). The highest measured concentration during 44 min was 23.5 mg/m³. Such a high exposure usually occurred only once a day when big sacks of solid anhydrides (maleic and phthalic) were emptied into the reactor kettle. After renovations, the concentration decreased to an overall mean of 1.2 mg/m³ ($n=3$), but it was still higher than the occupational exposure standard (OES) for momentary exposure to MA, 0.8 mg/m³ (0.2 ppm) [14].

In another plant for polymerisation of thermoplastics, the MA (an additive) concentrations in the workplace air were monitored six times (Table 2). The concentrations were at first mean 0.220 ± 157 mg/m³ (SD, $n=7$), which was around the level of a half of the OES value for 8 h work (0.4 mg/m³) [15]. The geometric mean (GM), geometric standard deviation (GSD) and the large concentration range may have indicated subtle leaks in the process. Then the circumstances stabilised, and the mean concentrations decreased, being repeatedly close to the detection limit of the method.

4. Conclusion

The present method describes the determination of maleic anhydride in the air. Gas chromatography with electron-capture detection is specific to maleic anhydride and unaffected by generic anhydrides. The concentration range of the determination covers the requirements of the exposure levels around the OES for MA (0.4 mg/m³ [15]), but allows also the determination of low concentrations at a few micrograms per cubic meter in the air. The method enabled measurements in long-term average exposures, but also in short-term exposures. The modified polymer tube is light and easy to wear device as a

personal sampler, it is also suitable for static area sampling.

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