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Determination of hexahydrophthalic anhydride in air using gas chromatography

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ABSTRACT

Two methods for the determination of hexahydrophthalic anhydride (HHPA) in air were developed. In a solid sorbent method, HHPA was sampled in Amberlite XAD-2 tubes, eluted in toluene and analysed by gas chromatography with flame ionization detection. The sampling rates were 0.2 and 1.0 l/min. At 15 $\mu\text{g}/\text{m}^3$ (relative humidity <2%) and 27 $\mu\text{g}/\text{m}^3$ (relative humidity 70%) no breakthrough was observed. However, at 160 $\mu\text{g}/\text{m}^3$ (relative humidity <2%), 6% breakthrough was found. The sampling efficiency of the sampling rates 0.2 and 1.0 l/min did not differ. In a bubbler method, HHPA was sampled in bubblers filled with 0.1 M sodium hydroxide solution. The sodium salt of hexahydrophthalic acid was formed. No breakthrough was observed using a sampling rate of 1.0 l/min. The samples were stable during storage for eight weeks in a refrigerator. The HHP acid was esterified with methanol–boron trifluoride and analysed by gas chromatography–flame ionization detection. Apparatus for the generation of standard atmospheres of HHPA, in the range of 10–3000 $\mu\text{g}/\text{m}^3$, was developed using the diffusion principle. For the solid sorbent method the precision (coefficient of variation) of the overall method was 2–7%, and for the bubbler method 3–19% (range 15–160 μg HHPA/ m^3 ; relative humidity = <2–70%). A comparison between the two methods was performed using the standard atmosphere. The concentrations found by the solid sorbent method were 86–98% of those found by the bubbler method (range 15–160 μg HHPA per m^3 ; relative humidity = <2–70%). In work environment air, 93% was found using the solid sorbent method relative to the bubbler method at a mean concentration of 330 $\mu\text{g}/\text{m}^3$ (coefficient of variation = 39%; range 200–540 $\mu\text{g}/\text{m}^3$). For both methods, concentrations > 3 $\mu\text{g}/\text{m}^3$ could be quantified at 60 min sampling with a sampling rate of 1.0 l/min.

INTRODUCTION

Hexahydrophthalic anhydride (HHPA), the saturated analogue of phthalic anhydride (PA), is used as a hardener in epoxy resins. HHPA epoxy resins have good mechanical and electrical insulation properties. Typical products made from HHPA epoxy resins are electrical capacitors and ignition systems.

It has been known for a long time that organic acid anhydrides are irritant to the eyes and to the mucous membranes in the respiratory tract [1]. HHPA has also like several other dicarboxylic anhydrides, been demonstrated to induce allergic rhinitis and asthma [2]. Studies on the chemically related methyltetrahydrophthalic anhydride [3,4] indicate that HHPA may be a sensitizing agent at low concentrations in air.

Organic anhydrides are reactive compounds. Free acids are formed by hydrolysis. The reaction with alcohols and primary and secondary amines results in the formation of esters and amides, respectively. Water is expected to be present in all work environment air. Alcohols and primary and secondary amines may also be present. The reactivity is expected to be strongly influenced by the presence of catalysts such as tertiary amines, which are also expected in the work environment. The toxicity of hexahydrophthalic acid (HHP acid) can be assumed to be low.

Some methods for the determination of acid anhydrides in air have been described in the literature. Most of them describe filter sampling methods of PA [5,6] and trimellitic anhydride [7–9]. The analyses are performed by gas chromatography (GC) or high-performance liquid chromatography (HPLC). PA has been sampled with Tenax as sorbent and analysed by GC with electron-capture detection [10]. Maleic anhydride has been sampled on XAD-2 Amberlite sorbent tubes treated with *p*-anisidine and analysed by HPLC [11].

Methyltetrahydrophthalic anhydride (MTHPA) has been sampled by two different methods [12]. In the first method, MTHPA was collected on XAD-2 tubes and the anhydride was analysed by GC with flame ionization detection (FID). In the second method, the anhydride was sampled in sodium hydroxide by bubblers and the corresponding acid was analysed by GC-FID, after derivatization with methanol-boron trifluoride.

The serious effects of HHPA generate a requirement for good methods of controlling the work environment. However, to our knowledge no methods of monitoring HHPA in air have been described in the literature. Moller *et al.* [2] reported that they have measured the concentration of HHPA in air by an impinger method from US National Institute of Occupational Safety and Health, but this method was not described. Pfäffli *et al.* [13] have monitored HHPA in air by a method used for the determination of PA.

In the present study two methods for the determination of HHPA in air are described and evaluated.

EXPERIMENTAL

Apparatus

For analysis of standard atmosphere samples, a Varian 3500 GC system (Varian, Palo Alto, CA, USA) equipped with a Varian FID system (time constant 50 ms), a Varian 8035 automatic on-column auto-sampler and a temperature-programmable capillary injector was used. The chromatograms obtained were evaluated with a Shimadzu C-R3A integrator (Shimadzu, Kyoto, Japan).

For analysis of work environment samples, a Carlo Erba GC system, Fractovap, Series 4160 (Carlo Erba, Milan, Italy), equipped with an FID system and on-column injector was used. The chromatograms were recorded on a BBS Goerz, Servogor 310 linear recorder.

For identification of hexahydrophthalic acid dimethylester (HHP acid-DME) a Shimadzu GC-MS QP1000 EI/CI quadropole mass spectrometer connected to a Shimadzu GC 9A GC system was used.

Sampling rates were maintained by portable pumps: GilAir (1.0 l/min; Gilian Instrument, Wayne, NJ, USA) and MSA Model C-210 (0.2 l/min; Mine Safety Applications, Pittsburgh, PA, USA).

Relative humidity (RH) was measured by hygrometer from Solomat (MPM 2000/2013 Thermo Hygro Anemo Tachometer; Solomat, Rowayton, USA). Phase separations were achieved with a Sigma 3E-1 centrifuge (Sigma, Harz, Germany).

Sample tubes and bubblers

For sampling in the solid sorbent method, Amberlite XAD-2 tubes (cat. No. 226-30, SKC, Eighth Four, PA, USA), and for sampling in the bubbler method 5-ml bubblers equipped with sintered glass filters (cat. No. L.9-751-1, Labglas Service, Stockholm, Sweden), were used.

Columns

Fused-silica capillary columns with chemically bonded stationary phases were used: for standard atmosphere sampling, CP-sil 8 CB (Chrompack, Middelburg, Netherlands) 25 m × 0.25 mm I.D. with a film thickness of 0.25 μm and, for work environment sampling, DB-5 (J & W Scientific, Folsom, CA, USA) 30 m × 0.32 mm I.D. with a film thickness of 1.0 μm.

Chemicals

Ethylacetate, methanol and toluene were from LabScan (Dublin, Ireland). Boron trifluoride, 14% in methanol, was from Sigma (St. Louis, MO, USA). HHPA (>98%), sodium bicarbonate, sulphuric acid, sodium hydroxide and sodium sulphate were from Merck (Darmstadt, Germany). HHP acid-DME was from SyntElec (Lund, Sweden).

Generation of standard atmosphere

HHPA in air was generated by the dynamic generation equipment shown in Fig. 1. Into a 250-ml vessel, placed in a water bath, two 4-ml test tubes containing HHPA were inserted. A stream of HHPA vapour was generated by blowing 2 l/min dried air into the vessel. The outlet was connected to a mixing chamber where the HHPA atmosphere was further diluted with air with a controlled RH. The humid air was generated by mixing dry air with air bubbled through deionized water. The outlet from the mixing chamber was connected to an all-glas 15-l cylinder which then contained the controlled atmosphere of HHPA. The RH was measured by a hygrometer. The cylinder had two outlets for simultaneous sampling. Excess air was removed through a third outlet. All connection tubes were made of PFTE (3.5–7 mm I.D.). All other equipment was glass.

Concentrations in the range 10–3000 μg/m³ (monitored by the solid sorbent method) were generated by the equipment. The different concentrations were obtained by varying the temperature in the water bath between 35 and 90°C and the flow of dilution air between 0 and 30 l/min. Relative humidity between <2 and 90% could be generated.

Work environment atmosphere

Air samples of HHPA were collected in a plant manufacturing electrical capacitors. Except for HHPA, the plant handled MTHPA, benzyldimethylamine, epoxy resins (epichlorhydrin and bisphenol A/aniline). The RH was 16–44%.

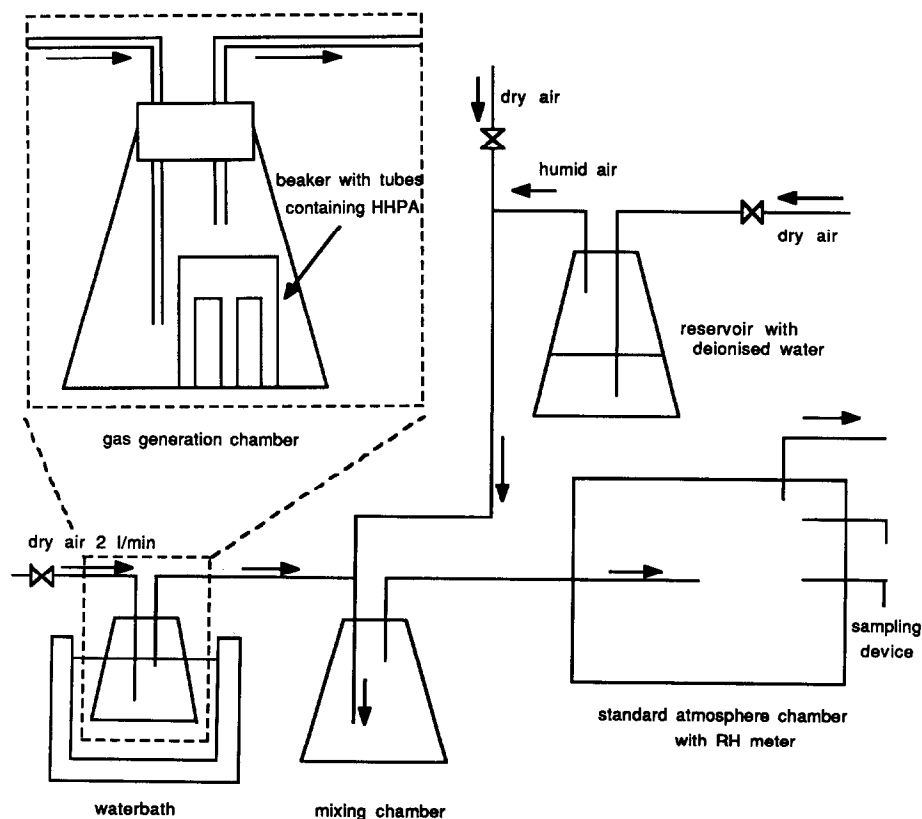


Fig. 1. Equipment for the generation of vaporous HHPA in air.

Procedure in the solid sorbent method

Sampling of HHPA was performed with XAD-2 tubes with one sampling layer and one control layer. The sampling rate was 0.2 l/min or 1.0 l/min.

After sampling, the XAD-2 tubes were sealed with plastic plugs and put into a sealed plastic vessel with a layer of dry silica gel on the bottom. The tubes were stored at -20°C .

Each XAD-2 layer was eluted in 1.0 ml of toluene for 8 min. Thereafter, the toluene was transferred into glass tubes with PFTE screw caps. The solution was analysed immediately after elution.

Procedure in the bubbler method

HHPA was sampled with midjet bubblers containing 5 ml of 0.1 M sodium hydroxide absorption solution in which HHP acid was formed. The sampling rate was 1.0 l/min.

After sampling, the bubblers were filled with 0.1 M sodium hydroxide to the original volume. All solutions were quantitatively transferred into glass tubes with PFTE screw caps and stored at 4°C .

The absorption solutions were acidified with 0.5 ml of 5 *M* sulphuric acid and extracted with 25 ml (15 ml + 10 ml) of ethylacetate. The ethylacetate was dried overnight with anhydrous sodium sulphate and evaporated to dryness in a stream of dry nitrogen. After evaporation, the residue was dissolved in 1.2 ml of methanol to which 2.0 ml of 14% boron trifluoride in methanol was added. Esterification was performed overnight in glass tubes with PTFE screw caps at 70°C. When the tubes had cooled, 4 ml of saturated sodium bicarbonate was added and the mixtures were extracted with 2 ml of toluene. After centrifugation, the toluene solutions were transferred to glass tubes and dried over anhydrous sodium sulphate. The samples were kept at -20°C until analysis.

Preparations of standard solutions

Standard solutions of HHPA were prepared by dissolving 100 mg of HHPA in 25 ml of toluene. This solution was then further diluted in toluene to appropriate concentrations.

Standard solutions of HHP acid-DME were prepared by reacting 100 mg of HHPA with 25 ml of aqueous 0.1 *M* sodium hydroxide. The HHP acid was then further diluted in the aqueous sodium hydroxide to appropriate concentrations. The standard solutions were worked up and analysed together with the samples as described above.

To determine the recovery of the work-up procedure of HHP acid-DME, standard solutions of HHP acid-DME were prepared in toluene. A 100-mg aliquot of HHP acid-DME was dissolved in 25 ml of toluene. The solution was then further diluted in toluene to appropriate concentrations.

Analysis

On the Varian equipment, 1.0 μ l of the toluene solutions was injected at a rate of 5 μ l/s into the column. The injector starting temperature was 100°C for 0.2 min, and thereafter the temperature was increased by 50°C/min to a final temperature of 160°C, where it was maintained for 8 min.

The column initial temperature was 100°C for 1 min. Thereafter the temperature was increased by 8°C/min until a final temperature of 135°C, which was maintained for 2 min. When analysing HHP acid-DME, an additional column programming step was added with an increase of the temperature of 40°C/min to a final temperature of 250°C, which was maintained for 2 min.

The detector temperature was 260°C, and the supply of hydrogen and air for the detector was 2 and 280 ml/min, respectively. As make-up gas, helium at a flow-rate of 40 ml/min was used. The gas flow of helium through the column was 2.0 ml/min.

On the Carlo Erba equipment, 1.0 μ l of the toluene solution was injected using the cold on-column technique. The column initial temperature was 122°C for 1 min and thereafter the temperature was increased by 10°C/min to the final temperature of 230°C, where it was maintained for 5 min.

The temperature of the detector was 260°C, the supply of hydrogen 12 ml/min and of air 280 ml/min. The flow of helium through the column was 3.0 ml/min.

RESULTS AND DISCUSSION

Standards

The identity of HHP acid-DME was confirmed by GC-mass spectrometry [14]. The purity of HHP acid-DME was checked using GC-FID and found to be *ca.* 97%.

Sampling considerations

Sampling using bubbler has been used for the determination of other anhydrides. The absorbing liquid used was an aqueous solution of sodium hydroxide. In the case of HHPA, the free sodium HHP acid is formed. Sodium HHP acid is expected to be stable in the sampling solution. The relatively fast hydrolysis of HHPA in the bubbler solution minimizes the possible interfering reactions by other co-occurring compounds present. However, a method based on the sampling in alkaline aqueous solutions can not separate HHPA and HHP acid in air. The amounts of HHPA and HHP acid are determined by the subsequent analysis.

Sampling of organic acid anhydrides has also been performed with sorbent tubes containing solid sorbents. With this procedure, the determination of anhydrides is feasible without interference from the possible presence of HHP acid. However, sample losses cannot be disregarded, as HHPA may react with other compounds also present in the sample. HHPA is sampled in a reactive form which may cause sample losses during storage. The subsequent determination ought therefore to be performed reasonably soon after sampling. The method is favoured by the simplicity of sampling, analysis and evaluation of the results.

Procedure in the solid sorbent method

Sampling efficiency. The sampling efficiency for different concentrations of HHPA and different RH in the air was determined by the analysis of the control layer. The results are summarized in Table I. Neither the concentration nor the RH seems seriously to affect the sampling efficiency. The sampling efficiency of the sampling rates 0.2 and 1.0 l/min was investigated. Seven parallel samplings with the different sampling rates were performed. The sampling time was 95 min and RH was < 2%. The estimated concentrations found by the different sampling rates were equal ($18 \mu\text{g}/\text{m}^3$) within the experimental errors.

TABLE I

SAMPLING EFFICIENCY OF THE SOLID SORBENT METHOD FOR DIFFERENT CONCENTRATIONS OF HHPA AND RELATIVE HUMIDITY IN AIR

The sampling rate was 1.0 l/min.

Concentration of HHPA in air ($\mu\text{g}/\text{m}^3$)	Relative humidity (%)	Sampling volumes (l)	Sampling efficiency ^a (%)	Number of determinations
15	<2	63	>80	7
27	70	59	>90	7
160	<2	51	94	7

^a Percentage of HHPA in the sampling layer compared with the totally sampled amount.

Recovery. The recovery of HHPA sampled on solid sorbent tubes was initially investigated by the application of 30 μl of a toluene solution containing 0.44 $\mu\text{g}/\mu\text{l}$ on loosely packed Pyrex glass wool. The glass wool was placed in a glass tube in glass to glass connection with a sorbent tube connected to a pump. HHPA was immediately transferred from the glass wool by suction of 6.01 of air for 30 min. Of the anhydride applied to the glass wool 76% was recovered from the XAD-2. When the glass tube containing the glass wool was shaken in toluene, no HHPA was found. However, when it was instead shaken in sodium hydroxide solution, 9% of the HHPA was found as HHP acid. The recovery was therefore found to be 85% [coefficient of variation (C.V.) 1%; $n = 5$; RH 40%].

Storage. The stability of HHPA on XAD-2 tubes was studied by the simultaneous sampling of pairs of sorbent tubes in the standard atmosphere. On tube of each pair was immediately analysed while the other tubes were kept in a freezer for 20 days until analysis. *Ca.* 10% of the sampled HHPA was lost, and the losses during storage were not influenced by the relative humidity in the sampled air. The RH was <2% ($n = 5$; sampling volume 58 l) and 70% ($n = 6$; sampling volume 60 l). The sampling rate was 1.0 l/min and the concentration *ca.* 20 $\mu\text{g}/\text{m}^3$. When storing HHPA in toluene at microgram per millilitre concentrations degradation of sample was found. At sub- $\mu\text{g}/\text{ml}$ concentrations up to 2%/h was lost when kept at room temperature. The loss was influenced by, for example, the condition of the toluene. Samples must therefore be analysed immediately after elution of the solid sorbent tube. When kept in a freezer, standard solutions could be stored up to ten days without noticeable degradation of the sample.

Procedure in the bubbler method

Sampling efficiency. The sampling efficiency was studied by sampling HHPA in the standard atmosphere with two bubblers, containing the alkaline-absorbing solution, coupled in series. All connections were glass to glass. Two different concentrations of HHPA were studied, 21 and 220 $\mu\text{g}/\text{m}^3$ ($n = 8$ for each; sampling volume 120 l; RH <2%). No HHP acid was found in any of the second bubblers.

Storage. No degradation of HHP acid in the absorption solution was found when stored in a refrigerator for eight weeks at concentrations of 0.16 $\mu\text{g}/\text{ml}$ ($n = 5$) and 2.5 $\mu\text{g}/\text{ml}$ ($n = 5$). Standard solutions of HHP acid-DME in toluene, containing 0.18 $\mu\text{g}/\text{ml}$ ($n = 5$) and 2.9 $\mu\text{g}/\text{ml}$ ($n = 5$), kept in a freezer were also stable.

Work-up procedure. The recovery for the work-up of absorbing solution spiked with 1.4 μg of HHPA was 88% (C.V. 4%) and 79% (C.V. 3%) when spiked with 22 μg of HHPA ($n = 10$).

Chromatography

Symmetrical peaks were obtained for HHPA as well as HHP acid-DME in the chromatographic system. No adsorption or decomposition was observed. When analysing the anhydride, no interfering peaks disturbed the evaluation of the chromatograms. When analysing the HHP acid-DME, on peak originating from the esterification step was eluted with the same retention time; this reduced the detection limit slightly (Fig. 2). A comparison between apolar columns of internal diameter 0.25 mm and a film thickness of 0.25 μm and internal diameter 0.32 mm and a film thickness of 1.0 μm was done. Significantly better resolution relative to the matrix was obtained

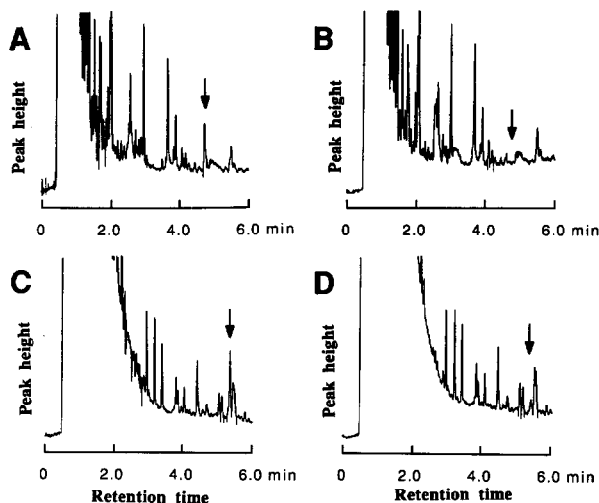


Fig. 2. Chromatograms of (A) 0.1 μg HHPA per millilitre of toluene and (B) blank sample of the solid sorbent method. (C) shows a chromatogram of HHPA-DME (about 0.1 $\mu\text{g}/\text{ml}$ in toluene) and (D) a blank sample of the bubbler method.

for the column with the internal diameter of 0.25 mm, which was also the minimal internal diameter of a capillary column that it was possible to use for automatic on-column injections. The on-column injection technique was chosen for the excellent repeatability achieved. At least 1000 injections were possible without noticeable degradation of the column. The chromatograms were hence easy to evaluate with the integrator.

Detection

Detection of HHPA was performed with FID, photoionization detection (PID) and electron-capture detection (ECD). PID was more than 10 times less sensitive than FID. ECD was much more sensitive than FID. However, ECD is complicated to use, unstable and sensitive to impurities. FID, which is easy to use, relatively sensitive and stable, was therefore chosen. The detection limits for HHPA in toluene using FID and calculated as three times the noise was *ca.* 0.1 $\mu\text{g}/\text{ml}$ (Fig. 2). However, owing to the instability of HHPA, concentrations lower than 0.2 $\mu\text{g}/\text{ml}$ were not quantified. The practical detection limit is defined by the sampling and the work-up conditions. The detection limit (three times the noise) for HHP acid-DME in toluene is about 0.1 μg of HHPA per millilitre (Fig. 2). Short time sampling (15 min) can be performed down to air concentrations of 13 $\mu\text{g}/\text{m}^3$ with both the bubbler and the solid sorbent methods. With 1 h sampling, concentrations $> 3 \mu\text{g}/\text{m}^3$ can be detected with both methods. For 8 h sampling it is advisable to use the low sampling rate for the solid sorbent method and to change the bubbler or XAD-2 tube at least once during the day.

Quantitative analysis

Calibration graph. Different amounts of HHPA were added to 5 ml of 0.1 M aqueous sodium hydroxide and the work-up procedure described above was used.

TABLE II

PRECISION AT DIFFERENT CONCENTRATIONS OF HHPA AND RELATIVE HUMIDITY IN AIR

The sampling rate was 1.01 l/min.

Concentration of HHPA in air ($\mu\text{g}/\text{m}^3$)	Relative humidity (%)	Sampling volumes (l)	Precision of XAD-2 (%)	Precision of bubbler (%)	Number of determinations
15	<2	63	2	12	7
27	70	59	7	19	7 ^a
160	<2	51	2	3	7

^a The precision of the bubbler method was calculated from six determinations.

Single samples at each concentration ($n = 7$) with duplicate injections were made. A linear relation passing through the origin was achieved at the investigated range of 0.6–320 μg of HHPA per sample. The correlation coefficient was 0.9996. HHPA was added to toluene to concentrations in the range of 0.44–440 μg of HHPA per millilitre. A linear calibration curve, passing through the origin, was found. The correlation coefficient was 0.9999.

Precision. HHPA was collected in solid sorbent tubes and bubblers for the estimation of the concentration in the standard concentration chamber. The precision of the determinations is presented in Table II. The result at RH = 70% indicates the minor influence of the relative humidity on the precision.

Comparison between the methods. Parallel samples were taken in the standard atmosphere on XAD-2 tubes and bubblers and the work-up procedures were then performed. The correspondence between the results obtained by the two methods was then compared. The low RH (<2%) was chosen to minimize the amount of HHP acid possibly present in the air. With a higher RH, a difference in the concentrations found by the two methods could demonstrate the presence of HHP acid in the air rather than a difference in determination of the anhydride. At 15 $\mu\text{g}/\text{m}^3$ ($n = 7$; sampling volume 63 l; RH <2%) the concentrations found by the solid sorbent method were 93% of those with the bubbler method, and at 160 $\mu\text{g}/\text{m}^3$ ($n = 7$; sampling volume 51 l; RH <2%) 98% and at 27 $\mu\text{g}/\text{m}^3$ ($n = 6$; sampling volume 59 l, RH 70%) 86%. This indicates decreasing recovery with the relative humidity for the solid sorbent method. However, the difference was not statistically significant. A comparison of samples taken simultaneously, by the two methods, in the work environment air was performed. The sampling rate for the solid sorbent tubes was 0.2 ml/min. No breakthrough was observed at any concentration monitored. The concentrations found by the solid sorbent method were 93% of that found by the bubbler method at a mean concentration of 330 $\mu\text{g}/\text{m}^3$ (C.V. = 39%; range 200–540 $\mu\text{g}/\text{m}^3$; sampling volume 19–46 l; $n = 8$). However, the possibility that other factories use other chemicals which can possibly interfere with the HHPA determinations must be considered. The results of the two methods were compared by the paired *t*-test (95% confidence limits; two-tailed). At none of the four conditions was there a significant difference between the methods.

CONCLUSIONS

The two methods for the monitoring of the HHPA in air were found to be reliable with detection limits much below the expected average found in the work environment. The methods were investigated for the concentration range 15–160 $\mu\text{g}/\text{m}^3$. However the studies in the work environment indicate that they are applicable at least up to 540 $\mu\text{g}/\text{m}^3$. RH < 70% did not seem to affect the sampling efficiency of the solid sorbent method. The high sampling rate (1.0 l/min) makes it possible to monitor the exposure for relatively short periods. For monitoring for a long time, using the solid sorbent method, a sampling rate of 0.2 l/min is preferable to minimize the breakthrough. The methods showed the same results (within the experimental errors) for the monitoring of HHPA concentration both in the standard atmosphere and when applied in the work environment. However, when both anhydride and acid are present in the air the total is obtained with the bubbler method. The solid sorbent method makes it possible to monitor HHPA as such and it has the advantages of somewhat better precision and a less time-consuming work-up procedure. The sampling solutions obtained for the bubbler method have the obvious advantage of being stable during storage.

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