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Monitoring 1,6-hexamethylene diisocyanate in air by chemisorption sampling

by Kurt Andersson, PhD,¹ Ann Gudéhn, BSc,² Christer Hallgren, BSc,¹ Jan-Olof Levin, PhD,¹ Carl-Axel Nilsson, PhD¹

ANDERSSON K, GUDÉHN A, HALLGREN C, LEVIN J-O, NILSSON C-A. Monitoring 1,6-hexamethylene diisocyanate in air by chemisorption sampling. *Scand j work environ health* 9 (1983) 497-503. A sampling procedure for 1,6-hexamethylene diisocyanate (HDI) in air is described. The diisocyanate is trapped on a chemisorption tube containing 9-(N-methylaminomethyl)anthracene adsorbed on Amberlite XAD-2. Recoveries in the laboratory experiments were 81-91 %. The chemisorption technique was evaluated in the field by measurements at two different factories using HDI as a hardener in two-component paints for vehicle refinishing. Simultaneous sampling with a fritted-glass bubbler and by the chemisorption technique showed equal collection efficiencies for HDI when 3.5- to 22-l air samples were used. For air samples exceeding 20 l the collection efficiency of the fritted-glass bubbler decreased. Several additional peaks appeared in the chromatograms from the fritted-glass bubblers. Statistical treatment of the data showed that these peaks are closely related to the amount of HDI.

Key terms: airborne isocyanates, 4,4'-diphenylmethane diisocyanate, isocyanate, toluene diisocyanate.

Aromatic and aliphatic diisocyanates have found widespread industrial use in the production of polyurethane materials, such as flexible and rigid foams, adhesives, elastomers, paints, and coatings. 1,6-Hexamethylene diisocyanate (HDI) is added to two-component paints used, eg, in the vehicle refinishing industry. Methods for analyzing and sampling diisocyanates, which may be toxic when inhaled (13, 14), are required.

A spectrophotometric method for determining aliphatic diisocyanates in air was introduced by von Eicken (5) and later modified (16, 20). The diisocyanates are hydrolyzed to the corresponding amines and then coupled with 1-fluoro-2,4-dinitrobenzene to form a colored derivative. Aromatic and aliphatic diisocyanates, their related oligomers, and the corresponding

amines all respond quantitatively to this method. Esposito & Dolzine (6) developed a gas-liquid chromatographic method for the determination of HDI in air. HDI was collected as the amine analogue and then derivatized with heptafluorobutyric anhydride and subsequently analyzed by gas liquid chromatography using electron capture detection.

Several methods using one-step derivatization with subsequent chromatographic analyses have been introduced for the determination of both aromatic and aliphatic diisocyanates. These compounds can now be selectively analyzed at low levels. The reagents used are N-*p*-nitrobenzyl-N-*n*-propylamine (4, 8, 9, 17), 1-naphthalenemethylamine (11), 9-(N-methylaminomethyl)anthracene (18), N-methyl-1-naphthalene methylamine (10), 1-(2-methoxyphenyl)piperazine (21), and 1-(2-pyridyl)piperazine (7).

The sampling of diisocyanates in workroom air has received less attention however, and, with a few exceptions (3, 15, 19), these methods suffer from the drawback of using liquid absorber samplers. We recently developed a sampling method using

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chemisorption (1), in which the diisocyanates are trapped on Amberlite XAD-2 coated with 1 % 9-(N-methylaminomethyl)anthracene (MAMA). The derivatives are desorbed with N,N-dimethylformamide and subsequently analyzed by high-performance liquid chromatography (HPLC). Chemosorption sampling has been evaluated in the field for toluene diisocyanate (1) and for 4,4-diphenylmethane diisocyanate (2). The purpose of this study was to evaluate the chemisorption sampling method for HDI.

Materials and methods

Chemicals

Acetonitrile (Rathburn Chemicals, HPLC grade), toluene (May & Baker, analytical purity), triethylamine (Merck), N,N-dimethylformamide (Mallinckrodt, analytical purity), and HDI (Fluka, puriss) were used without further purification. Water was purified in a Millipore Milli R/Q water purifier. 9-(N-methylaminomethyl)anthracene hydrochloride (MAMA · HCl) was purchased from Sangö & Zimerson (18).

Reagent solution

One hundred and twenty-five milligrams of MAMA · HCl was dissolved in 25 ml of 0.1-mol/l hydrochloride. The aqueous phase was washed twice with 12.5 ml of toluene. The toluene phases were discarded. The free amine was precipitated by the addition of 25 ml of 1-mol/l sodium hydroxide. The amine was extracted with two 15-ml portions of toluene, and the volume adjusted to 100 ml with toluene (reagent solution A). Twenty milliliters of reagent solution A was further diluted with toluene to contain a MAMA concentration of 10^{-4} mol/l.

Adsorbent

Amberlite XAD-2 (Rohm & Haas) is a cross-linked styrene divinylbenzene copolymer. For the elimination of salts and fines, the polymer was washed and decanted in water seven times, in methanol (puriss) five times, and in methanol (analytical purity) twice. The polymer was frac-

tioned and the beads between 20 and 50 mesh were collected. These were then Soxhlet-extracted twice for 12 h in diethyl ether (analytical purity) and finally dried overnight at 60°C.

Chemosorption tubes

Eighty milliliters of reagent solution A was added to 10 g of purified XAD-2. The toluene was evaporated in a rotary evaporator at 50°C. The chemisorbent (150 mg) was filled in a 6- \times -50-mm glass tube (inner diameter 4 mm) similar to an ordinary charcoal sampling tube. The tubes were stoppered at both ends with silanized glass wool.

Standard solutions

HDI was diluted in toluene to give 525, 105, and 10.5 μ g/ml. The urea-derivative standard solutions were prepared by the addition of 10 μ l of the HDI standard solutions to 10 ml of MAMA (10^{-4} mol/l) in toluene. The toluene was evaporated, and the residue dissolved in 2 ml of N,N-dimethylformamide.

Recovery studies

Ten microliters of the HDI standard solution was injected into a preheated (40°C) glass tube connected to the chemisorption tube; 15 l of air was pumped through the tube at a flow rate of 1 l/min.

Field measurements

Each experimental setup included one fritted-glass bubbler with 10 ml of MAMA (10^{-4} mol/l) in toluene and one chemisorption tube in parallel. The chemisorption tubes were backed up by a fritted-glass bubbler containing 10 ml of MAMA (10^{-4} mol/l) in toluene. Measurements were performed at two different factories (A and B) using HDI as a hardener in two-component paints for vehicle coating. Short periods (2–5 min) of spraying were generally required to repair damage to the body coating. The total sampling time varied between 3 and 60 min, and each sample included one to three periods of paint spraying. Sampling was performed in the ventilated spray-box in which the vehicles were sprayed. The paint used in factory A was Lesonal, the temperature was 20–22°C,

and the relative humidity 40–44 %. Factory B used Glassodur and Lesonal paints. The temperature was 22–24°C, and the relative humidity 38 %.

Analysis

The toluene in the fritted-glass bubbler reagent solutions was allowed to evaporate overnight in a hood, and the residue was dissolved in 2 ml of N,N-dimethylformamide. The chemisorption tubes were desorbed by the shaking of the chemisorbent with 2 ml of N,N-dimethylformamide for 30 min. The solutions were filtered through a Millex R -SR (0.5 µm) filter prior to the analysis. The chromatographic runs were performed with a Waters HPLC instrument, consisting of a WISP 710 A autosampler, a M6000 A solvent deliver system, a M440 ultraviolet-absorbance detector, and a data module. The instrument was further equipped with a Waters radial compression separation system with a C-18 reversed phase column (8 × 100 mm, 5 µm) operating at a flow rate of 1.5 ml/min [pressure approximately 600 pounds per square inch (4,137 · 10⁴ Pa)]. The chromatographic eluent consisted of 200 ml of water, containing 2.5 % triethylamine, with the pH adjusted to 3.0 with concentrated phosphoric acid. The water was diluted to 1.0 l with acetonitrile. The detector was operated at 254 nm, and 15 µl was injected. The minimum detectable quantity was 0.5 ng. Recoveries were determined with the use of the external standard method.

Data analysis

The chromatograms were analyzed by the PLS (partial least squares in latent variables) generalized pattern recognition method (12, 22). With this method one set of “dependent” variables (Y) can be related to another set of “independent” variables (X) measured on the same set of samples (1 to n). The PLS method simultaneously derives (i) a model which approximates the variation in the X variables in a way similar to factor and principal component analysis, and (ii) a relationship between Y and X. The former is described by the PLS scores t.

The HDI derivative peak (p1) and three additional peaks (p2–p4) were selected

from the HPLC chromatogram (fig 1), and the peak heights were measured. Information from the p2–p4 peaks was related to the amount of free monomeric HDI derivative.

Results and discussion

Recovery experiments

As can be seen from table 1, all the recoveries were high. The tubes with the

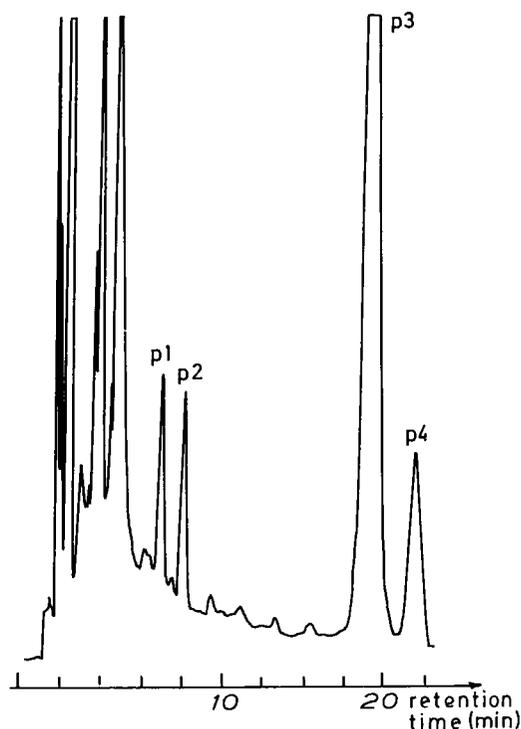


Fig 1. Chromatogram from a fritted-glass bubbler sample. The concentration of 1,6-hexamethylene diisocyanate (p 1) corresponds to 0.53 µg/ml.

Table 1. Recoveries of 1,6-hexamethylene diisocyanate (HDI) in the laboratory chemisorption experiments.

Amount of HDI added (µg)	Recovery (%)	Relative standard deviation (%)	Number of experiments
0.105	91	14	6
1.05	90	6	6
5.25	81	8	6
<i>Stored for one week in the dark at room temperature</i>			
1.05	83	5	4

higher amount of HDI, 5.25 μg , were connected to a backup chemisorption tube. No HDI derivative could be detected in any of the backup tubes. The amount of HDI added corresponded to 0.007, 0.07 and 0.35 mg/m^3 , respectively, for a 15-l air sample. Exposed chemisorption tubes can be stored for at least one week in the dark, with a slight decrease in recovery. It has previously been demonstrated (1) that unexposed chemisorption tubes are stable for at least two weeks if stored in the dark at room temperature.

Field studies

The amount of HDI derivative found in the fritted-glass bubbler solution was used as reference in the experiments and set at 1.00. The amount of HDI varied

between 0.34 and 1.10 μg when 3.5 to 22 l of air, corresponding to air concentrations of 0.014–0.139 mg/m^3 , was sampled. As can be seen from tables 2 and 3, there was excellent agreement in collection efficiency between the two sampling methods used for the 3.5- to 22-min sampling periods. However extension of the sampling period to 37–60 min resulted in considerably lower amounts of the HDI derivative in the fritted-glass bubblers (0.7–1.6 μg) compared with the chemisorption tubes (1.9–2.4 μg). No HDI could be detected in any of the fritted-glass bubblers used as backups.

Compared with the chromatograms from the chemisorption tubes (fig 2), the chromatograms from the fritted-glass bubblers contained several additional peaks (fig 1). To determine whether these peaks were related to the HDI content,

Table 2. Field sampling of 1,6-hexamethylene diisocyanate (HDI) with chemisorption tubes and fritted-glass bubbler samplers containing the reagent 9-(N-methylaminomethyl) anthracene.

Sample number	Sampling period (min)	Effective paint spraying (min)	Amount of HDI in chemisorption tubes (mg/m^3)	Amount of HDI in fritted-glass bubbler (mg/m^3)
1	7.7	5	0.139	0.136
2	7.7	5	0.130	0.136
3	7.7	5	0.143	0.143
4	20.0	6	0.015	0.019
5	20.0	6	0.014	0.017
6	22.0	4	0.035	0.037
7	22.0	4	0.035	0.034
8	22.0	4	0.033	0.035
9	36.9	6	0.054	0.019
10	36.9	6	0.058	0.025
11	36.9	6	0.049	0.035
12	60.0	10	0.042	0.018
13	60.0	10	0.038	0.013
14	60.0	10	0.039	0.027
15	11.5	3	0.048	0.040
16	11.5	3	0.035	0.042
17	11.5	3	0.030	0.031
18	19.0	7	0.058	0.056
19	19.0	7	0.048	0.053
20	19.0	7	0.053	0.042
21	7.0	4	0.106	0.104
22	7.0	4	0.094	0.106
23	7.0	4	0.080	0.080

Table 3. Collection efficiency of chemisorption tubes, compared with that of the fritted-glass bubbler, in field studies at two different factories.

Sampling technique	Sampling period (min)	Relative recovery	Relative standard deviation (%)	Number of experiments
Bubbler	3.5–22	1.00	—	17
Chemisorption	3.5–22	0.96	14	17
Bubbler	37–60	1.00	—	6
Chemisorption	37–60	2.30	25	6

we used a generalized pattern recognition technique. Using all peak heights simultaneously, this method recognizes similarities and dissimilarities in the pattern of peaks from each sample. With the chemometrical method PLS (12, 22) it is possible to recognize correlation patterns in a training set of data; these patterns are then used to predict properties in a test set. In the present case we wished to investigate correlations between the HDI peak height and the additional peaks (p2–p4). In a first step of statistical treatment, all the samples were used in a training set to see if different groupings of samples appeared. In a second step, the samples from factory A were compared with the samples from factory B.

The first PLS analysis resulted in a two-dimensional model. The plot, fig 3, can be seen as a two-dimensional projection of the three dimensional space spanned by the peaks p2–p4. Two classes of data emerged – one group including samples 1–8 from factory A and 15–23 from factory B, and a smaller group containing samples 9–14 from factory A.

In a second analysis, samples 1–8 from factory A were used as a training set, and samples 15–23 from factory B were used as a test set. The model built on the training set (sample 1–8) explained 93 % of the variance in the HDI peak height. With the use of the factory A model, amounts of HDI in the test set sample (numbers 15–23) were predicted from the p2–p4 peaks. The mean value of the predicted amounts of HDI was 116 % of the estimated value, with a relative standard deviation of 18. In other words the pattern of peaks in the chromatograms from the two industries was similar, and the three additional peaks were closely related to the amount of HDI. Each of the peak heights p2–p4 showed a linear relationship to p1.

Then a separate model was set up for samples 9–14. Seventy percent of the variance in p1 could be explained by this model. This model is not quite as good as the first, but it does show that the samples are similar within this group. In samples 9–14, 37–60 l of air was sampled in comparison with 5–22 l for the rest of the samples. On the assumption that p2–p4 are derivatives of isocyanate with the same detector response as for the p1 peak, the total amount of iso-

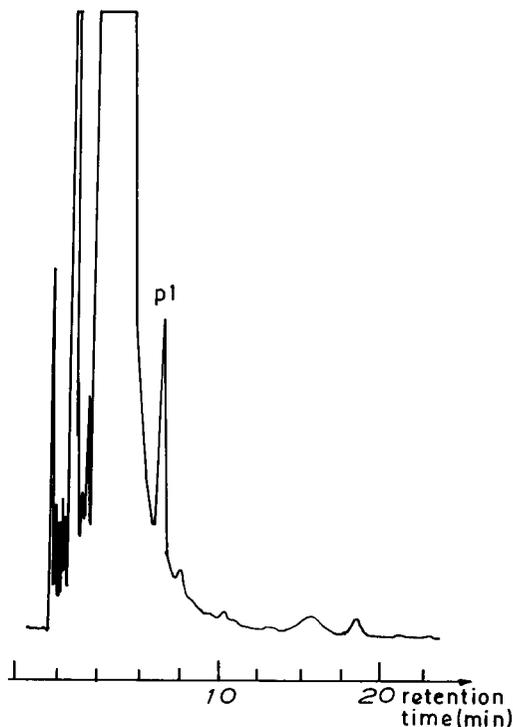


Fig 2. Chromatogram from a chemisorption tube sample. The concentration of 1,6-hexamethylene diisocyanate (p 1) corresponds to 0.55 $\mu\text{g/ml}$.

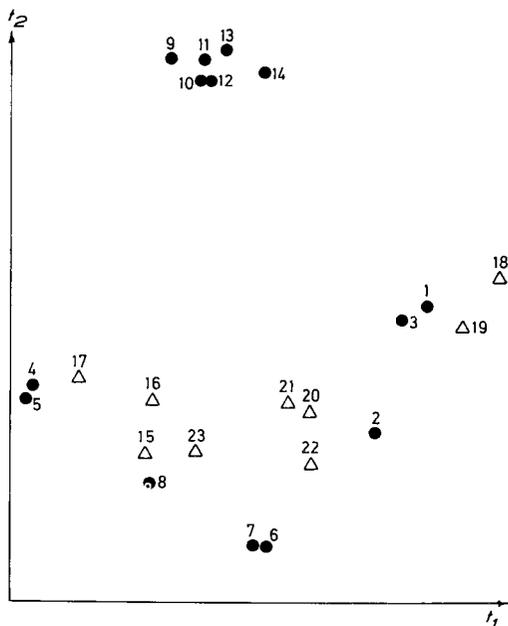


Fig 3. Principal component scores (t_1 and t_2) for samples 1 to 23. [For a detailed explanation of this type of plot, see Wold et al (22).]

cyanates can be calculated. In samples 9–14 the total amount was 4–6 µg compared to 3–12 µg in samples 1–8 and 15–23. Thus the difference in the patterns of the two classes cannot be explained by an insufficient amount of MAMA reagent.

Large air-sampling volumes change the pattern of p1–p4 in the chromatograms. This phenomenon may be caused by loss of substance from the fritted-glass bubbler solutions due, for example, to degradation of substance or breakthrough in the fritted-glass bubbler solutions.

Conclusion

Chemosorption is a convenient method for sampling HDI. The chemosorption tubes are easy to prepare, are stable enough to be stored before and after use, and HDI is effectively retained on the chemosorption tubes. The sampling is efficient even for large amounts of sampled air, and no complication is caused by additional peaks in the chromatograms. A fritted-glass bubbler containing MAMA reagent should not be used for sampling larger volumes of air than 20 l, since the collection efficiency of such a sampler decreases with increased sampling volume.

It is of the utmost importance to verify the additional peaks in the HPLC chromatograms from the solvent sampler. These peaks are suspected to be derivatives of polymeric HDI. If this should prove to be the case, the question should be considered whether these substances are respirable and whether it is relevant to measure them.

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