Liquid Chromatographic Determination of Hydrazine at Sub-Parts-per-Million Levels in Workroom Air as Benzaldazine with the Use of Chemosorption on Benzaldehyde-Coated Amberlite XAD-2

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Hydrazine is an important industrial chemical with many applications. It is used, for example, in the pharmaceutical, polymer, and dye industries (*1*). It is also widely used as a corrosion inhibitor in water boilers. Besides being reactive and explosive, hydrazine is highly toxic. It may cause skin sensitization as well as systemic poisioning (*2*). It is also a suspected human carcinogen, and the threshold limit value for workroom air is 0.1 ppm (0.1 mg/m^3) in the U.S. (*3*).

Several methods are available for the determination of hydrazine in air. The most widely used consists in liquid impinger sampling in hydrochloric acid, reaction with *p*-(dimethylamino)benzaldehyde, and spectrophotometric determination of the colored product (*4*). The method is not specific for hydrazine, however; hydrazine derivatives and amines may interfere. A more specific method has been developed by NIOSH (National Institute for Occupational Safety and Health), which involves trapping hydrazine (or alkyl hydrazines) on a sulfuric acid coated silica gel adsorbent. The hydrazine sulfate is desorbed with water and reacted with 2-furaldehyde to produce an aldazine, which is determined by gas chromatography (GC) (*5*). For personal exposure monitoring, solid sorbents are preferable for sampling, since liquid absorbers are difficult to handle in the field. However, the procedure of first desorbing hydrazine sulfate from the adsorbent and then making a derivative for GC is time-consuming and cumbersome. A combination of solid sorbent sampling and field colorimetric determination has also been used (*6*).

For some years, we have been studying the determination of reactive organics in air with the use of reagent-coated solid sorbents (chemosorption). The chemosorption tubes used for sampling are the same size as the standardized NIOSH charcoal tubes (*7*). A method for determination of low-molecular aldehydes in workroom air has been developed. The method utilizes hydrazone formation on an Amberlite XAD-2 adsorbent coated with (2,4-dinitrophenyl)hydrazine hydrochloride. The method has been used for determination of formaldehyde (*8*, *9*), acrolein (*10*), and glutaraldehyde (*10*) in air. Another chemosorption method has been developed for monitoring exposure to gaseous diisocyanates (*11*, *13*), which utilizes XAD-2 coated with 9-((*N*-methylamino)-methyl)anthracene for the formation of a urea derivative. Hydrazones and ureas are determined with high specificity and sensitivity by high-performance liquid chromatography (HPLC) with UV detection. We now wish to report a chemosorption method for the determination of hydrazine in workroom air. The method involves trapping hydrazine on benzaldehyde-coated XAD-2. The resulting azine is eluted from the adsorbent and determined by HPLC using UV detection.

EXPERIMENTAL SECTION

Chemicals. Solvents used were diethyl ether (May & Baker, p.a.), methanol (Merck, p.a.), ethanol (Kem-Etyl, spectr.), and *N*,*N*-dimethylformamide (Fluka, p.a.). Benzaldazine was prepared by dissolving 5.0 mL of benzaldehyde (Kebo Lab, puriss.) in 10.0 mL of 99% ethanol, acidifying with 1.5 mL of concentrated hydrochloric acid (Merck, p.a. 37%), and adding 1.2 mL of hydrazine hydrate (AnalaR, p.a.). The benzaldazine precipitated and was recrystallized from 99% ethanol; mp 91–92 °C (lit. (*4*) 93 °C).

Table I. Recovery of Benzaldazine from Benzaldehyde-Coated XAD-2

hydrazine added, μg	recovery, %	RSD,[a] %	n[b]
0.6	73	4	6
3.0[c]	83	13	4
15.0	84	6	6
3.0[d]	91	11	4

[a] Relative standard deviation. [b] Number of experiments. [c] Corresponds to 0.1 mg/m^3 in a 30-L air sample. [d] Exposed tubes stored for 1 week in the dark at room temperature.

A standard solution of benzaldazine in dimethylformamide (3.9 μg/mL) was prepared.

Chemosorption Tubes. Amberlite XAD-2 (Rohm & Haas, techn.) was purified by repeated washing with distilled water to remove inorganic salts. Fines were removed by decanting. The polymer was further washed with methanol five times, dried, and fractionated to produce the size distribution 20–50 mesh. Finally, the adsorbent was extracted twice in a Soxhlet apparatus for 24 h with diethyl ether and dried at 70 °C overnight. As an alternative commercially purified XAD-2 (Serva, analytical grade) can be used. Fifteen milliliters of ethanol was added to 10.0 g XAD-2. To this mixture a solution of 1.0 mL of benzaldehyde and 0.6 mL of concentrated hydrochloric acid in 10.0 mL of ethanol was added. The solvent was evaporated in a rotary evaporator at 35 °C, and the benzaldehyde-coated XAD-2 was filled in glass tubes, 60 × 4 mm (i.d.). The tubes were stoppered at both ends with Teflon wool. Each tube contained 200 ± 10 mg of chemosorbent.

Recovery Experiments. The chemosorbent tube was connected to a personal sample pump (SKC Model HFS 113UT) with the flow adjusted to 1.0 L/min. To the other end of the chemosorption tube was fitted a 50 × 4 mm (i.d.) Teflon tube. The pump was started, and varying amounts of hydrazine hydrate dissolved in ethanol were injected into the Teflon tube. The hydrazine was vaporized and drawn into the chemosorbent, and a total of 30 L of air was pumped through the tube.

Liquid Chromatography. The benzaldazine was eluted from the chemosorbent by shaking for 30 min with 5.0 mL of *N*,*N*-dimethylformamide. A 15-μL portion of this solution was injected into the liquid chromatograph. A Waters HPLC system consisting of one M-6000A pump, an M-710B autosampler, an M-720 system controller, an M-730 data module, and an M-440 UV detector was used. The column was a Waters Radial-PAK A (100 × 5 mm (i.d.), octadecylsilane, 10-μm particles). The mobile phase was 10% water in methanol, and the flow was 0.8 mL/min. Under these conditions, k' for benzaldazine was 1.3, and the retention time was 4.3 min. The benzaldazine was detected at 313 nm with a detection limit of approximately 3 ng, corresponding to 0.4 ng of hydrazine. Figure 1 shows chromatograms of desorbed air sample and chemosorption tube blank.

RESULTS AND DISCUSSION

The hydrazine chemosorption method was evaluated at different hydrazine levels in laboratory experiments. Table I shows the recovery of benzaldazine from chemosorption tubes. The amounts of hydrazine correspond to a range of 0.02–0.5 mg/m^3, calculated on a 30-L air sample. As the table shows, recoveries are generally high. The somewhat lower recovery at the lowest level is explained by the difficulty to generate small amounts of hydrazine quantitatively. Storing the exposed tubes for 1 week in the dark at room temperature

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Figure 1. Liquid chromatogram of desorbed 10-L air sample containing 0.1 mg/m^3 hydrazine (A) and chemosorbent tube blank (B).

Table II. Hydrazine Concentrations in Air in the Vicinity of a Water Boiler Containing Hydrazine as Corrosion Inhibitor (Sample Flow Rate 1.0 L/min)

tube no.	location[a]	sampling time, min	air concn, mg/m^3
1	beside container	30	<0.005
2	at feeding system	30	<0.005
3	beside boiler	30	<0.005
4	inside empty container	10	0.27
5		20	0.32
6		30	0.26
7		60	0.30

[a] See text for explanation.

does not lower recovery. Figure 1 shows a chromatogram of a desorbed air sample. As the figure shows, excess benzaldehyde does not interfere with the determination, nor does a relative humidity of 85% significantly affect the recovery. Other potential interferences were not investigated.

The method was also evaluated in an industry using hydrazine as corrosion inhibitor in a large water boiler. A solution of 15% hydrazine hydrate in water was fed into the system from a container via an automatic feeding system. No hydrazine could be detected in the air outside the container or beside the boiler. In the empty container, however, considerable amounts of hydrazine were found. The results are shown in Table II. In summary, the method described is a selective and sensitive method for the determination of hydrazine in air. The overall sensitivity of the method is about 5 μg/m^3, based on a desorption volume of 50 mL, an injection volume of 15 mL, and a 30-L air sample. Sensitivity can be further enhanced with the use of larger injection volumes and larger air samples. The use of a solid adsorbent for sampling makes the method especially suitable for personal sampling in the work environment.

Registry No. Hydrazine, 302-01-2; Amberlite XAD-2, 9060-05-3.

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Analysis of Heroin–Morphine Mixtures by Zero Order and Second Derivative Ultraviolet Spectrometry

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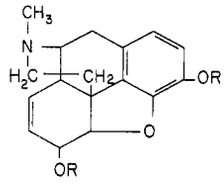
Morphine (Ia) is the most important alkaloid of opium and is a narcotic analgesic. Heroin (diacetylmorphine) (Ib) is also



Ia; R = H
b; R = COCH$_3$

an effective analgesic drug that induces a high level of addiction and subsequent illicit use. Today, heroin is recognized as one of the most widely abused drugs in the world. Its long history of abuse has produced numerous analytical techniques and procedures for its identification and determination in various matrices (*1*). These techniques range from color and microcrystalline tests to GC/MS procedures (*2*). In spite of the advent of many new highly sensitive analytical techniques, ultraviolet (UV) spectrometry, due to its simplicity and widespread availability, is frequently used for the analysis of unknown drugs (*3*). Bertulli et al. (*4*) reported a UV spectrometric method for the determination of single compounds

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