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Determination of airborne triethylenediamine and 2,2′-oxybis (N,N-dimethyl)ethylamine in the workplace

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Comprehensive industrial hygiene evaluations were performed in three flexible polyurethane foam manufacturing facilities. General area air samples were collected for determining aliphatic amines where these substances were used as catalysts in the foam. Because it was unclear which sampling medium was most appropriate to use when collecting these amines, several media were tried. In one comparison of performance, sample pairs consisting of a Thermosorb®/A tube and an acid-filled impinger were used to collect an aliphatic amine ether (2,2′-oxybis[N,N-dimethyl]ethylamine or bis[2-dimethylaminoethyl]ether) and an alicyclic amine (1,4-diazabicyclo[2,2,2]octane or triethylenediamine). Both samples in each pair were collected under identical conditions of sampling duration, flowrate, and environmental parameters such as temperature and humidity. Analysis of the Thermosorb/A tubes was performed with a gas chromatograph and a thermal energy analyzer (GC/TEA) with mass spectrometric confirmation of any detectable nitrogen-containing compounds. Analysis of the impinger samples was performed with a GC and a nitrogen-phosphorus detector with mass spectrometric confirmation. No nitrogen-containing compounds were detected using the Thermosorb/A samplers. In contrast, the acid impinger produced detectable results that were more consistent with our knowledge of the process. The difficulty with the Thermosorb/A sampler has not yet been identified. Because the field comparison using the acid impinger and Thermosorb/A tube was limited to only a few samples and only two aliphatic amines were analyzed, it should not be assumed that these data support the use of only the acid impinger for the collection of all volatile amines. These data support the conclusion that the acid impinger method for sampling provides a complementary approach to other methods that are used for the determination of certain amines in the workplace air. **Boeniger, M. F.; Choudhary, G.; Foley, G. D.**: Determination of airborne triethylenediamine and 2,2′-oxybis(N,N-dimethyl)ethylamine in the workplace. *Appl. Ind. Hyg. 2*:218–221; 1987.

Introduction

Aliphatic and alicyclic amines comprise a large class of compounds that are used widely in industry as curing agents or catalysts in the plastics and synthetic foam industry.[1] Most of these amines are capable of irritating the eye and skin after exposure to the gases or after direct contact.[2] The corneal effects have been commonly associated with a subjective but potentially dangerous temporary condition referred to as "halovision" which diminishes the vision and may cause the subject to see halos when looking at lights.[3–7] Some of the aliphatic amines have been associated with dermal and respiratory sensitization.[1,2,8] Few of these amines have been tested for carcinogenicity in laboratory animal experiments, but at least one aliphatic amine (triethanolamine) has been found to be carcinogenic.[9] An additional concern is that given the proper conditions, aliphatic amines may be nitrosated by nitrogen dioxide or similar nitrosating agents in the air to form carcinogenic nitrosamines.[10] Nitrogen dioxide, at concentrations sufficient to cause nitrosamine formation, is likely to be present in the air of most industrial workplaces.[10,11]

During 1985, air samples for several nonaromatic amines were collected as part of comprehensive exposure characterization surveys of three polyurethane foam manufacturing facilities. Although aliphatic amines are important industrial compounds and are toxicologically significant, there are few reports on determining these compounds in the air. Our interest in sample collection methods for aliphatic amines stemmed from our failure to detect amines using silica gel medium and Thermosorb®/A tubes in these three surveys. It was believed that the air concentrations of the amines should have been high enough to be detected. This belief lead to the use of an alternative air sampling medium.

Background

Because of a lack of specific published methods for each of the several amines of interest and the NIOSH laboratory's past favorable experience with collecting certain aliphatic amines, Thermosorb/A sampling tubes and large silica gel tubes were initially selected as suitable sampling media for the amines of interest. The Thermosorb/A tube contains a dry proprietary sorbent that is not related to silica gel.[12] The silica gel tube contained 520 and 260 mg of sorbent (SKC, Inc., Eighty Four, PA, catalog no. 226–15).

It was originally intended that sample pairs, using the two sampling media, would be collected in the three manufacturing sites and the results compared. Among the amines used in the three manufacturing facilities were triethylenediamine, 2,2'-oxybis(N,N-dimethyl)ethylamine, diethanolamine, triethanolamine, N-methylmorpholine, and triethylamine. A combined total of 47 silica gel and Thermosorb/A tubes were collected at these facilities at a flow rate of 1 lpm and 3 lpm, respectively, for 7 to 10.5 hours. Based upon the instrumental limits of detection and the air sample volumes, it was calculated that as little as 0.02 mg/m^3, or about 3–4 parts per billion of these amines could have been detected. The analysis, which included confirmation by mass spectrometry, indicated that no aliphatic amines or nitrogen-containing compounds were present in the samples. Because of our knowledge of the processes, reports of vision disturbances in the factories, and literature reporting airborne aliphatic amines in similar processes, it was decided that further investigation of alternative methods to sample nonaromatic amines was appropriate.

The purpose of this paper is to communicate comparative field sample results that were obtained by using two types of air sampling media to collect two aliphatic amines in the air. Thermosorb/A tubes and acid-filled impingers were used for comparison. The two tertiary aliphatic amines that were determined were 1,4-diazabicyclo(2,2,2)octane (DABCO or triethylenediamine) and 2,2'-oxybis(N,N-dimethyl)ethylamine (referred to hereafter as 2,2-oxybis). A comparison of the results suggests an unidentified problem with the Thermosorb tubes and supports the selection of the acid-filled impinger method for the collection of these particular amines. A description of the two methods of sampling and analysis and a discussion of the results from the field samples are presented.

Experimental

Field studies

Two different sample collection media were used concurrently in pairs to collect volatile aliphatic amines in a facility manufacturing flexible polyurethane foam. Triethylenediamine and 2,2-oxybis were used in the foam formulation. One sample collection medium consisted of acid-filled midget impingers while the other was a Thermosorb/A tube (Thermedics, Inc., Woburn, MA). Eight paired samples, each pair including only one of the above sampling media, were collected at various locations in the facility. Fifteen milliliters of a mixture containing 0.6 N H_2SO_4 and 0.6 N HCl (Marcali Solution) were added to each of the impingers.[13] The sampled air flow rates for the Thermosorb/A tubes and impinger samplers were both about 1 lpm. The flow rate for each sample was calibrated both before and after each air sample was collected. Post-sample flow rate generally did not differ from pre-sample flow rate by more than two percent.

Laboratory studies

The impinger samples were analyzed using a gas chromatograph (GC). The sampling and analytical method was based upon slightly modified methods reported previously by others.[14–16]. One milliliter of each of the impinger sample solutions was alkalinized with three drops of a saturated solution of sodium hydroxide and a 1 μL alioquot of the basic solution was injected directly into the gas chromatograph. A Hewlett-Packard 5890 Gas Chromatograph, equipped with a nitrogen-phosphorus detector in the nitrogen mode, was used in the analysis. The column chosen for this analysis consisted of 4% carbopack 20M/0.8% KOH on 60/80 Carbopack B packed in a six-foot coiled glass column (Supelco, Bellefonte, PA). The operating temperatures were as follows: oven, 210°C isothermal; injection port, 220°C; and detector 250°C. The helium carrier gas flow rate was set at 25 ml per minute. Recovery studies were performed for the two amines sought in this study.

The contents of the Thermosorb/A sampling tubes were desorbed with 2 ml of 0.05% KOH in methanol as described by NIOSH method P&CAM 221.[17] An aliquot of the sample extract was then analyzed in a GC programmed to run from 30° to 300°C in 30 minutes when using a SPB-5 large bore capillary column. A Thermal Energy Analyzer or TEA (Thermo Electron, Waltham, MA), set in the nitrogen mode, was used as the detector. Standard solutions of DABCO were injected to determine if the system was performing adequately. Spiking and recovery studies for the silica gel and Thermosorb/A sampling tubes were not performed since previous experience in our laboratories with other related amines indicated that these sampling media performed satisfactorily when using liquid spikes.

Results

Field studies

Analyses of Thermosorb/A sampling tubes from the survey produced results which were all below the limit of analytical detection. Upon desorbing the medium contained within the Thermosorb/A tubes, the extract from five of the eight samples formed a solid gel. This problem had not been seen in earlier surveys conducted in similar plants when 23 samples had been collected and analyzed. In an attempt to analyze the recent samples that formed a solid gel, a portion of the gel was dissolved in 2 ml of 0.05% KOH in methanol. All samples were then analyzed as stated before using GC-TEA in the nitrogen mode. Nitrogen-containing compounds were not detected in any of the samples. The samples that formed a solid were submitted for mass spectrometric solid probe analysis; however, the solid material could not be identified.

The results of the analyses of the acid-filled impinger samples were quite different from the analytical results of the Thermosorb/A samplers. Each impinger sample contained at least one of the two amines sought in the analysis. The highest analyte loadings for DABCO and 2,2-oxybis were 290 and 647 μg per sample, respectively. Air concentration results for the various sample locations are presented in Table I. The highest air concentrations of DABCO (616 μg/m^3) and 2,2-oxybis (1374 μg/m^3) were found near the foam-crushing units where halovision was most often reported by the workers.

Laboratory studies

Recovery studies of the acidic impinger sample medium, to which aliquots of both amines from standard solutions were added, revealed that 98 percent of the analytes were recovered over the range of 10 to

TABLE I
Air sampling results for two aliphatic amines using an acid impinger for sampling[A]

Sample location	Air concentration (μg/m³)			
	Acid impinger		Thermosorb/A tube	
	DABCO[B]	2,2-oxybis[C]	DABCO	2,2-oxybis
Seat assembly	170	180	F	F
Line 2 burlapping	40	ND[D]	F	F
Between line 1 & 4	130	270	ND[E]	ND
Foam crusher unit	230	560	F	F
Line 2 burlapping	40	ND	F	F
Center of carousel 3	420	900	ND	ND
Foam crusher	620	1370	ND	ND
Seat assembly	190	190	F	F

[A]Each air volume was approximately 0.500 m³.
[B]Triethylenediamine.
[C]2,2′-oxybis(N,N-dimethyl)ethylamine.
[D]Limit of detection was 1.4 μg/ml or about 42 μg/m³.
[E]Limit of detection for both compounds was about 10–50 μg/m³, depending upon the air volume.
[F]Upon extraction, these samples formed a solid gel which could not be analyzed according to the method.

200 μg per 10 ml sample. A calibration curve of the amine standards showed the limit of detection for DABCO to be 1.4 μg/ml and for 2,2-oxybis to be 1.5 μg/ml. The limits of quantitation were 4.7 and 4.9 μg/ml, respectively.

The recovery efficiency and limit of analytical detection for aliphatic amines collected on silica gel and Thermosorb/A tubes had previously been found in our laboratories to be somewhat dependent upon the particular analyte (unpublished). Nevertheless, the recovery of these aliphatic amines has typically been at least 80 percent with a limit of detection of 20 μg per sample. The Thermosorb/A tube collection method, coupled with the GC-TEA analysis, has been used in NIOSH laboratories to identify methylamine, diethanolamine, triethylamine, cyclohexylamine, and several other aliphatic amines in the past.

Discussion

In addition to the above field study in a polyurethane foam manufacturing facility, air samples for aliphatic amines also were collected on three occasions in other facilities using silica gel and Thermosorb/A collection media. In none of these other *facilities* were aliphatic amines detected, even when air samples were collected in areas where several different amines were stored in open vessels and an amine odor was evident. Poor analyte recovery has been reported for the silica gel tube by others who determined a 15 to 25 percent lower recovery of ethylenediamine in silica gel tubes compared to acid-filled impingers.[18] In contrast to the results obtained using the Thermosorb/A tube, it was possible in the most recent field evaluation to quantify two aliphatic amines by analyzing acid-filled impinger samples.

The experience described here is intended to alert others of these findings and to offer an alternative or additional method of sampling for the aliphatic amines identified. Since these findings were the result of an ancillary part of a larger industrial hygiene field survey, no effort has been made to validate either the impinger sampling method or the analytical method that is described here. Furthermore, it is not apparent from this limited work why aliphatic amines were not detected in the silica gel tube samples or in the Thermosorb/A sampling devices. Since the exact cause of difficulty has not yet been identified, it would not be prudent to dismiss the use of these solid sorbents for collecting DABCO or 2,2-oxybis until further study could be performed.

The impinger sampling and analytical method described here is proposed as a method for the collection of DABCO, 2,2-oxybis, and possibly similar relatively nonpolar volatile amines. The analytical procedure was unable to determine diethanolamine satisfactorily, which is a polar aliphatic amine, but other analytical instrumentation might allow for a determination from the abundant impinger sample solution. Therefore, the impinger sampling and analytical method described here is not indicated to be a universal method for determining all volatile aliphatic amines in air. For instance, a method to collect and analyze ethanolamines was recently published using methodology that was completely different from that described here.[19] Thus the user should be aware that a single, universal method does not exist for collecting air samples for the analysis of aliphatic and alicyclic amines.

Recommendations

The broad class of compounds which contain the amine group are varied in their physical and chemical properties. One sampling and analytical method will not suffice for determining all such compounds in the air. Unfortunately, methods have not been developed for all industrially significant amines. If time permits, a literature search can be performed to identify methods that have worked with similar amine compounds. But since workplace conditions are likely to differ from the conditions in laboratory studies, it is recommended that preparations be made to use several methods for collecting amines while in the field and that these results be compared. Professional judgment can then be used to determine if further developmental work is needed.

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