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DETERMINATION OF TOLUENEDIAMINES IN POLYURETHANE FOAMS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION

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SUMMARY

A method is presented for the determination of 2,4- and 2,6-toluenediamine (TDA) in aqueous extracts of polyurethane foams. Foam samples are extracted with methyl-*tert.*-butyl ether followed by back extraction into dilute hydrochloric acid. The method utilizes reversed-phase high-performance liquid chromatography with electrochemical detection. The lower limit of detection is 1.0 ppb (ng/g) for a 10.0-g sample. The response of TDA is linear over three orders of magnitude and recovery data averaged 50% for samples spiked in the 25–50 ppb range. Confirmation of peaks attributed to TDA in the chromatographic analyses was carried out using liquid chromatography–mass spectrometry.

INTRODUCTION

Flexible polyurethane foams have had wide application in a multitude of commercial products including furniture and automotive seating, mattresses and carpet padding. It is estimated that the U.S.A. alone will have consumed about $6.0 \cdot 10^8$ kg of flexible foam in 1988 for such consumer products [1]. Toluene diisocyanate (TDI) is used in the production of a significant portion of such foams. TDI-based products would be expected to contain residual amounts of toluenediamine (TDA) as a result of hydrolysis of the free unreacted isocyanate.

Aromatic amines such as TDA are of significant health concern because several studies have indicated toxic properties of TDA isomers. The 2,4-TDA isomer has been shown to be carcinogenic in animals[2–4], giving a positive Ames test[5] and to be responsible for reproductive toxicity in rats[6,7]. Several other toxic effects of 2,4-TDA have been reported[8–10]. The 2,6-TDA isomer has been identified as a suspected carcinogen in at least one animal study[11], but other reports indicate that 2,6-TDA causes no statistically significant differences in tumor occurrence from controls[12]. The 2,5-TDA isomer, a rarely occurring isomer in commercial TDA production, has also been indicated as a toxic agent [13,14].

Though the toxic effects of 2,4- and 2,6-TDA have not been demonstrated in

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humans, they appear potentially harmful. The analysis of amines such as TDA in polyurethane foams should be of increasing interest because there are many consumer goods containing polyurethanes which involve human contact and exposure. Thus, the availability of a sensitive analytical technique for monitoring TDA in polyurethane foams and other products used in consumer products is of substantial concern.

Very little has been published on the detection of aromatic amines in foams. We previously have published a fluorimetric thin-layer chromatographic (TLC) method for TDA analysis in foams but the sensitivity was poor[15]. Several reports have focused on TDA analysis in aqueous extracts from polyurethane food bags[16–18] and analysis of airborne diamines[19]. To obtain the detection limits reported in most of these studies, laborious concentration steps and large injection volumes were required. These methods were reported to have on column detection limits of 1 ng of TDA.

Toluenediamine analysis has been done using gas chromatography[20,16], TLC[15,21], and liquid chromatography with UV detection[18,19]. These methods require significant time in sample preparation or generally are not sensitive enough to detect aromatic amines at the concentration at which they exist in actual samples, *e.g.* at ppb[a] levels. Several workers report using high-performance liquid chromatography (HPLC) with electrochemical detection (ED)[18,19], but none for TDA analysis in foams. Because solid polyurethane foams present a significant challenge in preparation for analysis, a method for such analysis is desirable.

This report presents an HPLC method which can detect 1 ppb of 2,4- or 2,6-TDA in polyurethane foams (50 pg on column). This method utilizes ED of the aromatic amines to achieve this detection limit.

EXPERIMENTAL

Reagents and materials

Methanol, methyl-*tert.*-butyl ether (MTBE), hydrochloric acid, acetic acid and ammonium acetate were purchased from Baker Chemicals (Phillipsburg, NJ, U.S.A.). The 2,4- and 2,6-toluenediamine isomers were from Aldrich (Milwaukee, WI, U.S.A.) and used without further purification. Purity of the diamines was assessed by proton NMR. Acetonitrile was from Burdick & Jackson (Muskegon, MI, U.S.A.). The infusers were either purchased locally or constructed by a machine shop. The infuser consists of a heavy duty 600-ml beaker and a stainless-steel plunger that fits tightly into the beaker. The circular bottom of the plunger has a fine mesh wire which allows passage of solvent but retention of foam. Buffers were prepared with water purified by a Milli-Q water purification system (Millipore) and filtered through a nylon-66 filter (0.45 μm). Foams were prepared from prepolymer in our laboratory or purchased locally and represent a variety of industrial foams containing various additives. Polyurethane foams are typically composed of diols and triols derived from ethylene or propylene oxides and isocyanates (aromatic or aliphatic) such as TDI. To these structural components are added catalysts such as tin salts or amines. Other additives include dyes, pigments, antioxidants, and surfactants.

[a] Throughout this article, the American billion (10^9) is meant.

Equipment

The chromatographic system consisted of: an SSI 222B pump (Scientific Systems, State College, PA, U.S.A.), a WISP autosampler (Waters Assoc., Milford, MA, U.S.A.) and electrochemical detector (Model 400 EG&G PAR, Lawrenceville, NJ U.S.A.) equipped with a glassy carbon electrode, an LCI-100 integrator (Perkin-Elmer, Norwalk, CT, U.S.A.) and a Supelcosil C_{18} column (15 cm × 4.6 mm, 5 μm particle size) Supelco, Bellefonte, PA, U.S.A.). The detector was set at +875 mV *versus* Ag/AgCl and the output at 20 nA full scale. The eluent was 3% acetonitrile, 25 m*M* ammonium acetate, 1 m*M* propylamine, pH 5.5. The flow-rate was 1.0 ml/min and the injection volume was 50 μl. The liquid chromatography–mass spectrometry (LC–MS) experiments were conducted under the same chromatographic conditions and with a Finnigan TSQ 70 mass spectrometer equipped with a thermospray interface. LC–MS data were obtained by employing buffer ionization and scanning the third quadrupole from *m/z* 121 to *m/z* 500 in 1 s. The vaporizer temperature of the interface and the source block temperature were maintained at 118°C and 220°C, respectively during the experiments.

Extraction procedure

A 10.0-g foam sample is cut into 1-cm^3 pieces or smaller, or shredded in a bean grinder. The foam is placed into the infuser beaker and 60 ml of MTBE is added. The plunger is inserted and compressed such that the entire foam is submerged. The foam is compressed and released repeatedly for 5 min. The MTBE is expressed from the foam and decanted. This extraction is repeated two more times. The extracts are combined and blown down to *ca.* 80 ml. After transferring to a 125 ml separatory funnel, 4 ml of 20 m*M* hydrochloric acid (pH 2) is added and the mixture is extracted for 10 minutes on a mechanical shaker. After the phases have separated, the lower aqueous layer is removed and an additional 4 ml of 20 m*M* hydrochloric acid is added and the extraction is performed for an additional 10 min. The aqueous extracts are combined in a 10.0-ml volumetric flask (the organic phase is discarded) and the samples brought to volume with water. This extract should be protected from light and analyzed within 48 h.

Standard preparation

Standard stock solutions of 2,4- and 2,6-TDA are prepared in methanol at a concentration of 1 μg/μl and are stable for at least 4 weeks when kept refrigerated and protected from light. From this preparation, a 2 ng/μl intermediate standard was made in methanol. Appropriate dilutions from this stock are made in water to cover the concentration range of 0.5 to 50 pg/μl. The intermediate stock solution is stable for 1 week. Working standards are prepared fresh daily.

RESULTS AND DISCUSSION

The two major difficulties encountered in the analysis of toluenediamine in polyurethane foams were obtaining adequate sensitivity and developing a quantitative extraction protocol for the solid foam samples.

TABLE I

CONCENTRATION OF TDA ISOMERS IN FOAMS (ng/g)

Foam samples (10 g) were extracted with MTBE and analyzed by HPLC–ED as described in the text. Corrected values are based on 54% recovery of 2,6-TDA and 48% recovery of 2,4-TDA.

Foam	*2,6-TDA*	*2,6-TDA (corrected)*	*2,4-TDA*	*2,4-TDA (corrected)*	*Total (corrected)*
1	1.0	1.9	0.60	1.3	3.0
2	0.89	1.7	0.22	0.46	2.2
3	0.66	1.2	0.40	0.83	2.0
4	19	35	1.2	2.5	38
5	2.4	4.4	4.0	8.3	13
6	5.1	9.4	6.0	13	22
7	12	22	4.2	8.8	31
8	7.3	14	43	90	104

Electrochemical detection

The levels of TDA found in many foams were so low that conventional UV detection cited elsewhere [17] lacked the sensitivity for accurate quantitation at the ppb level. Our own experiments with UV detectors indicated a detection limit of around 100 ppb, well above the amounts that exist in many foams (Table I). Electrochemical detectors, in contrast, are extremely sensitive and are effective in measuring aromatic amines such as TDA by electrochemical oxidation. Several other laboratories[18,19] have succesfully used this mode of detection, though the applications were different. ED was found capable of detecting 50 pg of TDA on column (signal-to-noise ratio, S/N = 4), representing 1.0 ppb of TDA in a typical 10.0-g foam sample (Fig. 1).

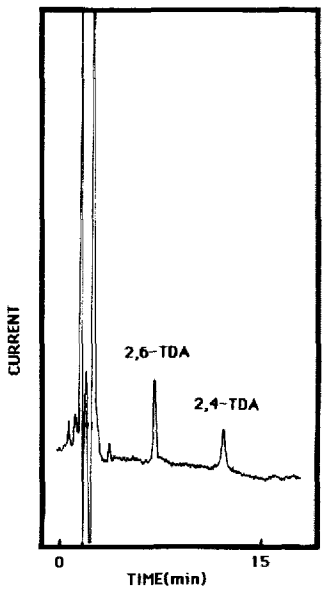

Fig. 1. Chromatogram of TDA standards. The chromatographic trace represents 1.0 ppb (50 pg on column) of each of the TDA isomers. Chromatographic conditions are given in the text.

Foam extraction study

Accurate foam analysis requires reproducible recovery and effective extraction of TDA from the solid foam matrix. Various solvents were examined for their effectiveness in extraction of TDA from spiked foams. The general protocol consisted of extraction of the foam with an organic solvent and back extraction into dilute hydrochloric acid. Organic solvents tested included MTBE, diethyl ether, ethyl acetate, chloroform methylene chloride and methanol. Also, 10–200 m*M* hydrochloric acid was tested, followed by back extraction into an organic solvent and then a final back extraction into dilute hydrocloric acid. Extractions with water and sterile saline solutions were also tested.

Recovery of TDA with methylene chloride and chloroform was poor (5–40%) and these solvents swelled the foam considerably, causing great difficulty in recovering the solvent from the foam. Ethyl acetate was judged as a poor solvent because its relatively high solubility in water (*ca.* 9%) did not allow a phase separation after the back extraction step. Diethyl ether gave relatively good results but MTBE was chosen because of its higher boiling point and the significantly cleaner chromatograms generated in its use (note Fig. 2). Overall, major considerations on the choice of solvent were immiscibility with water, volatility and efficacy in recovery of spiked TDA from the foam.

Further extraction studies indicated that three extractions of the foam with MTBE followed by two back extractions with dilute hydrochloric acid were sufficient in obtaining the maximum recovery. An additional important factor is the surface area of foam exposed. Cutting foam into small pieces or shredding of foam allowed greater recovery than that with large foam pieces.

High-performance liquid chromatography

LC analysis of TDA has been reported previously[18,19]. Both acetate and phosphate buffers have been employed. Acetate buffer at pH 5.5 with low concentrations of acetonitrile was well suited for good retention of TDA isomers and compatible with the electrochemical detector. The addition of 1 m*M* propylamine served to sharpen the TDA peaks thereby improving sensitivity slightly. Fig. 2 shows a typical chromatogram of a polyurethane foam.

Liquid chromatography–mass spectrometry

Many compounds may be extracted into the final aqueous fraction during the foam sample workup. Several peaks in addition to the TDA isomers are present, as noted in the chromatogram (Fig. 2). Co-elution of chromatographic peaks with standard materials does not constitute positive peak identification. Positive artifacts are possible, particularly in complex matrices. To confirm TDA isomers in foam extract, LC MS was performed.

LC–MS was conducted under the same chromatographic conditions as in the HPLC analysis. The thermospray LC–MS data were obtained with a Finnigan MAT TSQ-70 mass spectrometer equipped with a Finnigan thermospray interface utilizing buffer ionization. Fig. 3 shows a total-ion chromatogram and a single-ion trace of m/z 123 (MH^+ ion of TDA) of a foam extract. Only the protonated molecular ion of TDA was observed in the LC–MS mass spectrum with no fragmentation.

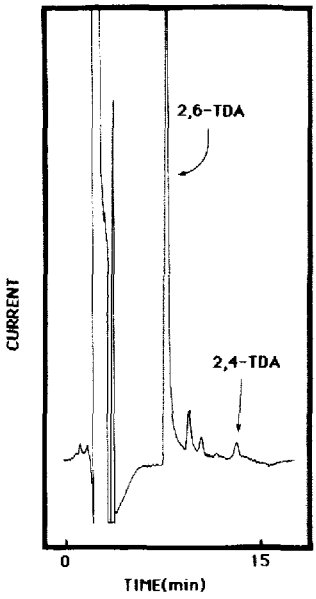

Fig. 2. Chromatogram of foam extract. The extract contained 20 ppb of 2,6-TDA and 1.5 ppb of 2,4-TDA.

Standard calibration

Response of TDA was linear in the range 0.5–500 ppb. Typically, a standard curve encompassed the range 0.5–50 ppb for a 20-nA full scale range on the electrochemical detector. Notably, even low concentrations of TDA (< 10 ppb) were stable for 2–3 days at room temperature. TDA was not irreversibly adsorbed to the glassware, as evidenced by comparison with silanized and untreated glass.

Sample preparation

Polyurethane foams typically contain significant moisture content. Freshly prepared foams contained approximately 40% water. Within 3 days at room temperature only about 10% moisture remained. Moisture content varied with relative humidity. No correction for this moisture was made for foams.

The foams were extracted as outlined in the methods section. After expression of MTBE, the foams were weighed and found to retain about 4 g solvent/10 g foam, or about 2% of the total solvent volume used in the three successive extractions. The results of LC–ED analysis from several foams are given in Table I. Corrected values of TDA below 1.0 ppb (ng/g), though less than the stated detection limit, are derived from peak areas where S/N is less than 4.

Precision and recovery

Precision was determined by analysis of six preparations of a single foam sample. Duplicate injections of each preparation were made. The precision of the method was 13% R.S.D.

Recovery was determined by spiking foams directly with TDA and then ex-

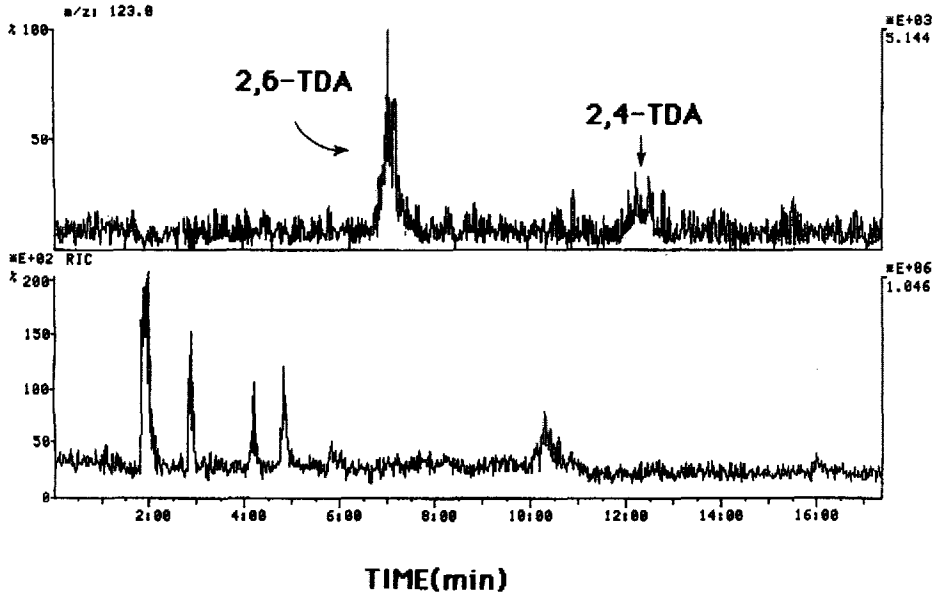

Fig. 3. Ion chromatograms from LC–MS analysis. Total (bottom) and selected (top) ion chromatograms from LC–MS foam extract. Conditions are given in the text.

tracting and analyzing by HPLC. Foams were spiked at 25 and 50 ppb. Results are summarized in Table II. Corrections were based on a typical TDA foam concentration.

It is unclear why the recovery of TDA from foams is so low, nevertheless it is

TABLE II

SPIKE AND RECOVERY DATA FOR 2,6-TDA AND 2,4-TDA

Foam samples (10 g) were spiked with 250 and 500 ng of TDA in methanol, extracted with MTBE and analyzed by HPLC–ED as described in the text.

Sample	*Recovery (%)*	
	2,6-TDA	*2,4-TDA*
1 at 25 ng/g	53	49
2	64	50
3	64	50
4	48	45
5	50	48
1 at 50 ng/g	55	48
2	51	49
3	59	55
4	60	57
5	40	32
	$\bar{x}$ = 54	$\bar{x}$ = 48

reproducible. Part of the difficulty may be in factors associated with the spiking of solid samples and spiking at such low levels. Extensive studies of the extraction steps showed very good recovery of TDA during the back extraction. The difficulty lies in the initial ether extraction step. It appears that the aromatic amines strongly adhere to the foam matrix in spite of the repeated extraction of shredded foam.

We reported in 1977[15] that several polyurethane foams contained up to 400 ppm of 2,4-TDA and 80 ppm of 2,6-TDA. The method, now obsolete, was based on methanol extraction and TLC with fluorimetric detection. Reinvestigation of this TLC procedure indicated that a urea derivative often overlapped the TDA spot causing gross overestimation of the TDA content. Later analysis of the same foams by an early version of the present HPLC method gave TDA values one to three orders of magnitude lower (0.1–5 ppm). We concluded that the TLC method had given artificially high values. This information, together with the present data indicate an apparent decline in free TDA over the last decade, but we are unable to conclude whether this reflects changes in foam-making technology or is simply an artifact of sample selection.

CONCLUSIONS

This is the first HPLC–ED method applied to the determination of TDA in polyurethane foams and provides the best sensitivity reported to date, allowing quantitative analysis of levels of TDA found in real samples. In addition, the presence of TDA isomers in the foam extract has been confirmed by LC–MS. Fig. 2 indicates that several other components are present in the foam extract. Attempts to identify any of these compounds were unsuccessful. It is assumed that they may be other types of aromatic amines or basic compounds.

Though this work was initially designed for analysis of relatively simple foams it appears to be applicable to many commercial foams based on our results with several industrial foams chosen at random. Our major interest was in foams that would be compatible with human tissues. This puts severe limitations on ingredients that may be used. In contrast, industrial foams may contain many components and additives such as dyes, antioxidants and surfactants. Such additives can contribute to problems with the extraction or interferences in chromatography though we experienced no significant problem with such. Thus, this HPLC–ED method provides excellent sensitivity for TDA analysis in a variety of commercial polyurethane foams.

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