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Organic analysis by ion chromatography
1. Determination of aromatic amines and aromatic diisocyanates by cation-exchange chromatography with amperometric detection

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Abstract

A method has been developed for the simultaneous determination of a range of aromatic amines using cation-exchange chromatography performed on a standard ion chromatography column using d.c. amperometric detection. The analytes separated were 2,4- and 2,6-toluenediamine (2,4- and 2,6-TDA), aniline, *o*-toluidine, benzidine, *p*-chloroaniline, 4,4′-diaminodiphenyl (4,4′-DDP), *m*-nitroaniline and 1-naphthylamine. A Dionex CS12 column was used with gradient elution from an initial eluent of 5% CH_3CN+35 m*M* H_2SO_4 to 27% CH_3CN+35 m*M* H_2SO_4 (at 35 min). Detection limits in the range 2.6–22.6 μg/l were observed for all analytes except *m*-nitroaniline, for which the detection limit was 201 μg/l. Linear calibrations and good precision were observed and the method was applied to the determination of benzidine, *p*-chloroaniline and 1-naphthylamine in wastewater samples. Further, the separation was also used (after some modification of the eluent conditions) for the determination of 2,4- and 2,6-toluene diisocyanate (2,4- and 2,6-TDI) and 4,4′-methylenediphenyl diisocyanate (4,4′-MDI) after their hydrolysis to 2,4-TDA, 2,6-TDA and 4,4′-DDP. Detection limits for 2,6- and 2,4-TDI and 4,4′-MDI were 3.8, 8.2, and 11.2 μg/l, respectively. The method was applied to the determination of diisocyanates in air.

Keywords: Amines; Diisocyanates; Isocyanates; Anilines

1. Introduction

Ion chromatography (IC) has developed into the method of choice for the simultaneous determination of mixtures of inorganic anions or cations. The technique has also often been extended to the determination of low molecular mass organic ionic species, such as C_1–C_5 carboxylic acids, sulfonic acids, amines, etc. These organic species are characterised by a predominance of their electrostatic features (i.e. the degree of charge) rather than other features, such as hydrophobicity. The stationary phases for IC have been developed extensively, such that current stationary phases are highly efficient and selective.

The application of IC to larger organic ions is

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much less common, due probably to the relatively low sensitivity with which these species can be detected using conductometric methods. However, there are broad opportunities to utilise the highly efficient ion-exchangers developed for IC for the determination of larger organic ions, especially if sensitive detection methods are used. In this paper we demonstrate the utility of this approach by investigating the separation of aromatic diisocyanates and aromatic amines by cation-exchange IC using amperometric detection.

Aromatic amines, such as 2,4-, 2,6-toluenediamine (2,4- and 2,6-TDA), aniline, *o*-toluidine, benzidine, *p*-chloroaniline, 4,4′-diaminodiphenyl (4,4′-DDP), *m*-nitroaniline and 1-naphthylamine, are involved in many industrial processes. These species are also used widely as intermediates in the synthesis of dyestuffs, cosmetics, medicines and rubber [2–4]. They can be released into the environment directly as industry waste [1], or indirectly as breakdown products of herbicides and pesticides. Due to their high solubility in water, aromatic amines can readily permeate through soil and contaminate ground water, ultimately being present at trace levels in drinking water [5]. They are strongly toxic and are suspected carcinogens [6]. In view of the environmental importance of these compounds, a rapid and sensitive method of analysis is needed to detect them in water samples.

Aromatic isocyanates are used predominantly in the production of polyurethane polymers, elastomers, flexible and rigid foams, and glues. 4,4′-Methylenediphenyl diisocyanate (MDI),and 2,4- and 2,6-toluene diisocyanate (TDI) are the most frequently used monomer isocyanates. Occupational exposure to these compounds is a recognised hazard [7–9], with high concentrations of TDI causing irritation of the mucous membranes, exacerbation of asthma and possibly also progressive impairment of pulmonary function [10].

The most common techniques for the determination of aromatic amines in environmental waters are gas chromatography (GC) coupled with different detectors (usually after derivatisation and often involving hazardous reagents) [3,11], high-performance liquid chromatography (HPLC) [12–14], capillary zone electrophoresis (CZE) [15], and ultraviolet spectrophotometry [16]. Procedures for the determination of TDI and MDI monomers include colorimetric procedures [17–19], GC [20,21], thin-layer chromatography [22] and more recently, HPLC with ultraviolet [23] or fluorescence detection [24]. These methods have been applied to commercial polyurethanes [25,26], urine and plasma [10,27–30]. However, there is no suitable method available for the simultaneous determination of 2,6-TDI, 2,4-TDI and 4,4′-MDI in air samples. However, TDI and MDI can be readily hydrolyzed into TDA and DDP [10,17,18], so these diisocyanates can be determined by monitoring the resultant aromatic amines.

The purpose of the present study was to develop an IC method using d.c.-amperometric detection for the determination of 2,4-TDA, 2,6-TDA, aniline, *o*-toluidine, benzidine, *p*-chloroaniline, 4,4′-DDP, *m*-nitroaniline and 1-naphthylamine in water samples. This approach was then to be applied to the determination of TDI and MDI after hydrolysis of these species to TDA and DDP.

2. Experimental

2.1. Reagents

Stock solutions containing 2,4-TDA, 2,6-TDA, aniline, *o*-toluidine, benzidine, *p*-chloroaniline, 4,4′-DDP, *m*-nitroaniline and 1-naphthylamine, sulfuric acid, sodium sulfate and acetonitrile were prepared from analytical reagent chemicals (purchased from Shanghai Chemical Reagents, Shanghai, China). All solutions including eluents, stock solutions, and standard solutions were prepared with doubly distilled water.

2.2. Instrumentation

The ion chromatograph used in these experiments was a Dionex (Sunnyvale, CA, USA) Model DX500 micro-column instrument equipped with a GP50 gradient pump, an ED40 electrochemical detector with glassy carbon electrode, a Dionex IonPac CG12 (50×2 mm, I.D.) guard column and an IonPac CS12 (250×2 mm, I.D.) analytical column. The sample injection volume in all cases was 25 μl. Data were acquired by using Peaknet 5.0 software installed on a Dell P-III 550 computer.

2.3. Wastewater and air samples

Wastewater samples were filtered through a 0.45 μm membrane filter and injected directly onto the column. To hydrolyze the 2,4-TDI, 2,6-TDI and 4,4′-MDI, a 5-ml solution containing 3.5% (v/v) hydrochloric acid and 4.4% (v/v) acetic acid was placed into an impinger, which was then connected to a pump sampling at 1 ml/min of air, with the sampled air passing through the impinger solution through this solution. After 2 h, hydrolysis was complete and the solution was filtered through a 0.45 μm membrane filter and injected directly.

3. Results and discussion

3.1. Gradient elution separation of aromatic amines

The separation of the aromatic amines was approached using cation ion-exchange chromatography with mixtures of sulfuric acid and acetonitrile as eluent. The role of the sulfuric acid was to protonate the analytes and to also provide H^+ as the eluent competing ion. The CH_3CN was added to reduce hydrophobic absorption of the analytes and to decrease the retention times. The optimal gradient profile is shown in Table 1, and Fig. 1 shows the separation obtained under these conditions using amperometric detection. Voltage at a glassy carbon electrode with a working voltage of 1.00 V was chosen as the best signal–noise ratio for all anilines.

Using the separation conditions shown in Table 1, linear calibration plots (R^2>0.989) were obtained for all analytes when peak area was plotted against analyte concentration. Detection limits determined at a signal-to-noise ratio of 3 for 2,4-TDA, 2,6-TDA, aniline, *o*-toluidine, benzidine, *p*-chloroaniline, 4,4′-DDP, *m*-nitroaniline and 1-naphthylamine were 3.5, 7.3, 5.0, 7.4, 21.2, 16.3, 2.6, 201, and 22.6 μg/l, respectively. The percentage relative standard deviations determined for 10 replicate injections were in the range 0.08–0.62% for retention times, 4.0–8.1% for peak height, and 2.5–7.8% for peak area.

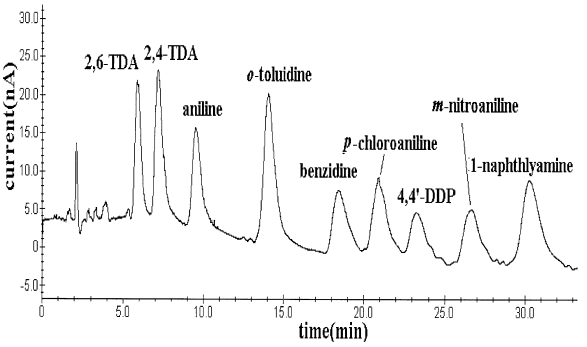

Fig. 1. Separation of a standard solution of aromatic amines. Conditions: column, Dionex IonPac CG12 (50×2 mm) and CS12 (250×2 mm); eluent, gradient from 5% CH_3CN+35 m*M* H_2SO_4 to 27% CH_3CN+35 m*M* H_2SO_4; flow-rate, 0.25 ml/min; detection, amperometric detector with glassy carbon electrode operated at 0.80 V vs. saturated calomel electrode (SCE); sample, 25 μl containing 1.0 μg/ml of each amine.

The separation shown in Fig. 1 can be applied to the determination of any of the constituent analytes. As an example, a wastewater sample was analysed and the results shown in Table 2 were obtained for the raw wastewater and the same sample spiked with benzidine, *p*-chloroaniline and 1-naphthylamine. Recoveries were in the range 99.95–100.9% for an added benzidine, *p*-chloroaniline and 1-naphthylamine concentration of about 1 μg/ml.

3.2. Chromatographic determination of diisocyanates

Under acidic conditions, 2,4-TDI, 2,6-TDI and

Table 1
Gradient profile for separation of aromatic amines by cation-exchange IC

Time (min)	Flow (ml/min)	A (%)	B (%)	C (%)	Comment
Initial	0.5	52	35	12	
0	0.5	52	35	12	Sample injection
0.5	0.5	52	35	12	
35	0.5	38	35	27	Start of step gradient
35.1	0.5	52	35	12	End of step gradient

Table 2
Analysis of wastewater

Species	Concentration found in wastewater (μg/ml)	Concentration of added standard (μg/ml)	Recovery (%)
Benzidine	0.146	1.15	100.2
p-Chloroaniline	0.129	1.14	100.9
1-Naphthylamine	0.679	1.64	99.9

4,4′-MDI (structures shown in Fig. 2) are hydrolysed to 2,4-TDA, 2,6-TDA and 4,4′-DDP [10,17,18]. The separation of these amines shown in Fig. 1 provides a means to indirectly determine the diisocyanates. However, it was necessary to modify the separation conditions in order to improve the separation of 2,4-TDA and 2,6-TDA and also to decrease the analysis time. For these reasons, eluents comprising

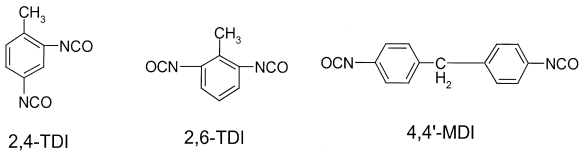

Fig. 2. Structures of 2,4-TDI, 2,6-TDI and 4,4′-MDI.

sulfuric acid, sodium sulfate and acetonitrile were investigated. Table 3 shows retention behaviour of 2,4-TDA and 2,6-TDA when these eluent parameters were varied, whilst Fig. 3 shows the effect of acetonitrile concentration on the retention time of 4,4′-DDP. These data show that addition of relatively large amounts of acetonitrile to the eluent were necessary to elute 4,4′-DDP in a reasonable time, and this eluent parameter was also the most effective means of improving the resolution of 2,4-TDA and 2,6-TDA. Simultaneous determination of 2,4- and 2,6-TDA and 4,4′-DDP could be accomplished using a step-gradient in which an initial eluent composition of 3% CH_3CN, 12 m*M* H_2SO_4 and 25 m*M* Na_2SO_4 was replaced after 8.0 min with an eluent comprising 30 m*M* H_2SO_4 and 40% CH_3CN. These conditions

Table 3
Effects of concentration of acetonitrile, sulfuric acid and sodium sulfate on retention time and resolution

Eluent parameter	Retention time of 2,6-TDA (min)	Retention time of 2,4-TDA (min)	Resolution
% (v/v) CH_3CN (eluent also contained 10 m*M* H_2SO_4 and 40 m*M* Na_2SO_4)			
1	11.72	19.96	1.486
3	9.45	13.9	1.037
5	8.6	11.9	0.753
8	7.65	10.15	0.692
10	7.95	10.68	0.773
12	8.62	11.68	0.887
15	7.93	10.43	0.679
[H_2SO_4] (m*M*) (eluent also contained 3% (v/v) CH_3CN and 40 m*M* Na_2SO_4)			
7	19.85	12.75	1.259
10	14.32	9.82	1.037
12	12.18	8.47	1.038
15	9.83	7.08	0.827
17	10.8	7.35	1.000
20	9.45	6.53	0.964
[Na_2SO_4] (m*M*) (eluent also contained 3% (v/v) CH_3CN and 12 m*M* H_2SO_4)			
20	16.35	10.87	1.166
25	13.48	9.45	1.040
30	12.73	8.87	1.038
35	12.17	8.5	1.003
40	12.18	8.47	1.038

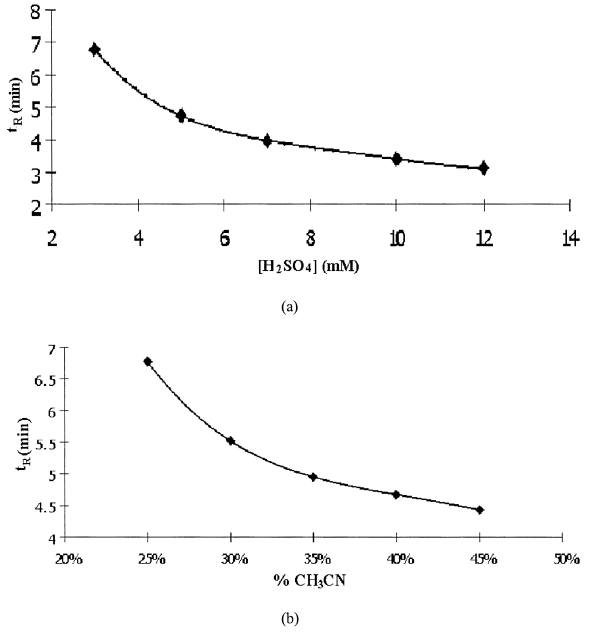

Fig. 3. Effects of (a) [H_2SO_4] (at 25% CH_3CN) and (b) % CH_3CN (at 30 m*M* H_2SO_4) on the retention of 4,4′-DDP.

were obtained by simultaneous optimization of all eluent parameters and the chromatogram obtained under the optimal conditions is given in Fig. 4.

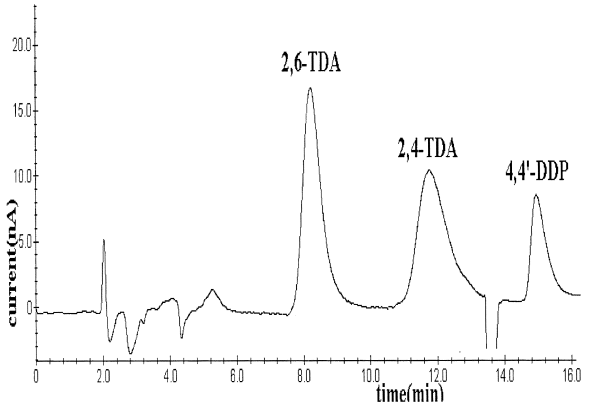

Fig. 4. Separation of a standard solution containing 2,4-TDA, 2,6-TDA and 4,4′-DDP. Conditions: column, Dionex IonPac CG12 (50×2 mm) and CS12 (250×2 mm); eluent, step-gradient from initial conditions of 3% CH_3CN+12 m*M* H_2SO_4, changing at 8 min to 40% CH_3CN+30 m*M* H_2SO_4; flow-rate, 0.25 ml/min; detection, amperometric detector with a glassy carbon electrode operated at 0.80 V vs. SCE; sample, 25 μl containing 2 μg/ml 2,4-TDA, 2 μg/ml 2,6-TDA and 6 μg/ml 4,4′-DDP.

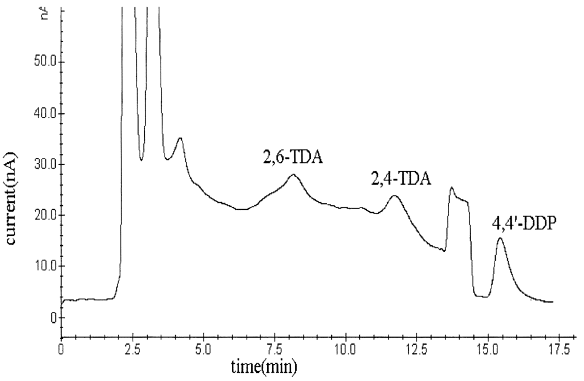

Fig. 5. Chromatogram of 2,6-TDA, 2,4-TDA and 4,4′-DDP in an air sample. Conditions as for Fig. 4. Sampled air was passed through an impinger containing 5 ml 3.5% (v/v) hydrochloric acid and 4.4% (v/v) acetic acid at 1 ml/min for 2 h, with the solution then filtered through a 0.45 μm membrane filter and injected directly.

Using the optimal separation conditions, calibrations for 2,6-TDA and 2,4-TDA were prepared over the range 0.1–4.0 μg/ml and for 4,4′-DDP over the range 0.3–12.0 μg/ml. These calibrations were linear for both peak heights (R^2>0.997) and peak areas (R^2>0.997). Detection limits determined at a signal-to-noise ratio of 3 for 2,6-TDA, 2,4-TDA and 4,4′-DDP were 2.7, 5.7 and 8.8 μg/l, respectively, which corresponded to detection limits for 2,6-TDI, 2,4-TDI and 4,4′-MDI of 3.8, 8.2 and 11.2 μg/l, respectively. Precision studies for 10 replicate injections gave percentage relative standard deviations for the three analytes in the range of 1.2–4.1% for retention time, 1.6–3.5% for peak area, and 1.7–4.4% for peak height.

The proposed method was applied to the determination of diisocyanates in air samples by their conversion to amines in the impinger solution (Fig. 5). Results are given in Table 4, which shows that detectable amounts of the diisocyanates were measured and recoveries in the range 99.6–105.9% were obtained for 2,6-TDA, 2,4-TDA and 4,4′-MDI added to the impinger solution.

4. Conclusions

Simultaneous determination of 2,4-TDA, 2,6-TDA, aniline, *o*-toluidine, benzidine, *p*-chloroaniline, 4,4′-DDP, *m*-nitroaniline and 1-naphthyl-

Table 4
Determination of diisocyanates in air samples

Analyte	Concentration of amines in impinger solution (μg/l)	Concentration of diisocyanate in air (mg/m^3)	Concentration of added standard to impinger solution (μg/l)	Recovery (%)
2,6-TDA	319.9	24.7	500	105.9
2,4-TDA	763.0	43.9	500	99.6
4,4′-DDP	5199	273.5	3000	103.3

amine was achieved using cation-exchange IC with detection by d.c.-amperometry. The separation of this group of moderately large organic ions shows that the IC stationary phases developed primarily for the separation of inorganic ions can also be used for organic species. Moreover, the developed separation of aromatic amines was found to be applicable to the determination of several diisocyanates after their hydolysis to amines.

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