Determination of *N,N*-Dimethyl-o-Toluidine and *N,N*-Diethyl-p-Toluidine in Ethylene Gas Samples

INTRODUCTION

Amines are found throughout nature and are synthesized for many commercial applications. They are used as pharmaceuticals, anti-corrosive agents, and chemical intermediates, and can indicate food spoilage. Ion chromatography (IC) with either suppressed conductivity or integrated amperometry detection is an excellent technique for determining amines in a variety of samples, even at low concentrations.[1-3] Dionex has designed high-performance cation-exchange columns, the IonPac® CS17 and IonPac CS18, to separate amines from common inorganic cations and ammonium and deliver good peak shapes. Although these columns can be used for a number of amines with a weak (< 50 mM) methanesulfonic acid (MSA) eluent, some amines do require the addition of an organic solvent, usually acetonitrile, to the eluent to achieve good peak shape and shorten analysis time. There are also some amines that can be detected successfully by UV absorbance. Here is shown the separation and detection of two such amines: *N,N*-dimethyl-o-toluidine and *N,N*-diethyl-p-toluidine. These amines are separated on a CS17 column with an MSA gradient and 9% acetonitrile, and are detected by absorbance at 210 nm. This method was used to monitor *N,N*-dimethyl-o-toluidine and *N,N*-diethyl-p-toluidine in ethylene gas. The gas was bubbled into a solution of MSA to trap the amine impurities.

EXPERIMENTAL

Equipment

Dionex ICS-3000 Reagent-Free™ Ion Chromatography system with:

> DP Dual Pump module[a]
>
> DC Detector/Chromatography module
>
> AS Autosampler[b]

PDA-100 Photodiode Array Detector[c]

Chromeleon® 6.8 Chromatography Management Software

[a]*For this application, a Single Pump (SP) module can also be used.*
[b]*An AS40 Autosampler can also be used for this application.*
[c]*A VWD Variable Wavelength Detector can also be used for this application if spectral identification is not needed.*

Reagents and Standards

Deionized (DI) water, Type I reagent grade, 18 M -cm resistivity or better

N,N-dimethyl-o-toluidine ($C_9H_{13}N$)

N,N-diethyl-p-toluidine ($C_{11}H_{17}N$)

Methanesulfonic acid (MSA) (CH_4O_3S)

Acetonitrile (CH_3CN)

All compounds were ACS reagent grade or better from reliable sources. The N,N-dimethyl-o-toluidine ($C_9H_{13}N$) and N,N-diethyl-p-toluidine ($C_{11}H_{17}N$) were gifts from a Dionex customer, but N,N-dimethyl-o-toluidine can be obtained from Sigma-Aldrich (St. Louis, MO, USA) and both compounds from R.S.A. Corporation (Danbury, CN, USA).

Conditions

Column: IonPac CS17 2 × 250 mm (P/N 060561)*

Eluents: (E1) DI water
(E2) 100 mM Methanesulfonic acid
(E3) 90% Acetonitrile

Gradient Steps:

Time (min)	%E1	%E2	%E3
–7.0	86	4	10
0.0	86	4	10 (inject)
3.5	86	4	10
12.0	10	80	10
15.9	10	80	10
16.0	86	4	10

Flow Rate: 0.4 mL/min

Inj. Volume: 100 µL

Column Oven: 40 °C

System Backpressure: 2400-2800 psi

Detection: UV at 210 nm (PDA mode)

A guard column was not used for this application in order to keep the backpressure under 3000 psi. The system and column can accommodate higher backpressures but all fittings must be tight to avoid leaks.

Preparation of Reagents

Methanesulfonic acid (MSA) 100 mM

Dissolve 9.610 g of MSA in a 1 L volumetric flask containing approximately 300 mL of deionized water. Bring to volume with deionized water, mix well, degas, and transfer to an eluent bottle.

90% Acetonitrile

Mix 900 mL of acetonitrile and 100 mL of deionized water. Mix well and degas.

Preparation of Standard Solutions

Stock Standards

Prepare 1000 mg/L standards for each of the analytes in eluent (4 mM MSA, 9 % acetonitrile). Standards should be prepared from the highest purity compounds available. Table 1 provides the amounts needed to prepare 100 mL of each standard. Concentrated standards are stable for at least one month when stored at 4 °C.

Table 1. Masses of Compounds Used to Prepare 100 mL of 1000 mg/L Amine Standards		
Analyte	**Compound**	**Amount (g)**
N,N-dimethyl-o-toluidine	N,N-dimethyl-o-toluidine	0.100
N,N-diethyl-p-toluidine	N,N-diethyl-p-toluidine	0.100

Secondary Standards

The stock standards are used to prepare the calibration standards listed in Table 2. For example, the level 3 standard is prepared by adding 1 mL each of the 1000 mg/L stock standards of N,N-dimethyl-o-toluidine and N,N-diethyl-p-toluidine to a 100 mL volumetric flask and then bringing to volume with eluent (4 mM MSA, 9 % acetonitrile).

Table 2. Standard Concentrations for Method Calibration			
Analyte	**Concentration (mg/L)**		
	Level 1	**Level 2**	**Level 3**
N,N-dimethyl-o-toluidine	1	5	10
N,N-diethyl-p-toluidine	1	5	10

Column:	IonPac CS17 (2 mm)		
Eluent:	(E1) Water		
	(E2) 100 mM MSA		
	(E3) 90% CH₃CN		

Gradient Steps: Time (min)	%E1	%E2	%E3
−7.0	86	4	10
3.5	86	4	10
12.0	10	80	10
15.9	10	80	10
16.0	86	4	10

Temperature:	40 °C
Flow Rate:	0.4 mL/min
Inj. Volume:	100 µL
Detection:	UV, 210 nm
Sample:	MSA blank
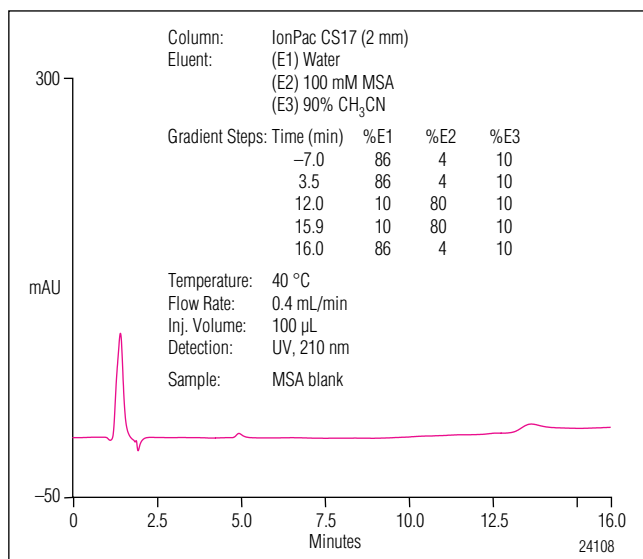
Figure 1. Chromatography of the MSA blank.

Preparation of Samples

A Milligan gas washing tower (scrubber) was charged with 100 mL of 25 mM MSA solution. Prior to bubbling the gas through the MSA solution in the Milligan bottle, a sample was removed to serve as a blank. To trap the amines, the ethylene gas was bubbled (scrubbed) through the bottle at a flow rate of 200 mL/min (steady stream of bubbles) until the sample cylinder was empty. These samples were kindly provided by a customer.

RESULTS AND DISCUSSION

Figures 1 and 2 show the results of the method development for the separation of *N,N*-dimethyl-o-toluidine and *N,N*-diethyl-p-toluidine on the IonPac CS17 column. The separation uses a short isocratic 4 mM MSA eluent followed by a gradient from 4 to 80 mM MSA all in the presence of 9% acetonitrile. The acetonitrile is added to ensure the best peak shapes for these hydrophobic amines. Figure 2 shows the baseline separation of the amines at three concentrations. While wavelength scans of these amines (Figures 3 and 4) reveal that they can be detected at approximately 260 nm, 210 nm was chosen for the best sensitivity. The choice of 210 nm will reduce the selectivity of the detection, but analysis of an MSA blank (Figure 1) reveals that there are no interfering peaks at the retention times of *N,N*-dimethyl-o-toluidine and *N,N*-diethyl-p-toluidine. The spectral scans were added to a library used for confirming the presence of these amines in samples.
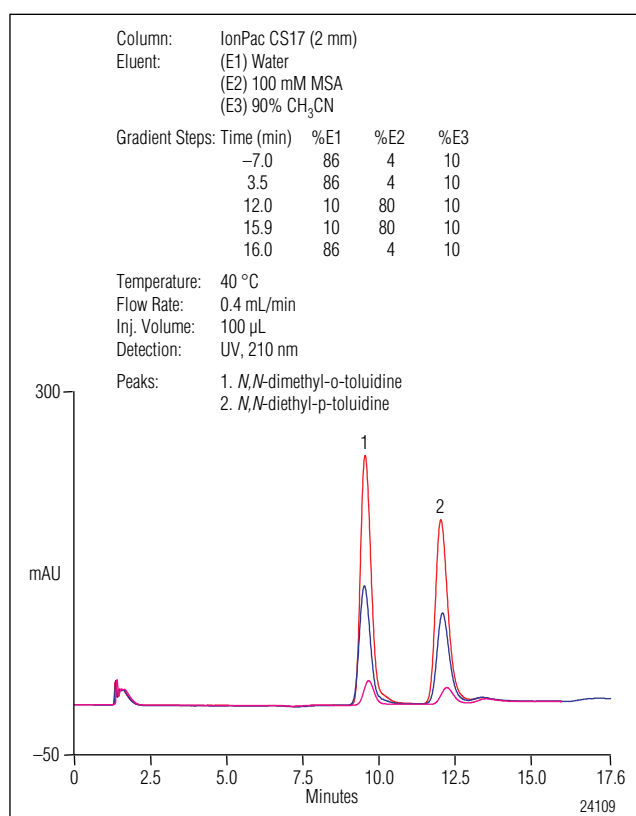

Column:	IonPac CS17 (2 mm)		
Eluent:	(E1) Water		
	(E2) 100 mM MSA		
	(E3) 90% CH₃CN		

Gradient Steps: Time (min)	%E1	%E2	%E3
−7.0	86	4	10
3.5	86	4	10
12.0	10	80	10
15.9	10	80	10
16.0	86	4	10

Temperature:	40 °C
Flow Rate:	0.4 mL/min
Inj. Volume:	100 µL
Detection:	UV, 210 nm
Peaks:	1. *N,N*-dimethyl-o-toluidine
	2. *N,N*-diethyl-p-toluidine

Figure 2. Separation of three mixed standard solutions of N,N-*dimethyl-o-toluidine and* N,N-*diethyl-p-toluidine (1, 5, and 10 mg/L each) using the method in Figure 1.*

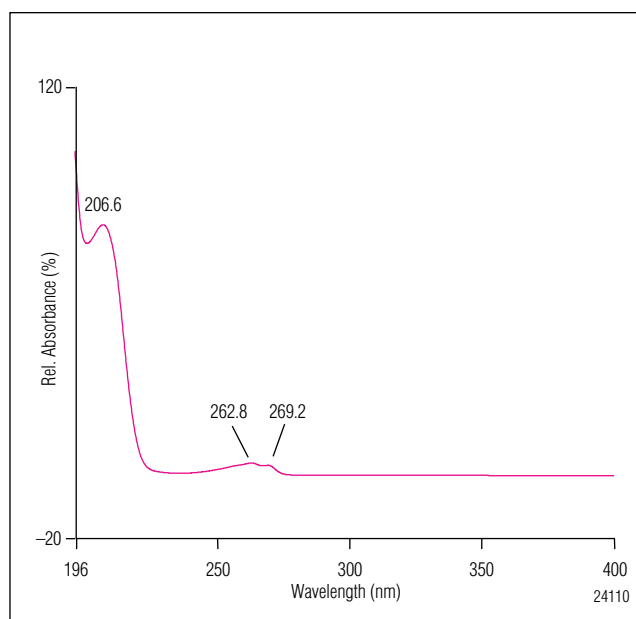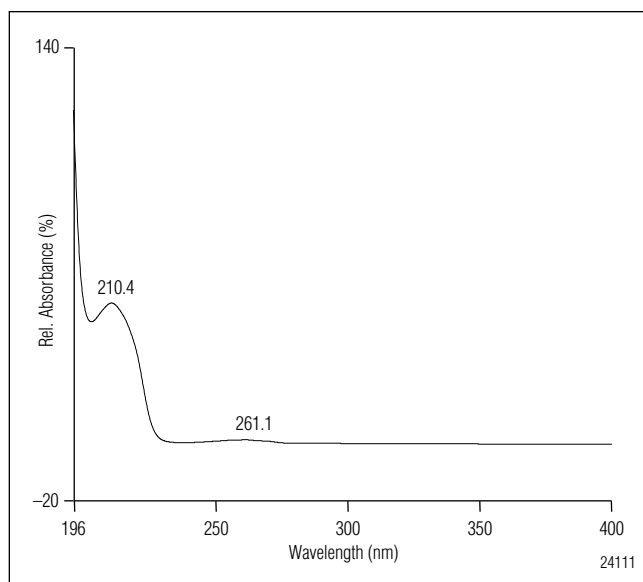Figure 3. Spectral scan of N,N-*dimethyl-o-toluidine (5 mg/L).*

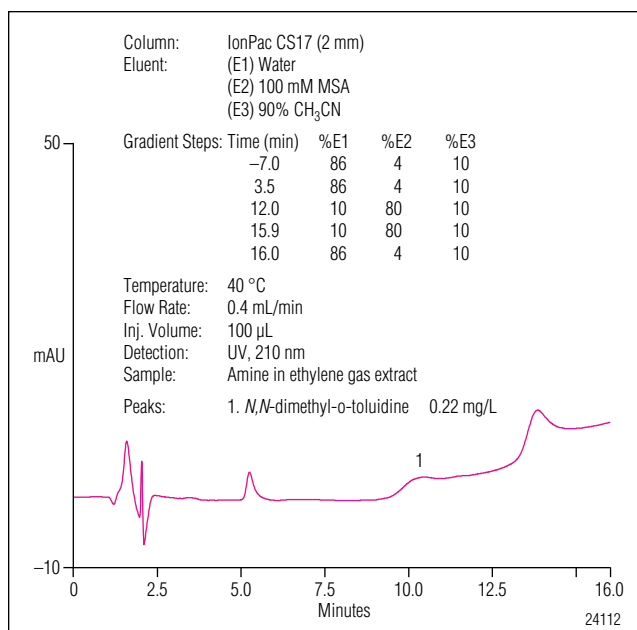Figure 4. Spectral scan of N,N-*diethyl-p-toluidine (5 mg/L)*.

Figure 5. Chromatogram of the extract (scrubbed) of an ethylene gas sample using the method in Figure 1.

Table 3. Method Calibration Results as Reported by Chromeleon				
Peak Name	**Coeff.Det. %**	**R-Square %**	**Offset**	**Slope**
N,N-dimethyl-o-toluidine	99.9911	99.9910	−0.6125	8.9901
N,N-diethyl-p-toluidine	99.9880	99.9880	−1.3458	8.3587

Prior to sample analysis the system was calibrated using single injections of three concentrations of the two amines shown in Table 2 and Figure 2. Calibration (linear) results are shown in Table 3. Fourteen samples were analyzed, seven scrubbed ethylene gas samples and their seven corresponding blanks. *N,N*-diethyl-p-toluidine was not detected in any of the samples, but three samples had *N,N*-dimethyl-o-toluidine, all below the lowest concentration of the calibration standards. Figure 5 shows a chromatogram of one of the samples that had *N,N*-dimethyl-o-toluidine. Its presence was confirmed by a spectral match with the library.

This application update shows that IC columns designed for determining amines with suppressed conductivity and IPAD can also be used with MSA gradients and UV absorbance detection to determine amines not commonly determined by IC.

REFERENCES

1. Dionex Corporation. *Determination of Cations and Amines in Hydrogen Peroxide by Ion Chromatography Using a RFIC™ (Reagent-Free) System.* Application Update 155; LPN 1832. Sunnyvale, CA, 2006.
2. Dionex Corporation. *Determination of Biogenic Amines in Alcoholic Beverages by Ion Chromatography with Suppressed Conductivity and Integrated Pulsed Amperometric Detection.* Application Note 182; LPN 1888. Sunnyvale, CA, 2007.
3. Dionex Corporation. *Determination of Biogenic Amines in Fermented and Non-Fermented Foods Using Ion Chromatography with Suppressed Conductivity and Integrated Pulsed Amperometric Detections.* Application Note 183; LPN 1889. Sunnyvale, CA, 2007.

Passion. Power. Productivity.

DIONEX