Printed in the Republic of Korea
ANALYTICAL SCIENCE & TECHNOLOGY
Vol. 20, No. 3, 255-260, 2007

Notes

Simultaneous determination of low molecular weight amines and quaternary ammonium ions by IC/ESI-MS

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(Received May 9, 2007; Accepted May 31, 2007)

Abstract: A new method for the simultaneous determination of low molecular weight amines and quaternary ammonium ions based on the separation by IC with a suppressor and the detection by MS with ESI has been developed. The method has been applied to the analysis of a mixture containing tetramethylammonium ion, tetraethylammonium ion, tetrapropylammonium ion, triethanolamine, trimethylamine and triethylamine. The constituents were separated by isocratic elution using an IonPac CS17 column, a cation-exchange column, and detected by conductivity and mass spectrometry. The newly developed method for the six components demonstrated that the repeatability in terms of relative standard deviation for three measurements was in the range of 0.1-0.5 %. The detection limits were between 0.2 and 0.9 μg/mL by the IC/ESI-MS.

Key words : IC/ESI-MS, low molecular weight amine, quaternary ammonium ion

Introduction

Amines and their derivatives are compounds which are widely used as raw materials or intermediates in the manufacture of industrial chemicals, e.g., medicines, pesticides, dyestuffs and corrosion inhibitors.[1] These amines are discharged into the many different matrices such as natural and waste waters or gaseous emission from several industries and wastewater treatment plants.[2-3] The occurrence and determination of low molecular weight amines have received a great deal of attention in recent years.

To date several analytical techniques for the determination of low molecular amines have been used, including gas chromatography,[4] high performance liquid chromatography,[5] capillary electrophoresis[6] and ion chromatography.[7]

The analyses of most of the amines and quaternary ammonium ions by LC methods have always been difficult due to the lack of a suitable chromophore and the peak shape with asymmetry or tailing.[8-9] For this reason most of these methods incorporate a derivatization before the chromatographic step to increase sensitivity of the analysis. LC-MS methods are now available by ion chromatography (IC) and mass spectrometry (MS) for the separation and detection of ionic compounds, respectively.[10] However, the eluents mostly used in the IC are not compatible with MS, that is, the eluents containing

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high salt concentrations are used in IC, which makes it difficult to interface the two techniques. To make the IC eluent compatible with MS, a desalting device, called suppressor, should be used to remove salts from the eluent before it enters MS. Recently MS offers two interfaces, electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), both of which can be operated in the positive ion mode. Often, an appropriate selection for a given analyte can be made by considering that ESI transfers ions from the solution into the gas phase, whereas APCI ionizes the analyte in the gas phase. As a rule, analytes occurring as ions in solution may be best analyzed by ESI, while non-ionic analytes may be well suited for APCI.

In the past several years, there have been many publications to explore the feasibility of coupling an IC to ESI interface to obtain on-line mass analysis from organic ions dissolved in the chromatographic effluent. These publications were to study common organic anions, including byproduct anions, perchlorates, bromates, oxyhalides and haloacetic acids.[11-16] To the best of our knowledge no attempt has been made to study cations, especially low-molecular weight amines and quaternary ammonium ions by IC/ESI-MS. However, some investigations regarding to biogenic amines were reported.[17] The purpose of this study was for the first time to examine the applicability of the separation and the detection of cations such as low-molecular weight amines and quaternary ammonium ions by an IC/ESI-MS coupling method.

2. Experimental

2.1. Chemicals

Water of 18 MΩ obtained from Milli-Q system (Millipore, USA) was used to prepare eluent and all solutions. Methanesulfonic acid was from Fluka (Steinheim, Germany). Acetonitrile was of HPLC grade (Burdick & Jackson, Korea). Ammonium chloride was obtained from the DC Chemical (Seoul, Korea). Trimethylamine, tetramethylammonium hydroxide, tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium hydroxide, triethylamine, triethanolamine, tripropylamine and tributylamine were obtained from Aldrich (Milwaukee, USA).

2.2. Preparation of sample solutions for IC/ESI-MS

Stock solutions of the compounds used in this study, each of 100.0 μg/mL, were prepared by deionized water and stored in the dark at 4 °C for further use. Working standard solutions were prepared daily by appropriate dilution of the stock

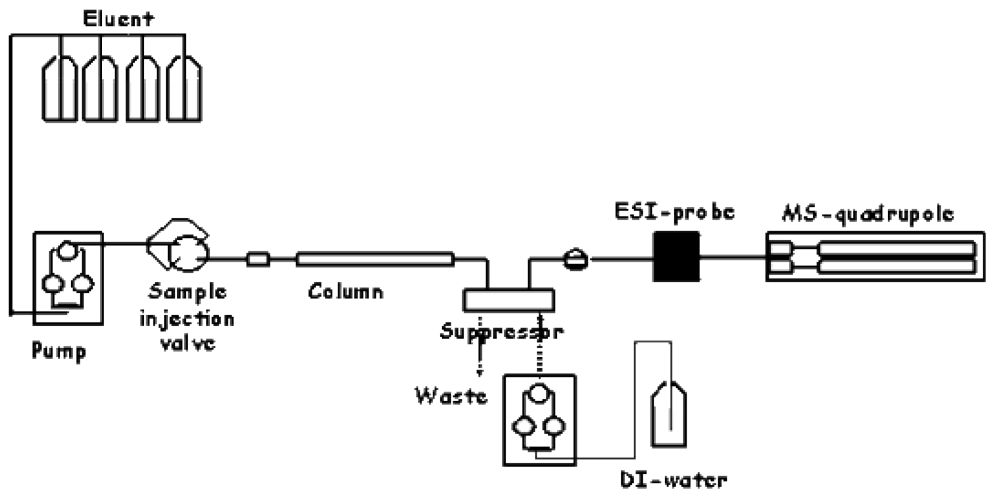

Fig. 1. Schematic diagram of the IC/ESI-MS system.

solutions. The mixed standard solution was composed of amines and quaternary ammonium ions including NH_4^+ ion.

2.3. IC/ESI-MS analysis

The analyses were performed on a DX-120 ion chromatograph (Dionex, USA) equipped with a conductivity detector and a Quattro micro quadrupole mass spectrometer (Micromass, UK). A Dionex IonPac CS17 analytical column and its guard column CG17 were used. The eluent used was a mixed solvent of 10:90 acetonitrile/water with 12 mM methanesulfonic acid. Background conductivity was suppressed with a CSRS 4 mm suppressor operated in the external water mode. All eluate from the suppressor was introduced into the mass spectrometer equipped with an electrospray interface. The ESI-MS was operated in the positive-ion mode. The capillary voltage was set to 3.2 kV. Desolvation temperature of 500 °C and desolvation gas flow of 560 L/h were selected. The MS data were measured using total ion chromatogram (TIC) and single ion chromatogram (SIC). A diagram of the coupled IC/ESI-MS system is schematically shown in *Fig.* 1.

3. Results and Discussion

When a working standard solution was introduced directly into the MS ion source, the molecular ion and/or characteristic fragment ions were formed depending on the cone voltage. The typical mass spectra of the working standard solutions obtained at the cone voltages of 25 and 50 V are shown in *Fig.* 2. At the low cone voltages up to 25 V, the molecular ions were predominantly produced. However, at a higher cone voltage such as 55 V, the fragment ions were additionally produced and thus the analyses of

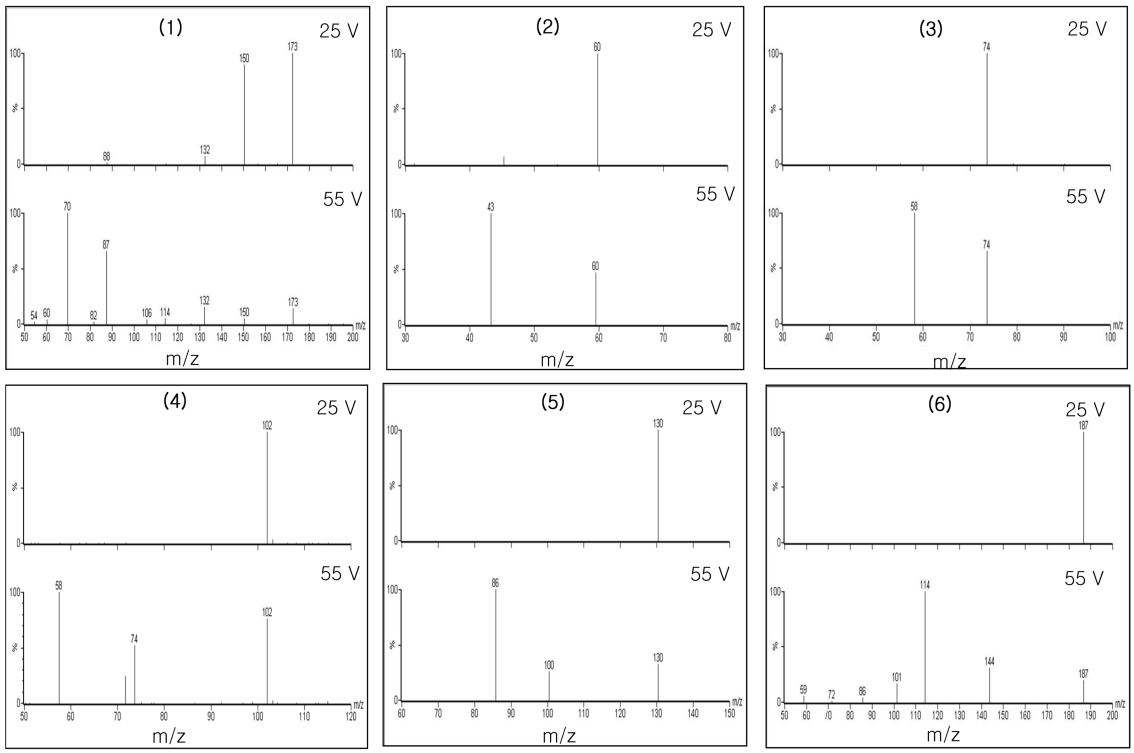

Fig. 2. Mass spectra of the standard amines and quaternary ammonium ions measured at the cone voltages of 25 and 55 V. Each solution of 10 μg/mL in water was introduced into the MS with a syringe pump. Compounds: (1) triethanolamine; (2) trimethylamine; (3) tetramethylammonium ion; (4) triethylamine; (5) tetraethylammonium ion; (6) tetrapropylammonium ion.

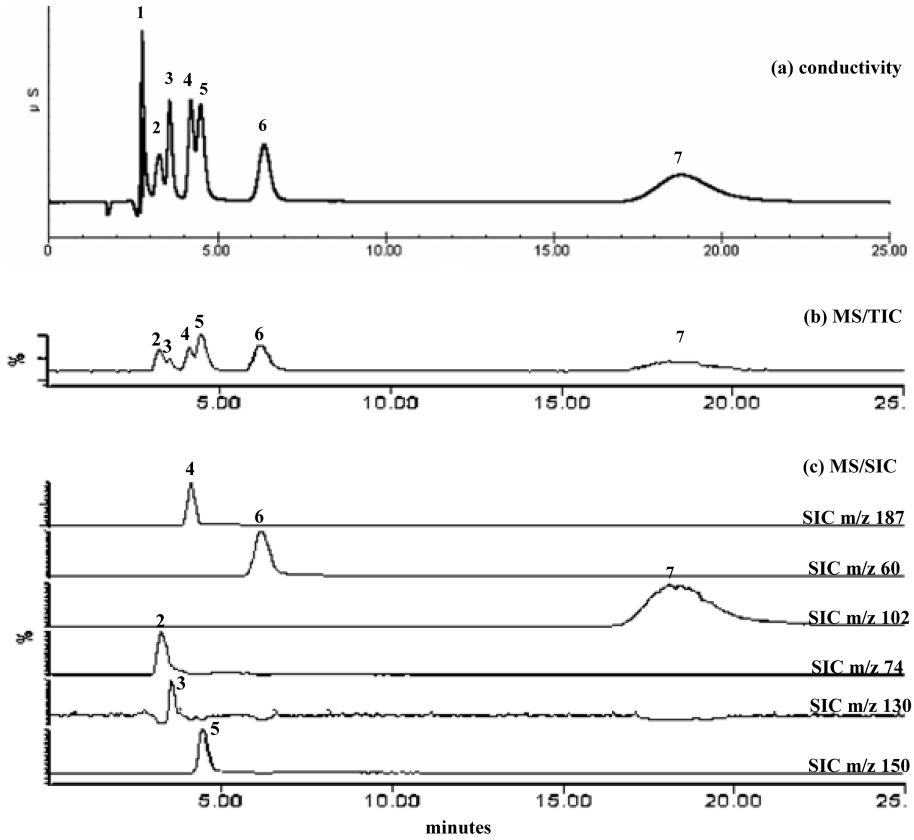

Fig. 3. Chromatograms of the mixed standard solutions containing amines and quaternary ammonium ions detected by (a) conductivity, (b) mass spectrometry using total ion chromatogram (TIC), and (c) mass spectrometry using single ion chromatogram (SIC). Peaks: 1, ammonium ion; 2, triethanolamine; 3, trimethylamine; 4, tetramethylammonium ion; 5, triethylamine; 6, tetraethylammonium ion; 7, tetrapropylammonium ion.

them were useful to identify the compounds. *Fig.* 2 shows that the mass spectra of triethanolamine produced a variety of the fragment ions at 50 V, whereas that obtained at 25 V showed essentially two main peaks appearing at *m/z* 150 and *m/z* 173. The former is clearly the peak of $[M+H]^+$. However, the identification of the latter peak is uncertain. It appears the peak at *m/z* 173 to be the adduct ion of $[MH+Na]^+$. The mass spectra of trimethylamine consisted of the protonated molecular ion of *m/z* 60 and a characteristic ion of *m/z* 43. The fragment ion of *m/z* 43 corresponds to $[M-CH_4]^+$. Tetramethylammonium yielded the molecular ion of *m/z* 74 and a characteristic ion of *m/z* 58. The fragment ion of *m/z* 58, corresponding to $[M-CH_4]^+$, was produced by the direct cleavage of tetramethylammonium ion. Triethylamine can be identified by the protonated molecular ion appearing at *m/z* 102 and a characteristic ion of *m/z* 72 among other fragment ions. The peak at *m/z* 72 corresponds to the fragment ion, $[M-C_2H_5]^+$. In the case of tetraethylammonium ion, the characteristic peaks at *m/z* 100 and 86 in addition to the molecular ion of *m/z* 130 were formed. The peak at *m/z* 100 corresponds to $[M-C_2H_6]^+$. Tetrapropylammonium ion produced the molecular ion peak at *m/z* 187 and characteristic ions of *m/z* 144 and 114. The peak at *m/z* 144 is the fragment ion that corresponds to $[M-C_3H_7]^+$.

Fig. 3 shows typical chromatograms of the mixed standard solutions detected by three different methods, that is, suppressed conductivity, MS detection using total ion chromatogram (TIC) and MS detection with

Table 1. Linearity, repeatability and detection limit of the IC/ESI-MS method

Components	Linearity range	RSD	DL
	(μg/mL)	(%)[a]	(μg/mL)[b]
Tetramethylammonium ion	0.2-5.0	0.2	0.3
Tetraethylammonium ion	0.2-5.0	0.2	0.3
Tetrapropylammonium ion	0.2-5.0	0.5	0.9
Triethanolamine	1.0-20.0	0.5	0.9
Trimethylamine	0.2-5.0	0.1	0.2
Triethylamine	0.2-5.0	0.2	0.3

[a]The number of measurements, N=3. [b]Two times of the standard deviations above the blank signal, 2σ.

single ion chromatogram (SIC). The mixed standard solution was composed of NH_4^+, three quaternary ammonium ions, and three amines. It is noted that all the components except tetrapropylammonium ion were separated within 7.5 min. A preliminary experiment showed that tetrabutylammonium ion, tripropylamine and tributylamine contained in the mixed standard solution were retained in the column for more than one hour (not included in the figure) and thus these compounds were excluded from the mixed standard solution in the subsequent analyses. The NH_4^+ ion peak at 2.9 min was not detected by the MS methods because of its low *m/z*. The peaks of triethanolamine and trimethylamine and those of tetramethylammonium ion and triethylamine were not resolved in the TIC, but all the components were well resolved in the SIC.

The linearity, repeatability and detection limit (DL) of the IC/ESI-MS coupling method were examined. The results are summarized in *Table* 1. The table shows that the linearities based on the peak areas were maintained between 0.2 and 5.0 μg/mL for tetramethylammonium ion, tetraethylammonium ion, tetrapropylammonium ion, trimethylamine, and triethylamine, whereas that of triethanolamine showed a linearity in the range of 1.0-20.0 μg/mL. Data obtained from the calibration curves were subjected to the linear regression analysis and revealed that their correlation coefficients were found to lie above 0.97. The repeatability expressed as the relative standard deviation (RSD) of the peak area was obtained to be 0.5 % for triethanolamine and tetrapropylammonium ion, but lower than 0.2 % for the other compounds. The detection limits for triethanolamine and tetrapropylammonium ion showed a high value of 0.9 μg/mL, but those for the others were only ranged between 0.2 and 0.3 μg/mL.

4. Conclusions

We have newly developed a method of simultaneous determining low molecular weight amines and quaternary ammonium ions in a mixture containing tetramethylammonium ion, tetraethylammonium ion, tetrapropylammonium ion, triethanolamine, trimethylamine, and tripropylamine by the IC/ESI-MS. In particular, the method does not involve any chemical derivatizations. Methanesulfonic acid in the eluent and a membrane cationic suppressor in the IC enabled the simultaneous analysis to be possible by minimizing background spectral interferences. The IC/ESI-MS method can be well applied to the analyses of low molecular weight amines and quaternary ammonium ions that are present in air, water, organic solvents, or raw materials from industrial and environmentally hazardous areas.

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