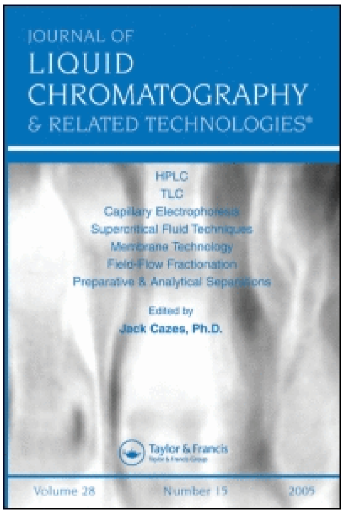

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A Reversed-Phase Ion-Pair HPLC Assay of the Products of the Reaction Between Carbon Disulfide and Ammonia

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A Reversed-Phase Ion-Pair HPLC Assay of the Products of the Reaction Between Carbon Disulfide and Ammonia

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ABSTRACT

A simple, rapid, and reproducible reversed phase ion-pair chromatography method was developed for the simultaneous determination of $(NH_4)_2CS_3$, $(NH_4)_2S$, NH_4SCN, and $NH_2CS_2NH_4$, in the reaction system of carbon disulfide and ammonia. The best analytical results were obtained by using a C_{18} column with a mobile phase of methanol : water : tetramethylene-oxide (20 : 79 : 1, v/v/v), ammonium tetrabutyl bromide (0.003 mol L^{-1}), and KH_2PO_4–K_2HPO_4 buffer solution (0.006 mol L^{-1}, pH 6.64). Total analysis time was about 24 min. The precision, accuracy, and detection limit of the method were reported and discussed. The proposed method can be readily utilized for analysis of $(NH_4)_2CS_3$, $(NH_4)_2S$, NH_4SCN, and

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$NH_2CS_2NH_4$, and the detection results provided important data for research on the reaction mechanism.

Key Words: $(NH_4)_2CS_3$; $(NH_4)_2S$; NH_4SCN; $NH_2CS_2NH_4$; Reversed-phase ion-pair chromatography; Detection.

INTRODUCTION

Ammonium thiocyanate is an important chemical,[1,2] which is normally prepared by the reaction of ammonia with carbon disulfide. According to the literature,[3,4] the reaction process is two-step and can be described as follows:

$$2NH_3 + CS_2 = NH_2CS_2NH_4 \quad (1)$$

$$NH_2CS_2NH_4 = NH_4SCN + H_2S \quad (2)$$

We reinvestigated the reaction, and the initial analysis of the synthesized samples by IR, MS has confirmed the existence of $(NH_4)_2CS_3$, $(NH_4)_2S$, NH_4SCN, and $NH_2CS_2NH_4$ in the same reaction system, which show that the reaction, in a strict sense, was not a two-step reaction. The aim of this paper is to demonstrate the existence of the four components and to take further steps to provide a quantitative method of the components. We think that it can contribute to the understanding of the reaction mechanism and kinetics. In Petrunina's work, a titrimetric method was used to determine the mixture of NH_4SCN, $(NH_4)_2S$, NH_3, and H_2S, step by step, with many kinds of reagents.[5] Berestetskii reported a potentiometric titration of S^{2-}, SCN^-, $S_2O_3^{2-}$ by an indicator electrode of carbon.[6] However, there is no report of simultaneous determination of the four components.

The HPLC has been confirmed to be a useful method for the speciation and mixture separation,[7,8] and reversed phase ion pair chromatography (RPIPC) has also been widely used in the separation and detection of polar compounds.[9,10] In this research, the RPIPC method was found to be suitable for the simultaneous separation of $(NH_4)_2CS_3$, $(NH_4)_2S$, NH_4SCN, and $NH_2CS_2NH_4$ with ammonium tetrabutyl bromide (TBA) as ion-pair reagent and tetramethylene-oxide as organic modifier reagent. The method has been applied for the detection of the four components with satisfactory results.

EXPERIMENTAL

Apparatus

The chromatographic system consisted of Shimadzu commercial components: a solvent-delivery pump, a SPD-6AV UV-VIS detector, operating at 220 nm. The data was collected and analyzed using CR-3A system (Kyoto, Japan). The chromatographic column was 25.0 cm × 0.46 cm 5 μm Elite® C_{18} [Elite Scientific Instruments Co. Ltd. (Dalian, China)].

The sensitive UV absorption wavelengths were determined by a Tianmei® 8500 spectrophotometer (Shanghai, China). The pH was measured with a Tianmei® PHS-3C acidometer (Shanghai, China).

The mass spectrum analysis was obtained with a VG70EH® mass spectrometer (England), and the enrichment of the sample was performed with a SANYO F-20S® freeze dryer (Japan).

Chemicals and Reagents

Ammonium sulfide was kindly provided by Dagang Chemical Reagents Company (Tianjin, China), and ammonium thiocyanate was purchased from Double Circle Chemical Reagents Company (Beijing, China).

Methanol was of HPLC grade, purchased from Concord®(Tianjin, China). All the other chemicals were commercial analytical reagents. Doubly distilled water was used for preparing the mobile phase.

$(NH_4)_2CS_3$ was synthesized from CS_2 and $(NH_4)_2S$ according to Ref.[11] and the yield was calculated based on CS_2.

Preparation of Samples

The mixture of CS_2 with different solvents (1 : 3, v/v) was added to the reactor; then, dry NH_3 gas was led into the reactor through a glass tube and a bubbler. The temperature was controlled at -30°C by a thermostatic bath. In the reaction, cyclohexene, ethyl ether, alcohol, nitrobenzene, water, and KNO_3-H_2O (7%) were used as solvent, respectively. The reaction was completed when CS_2 disappeared; the products were stored at $-18 \sim -20$°C.

Chromatographic Conditions

Chromatographic analysis was carried out at ambient temperature. The compounds were separated with a mobile phase consisting of methanol : water : tetramethylene-oxide (20 : 79 : 1, v/v), TBA ($0.003\,\mathrm{mol\,L^{-1}}$), and $KH_2PO_4-K_2HPO_4$ buffer solution ($0.006\,\mathrm{mol\,L^{-1}}$, pH 6.64). The flow rate was $1.0\,\mathrm{mL\,min^{-1}}$. The column effluents were monitored spectrophotometrically at a wavelength of 220 nm. Each solution, 10 μL, was injected and chromatograms were recorded.

Stock Solution and Standards

$NH_2CS_2NH_4$ was a salt of NH_2CSSH. However, $NH_2CS_2NH_4$ was not commercially available. So, the establishment of an analysis method was based on $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN. The qualitative analysis of $NH_2CS_2NH_4$ was carried out according to the determination of sample and chromatographic effluents.

Stock solutions of $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN were prepared separately in water. Standard solutions were prepared with mobile phase with varying the concentration of $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN in the range of 0.10–250 $\mu g\,mL^{-1}$. Injections were made with each solution and peak area was plotted against the corresponding concentration to obtain the calibration graph.

Based on the experimental results, calibration curves were obtained and characterized with their regression coefficients, slopes, and linear ranges (as shown in Table 1). The linearity of each component was 38–1714 ng for $(NH_4)_2CS_3$, 17–3406 ng for $(NH_4)_2S$, and 38–3809 ng for NH_4SCN, respectively. The calibration curve equation was $y = mx + n$, where y represented the peak area and x represented the mass (μg) of the component. The detection limits (DLs) of the procedure were calculated on the peak area using the following Eq. (3):

$$\mathrm{DL} = \frac{3\mathrm{s}}{m} \tag{3}$$

where s, the noise estimate, is the standard deviation of the peak areas (five injections) of the component and m is the slope of the corresponding calibration curve.

Application of the Proposed Method to Standards

To estimate the retention behavior of $NH_2CS_2NH_4$, $(C_2H_5)_2NCS_2Na$, the derivative of $NH_2CS_2NH_4$, was analyzed together with $(NH_4)_2CS_3$, $(NH_4)_2S$,

Table 1. Characteristics of the regression equations of $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN.

Component	Regression equation	Correlation coefficient	Detection limit (ng)
$(NH_4)_2CS_3$	$y = 128{,}660x + 34{,}871$	0.9999	1.3
$(NH_4)_2S$	$y = 105{,}633.7x - 3{,}249.7$	0.9989	1.0
NH_4SCN	$y = 106{,}675x + 77{,}398$	0.9998	1.2

and NH_4SCN. With an injection of 10 μL of the mixture, the chromatograms of the four components were obtained (Fig. 1).

Application of the Proposed Method to Synthesis Samples

The synthesis samples were dissolved in water and diluted to 500 mL; then, a 1 mL sample was transferred into a 50 mL volumetric flask, diluted to the mark with the mobile phase. The chromatograms of the sample were obtained as shown in Fig. 2. The amount of $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN in the reaction mixture were calculated according to the linear regression equation.

A water solution of the sample (30 mL) was transferred to a 50 mL distillation flask. During distillation under reduced pressure, when the temperature was controlled below 80°C, no isomerized product (NH_2CSNH_2) of NH_4SCN was produced.[12] $(NH_4)_2CS_3$ and $NH_2CS_2NH_4$ were completely converted to NH_4SCN.[4,11] After filtration and washing with water (30 mL), 1 mL of the filtered solution was added to a 50 mL volumetric flask and diluted to the mark with the mobile phase. The total amount of NH_4SCN in the distilland was calculated according to the linear regression equation, and the content of $NH_2CS_2NH_4$ in the reaction mixture was calculated according to Eq. (4).

$$m\,(NH_2CS_2NH_4) = m\,(NH_4SCN)_2 - m\,(NH_4SCN)_1 - m\,((NH_4)_2CS_3) \qquad (4)$$

where $m\,(NH_2CS_2NH_4)$ is the mass of $NH_2CS_2NH_4$ in 1 mL aqueous solution of the sample, $m\,(NH_4SCN)_2$ is the mass of NH_4SCN detected in the distilland, $m\,(NH_4SCN)_1$ is the mass of NH_4SCN detected in 1 mL aqueous solution of the sample. $m\,((NH_4)_2CS_3)$ is the mass of $(NH_4)_2CS_3$ detected in 1 mL aqueous solution of the sample.

Recovery Studies

To study the accuracy of the proposed method, recovery experiments were carried out by the standard addition method. Known amounts of $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN were added to the synthesis samples and the mixtures were analyzed by the proposed method. From the total amount found, the percentage recoveries were calculated, and the results are shown in Table 2. The RSD of the recoveries was 3.1% for $(NH_4)_2CS_3$, 2.9% for $(NH_4)_2S$, and 2.6% for NH_4SCN, respectively.

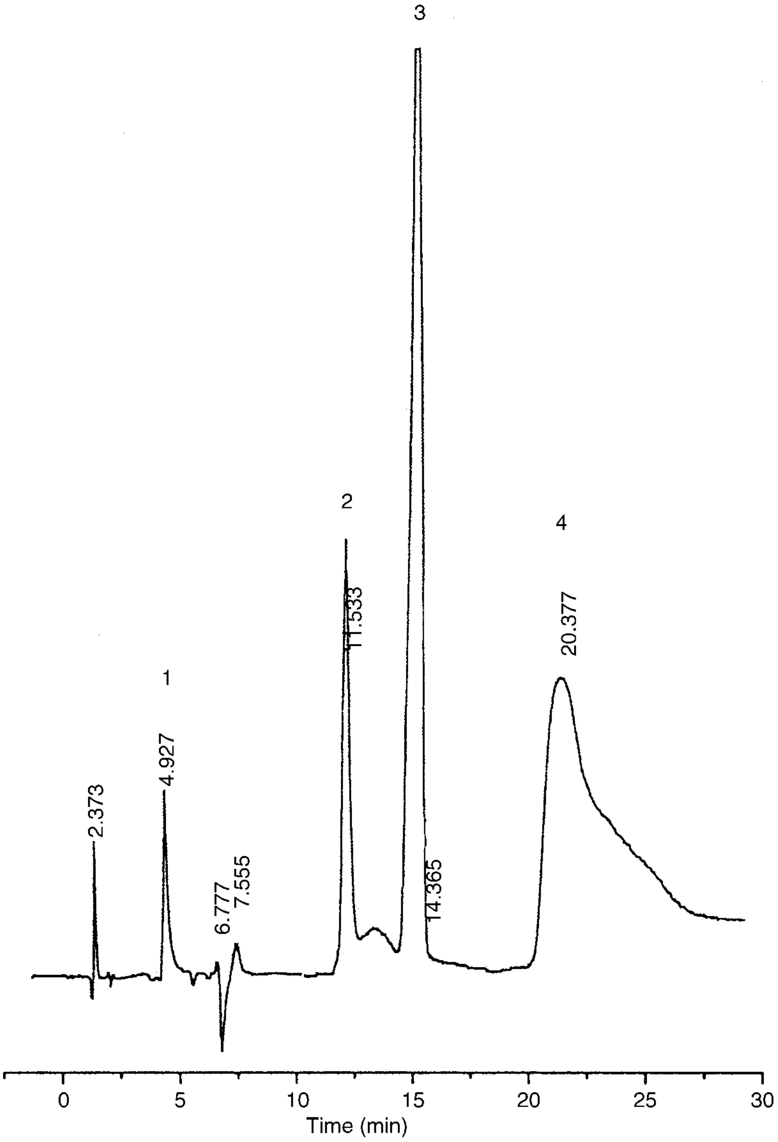

Figure 1. Chromatograms obtained from the separation of standard solution of $(NH_4)_2CS_3$ (1), $(NH_4)_2S$ (2), NH_4SCN (3), and $(C_2H_5)_2NCS_2Na$ (4).

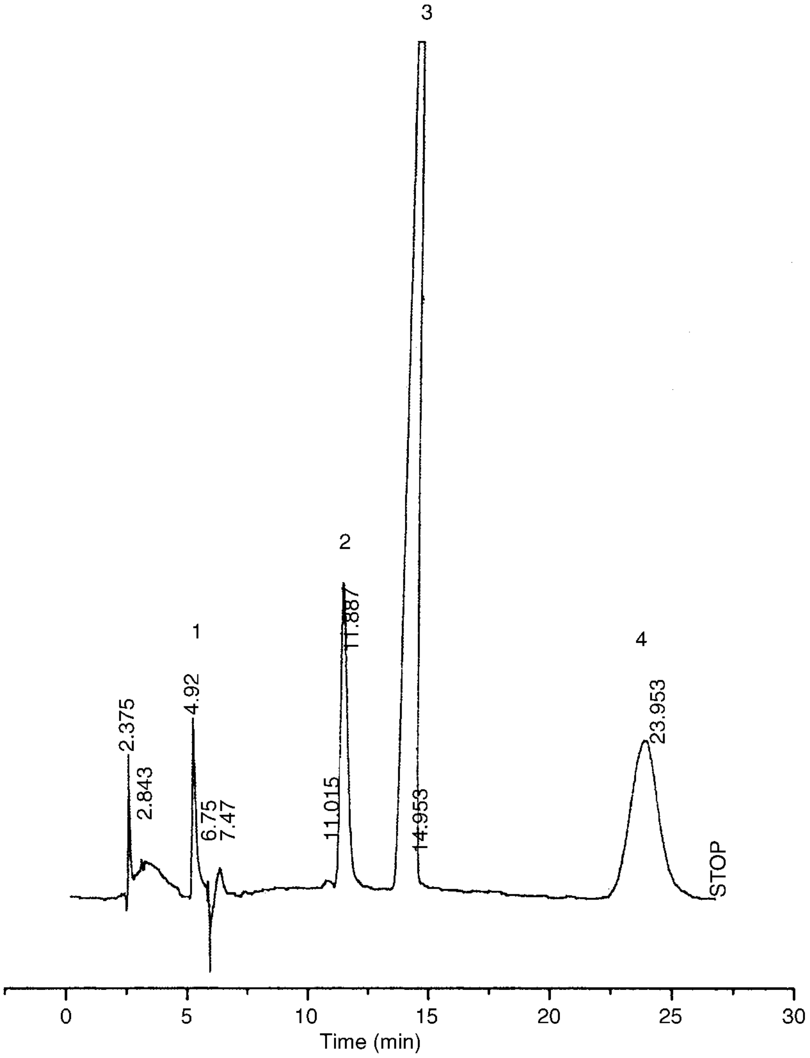

Figure 2. Chromatograms obtained from the separation of reaction mixture of $(NH_4)_2CS_3$ (1), $(NH_4)_2S$ (2), NH_4SCN (3), and $NH_2CS_2NH_4$ (4).

RESULTS AND DISCUSSION

The spectra of TBA, $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN were recorded within the wavelength range 200–350 nm. The wavelengths of maximum

Table 2. Results of the determination and the recovery analysis of $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN.

Component	Component added (μg mL^{-1})	Component detected (μg mL^{-1})	Recovery (%)	RSD of recovery (%) ($n = 4$)
$(NH_4)_2CS_3$	10	9.8	98.0	3.1
	20	20.3	101.5	
	30	30.5	101.6	
$(NH_4)_2S$	10	9.6	96.0	2.9
	20	19.7	98.5	
	30	28.7	95.7	
NH_4SCN	10	10.3	103.0	2.6
	20	20.5	102.5	
	30	30.8	102.7	

absorption were 209 nm for TBA, 219 nm for $(NH_4)_2CS_3$, 226 nm for $(NH_4)_2S$, and 221 nm for NH_4SCN, respectively. To ensure adequate sensitivity for all components except TBA, 220 nm was selected as the detection wavelength.

The dependence of the capacity factors of $(NH_4)_2CS_3$, $(NH_4)_2S$, and NH_4SCN on pH was studied with a mobile phase containing 79% water, 20% methanol, 1% tetramethylene-oxide, and 0.003 mol L^{-1} TBA. When pH was varied from 6.10 to 7.17, the retention time of $(NH_4)_2S$ and NH_4SCN decreased. Through the uniform experiment $U_7(7^6)$,[13] the mobile phase pH was maintained at 6.64 with $KH_2PO_4-K_2HPO_4$ as buffer.

The effect of mobile phase composition on capacity factors was investigated with methanol's content ranging from 10% to 50% (v/v), and tetramethylene-oxide's content ranging from 0% to 3% (v/v). The retention time of $(NH_4)_2S$ and NH_4SCN decreased slowly as the content of methanol was increased from 10% to 50%. However, when 1% of tetramethylene-oxide was added, the capacity factor of NH_4SCN was decreased about 30%, with a retention time of 15 min. To ensure the rapid analysis of the components, water containing 20% methanol and 1% tetramethylene-oxide was used for subsequent measurements.

The TBA concentration played an important role in the separation of the four components. When the flow rate was 1.0 mL min^{-1}, the volume ratio of water, methanol, and tetramethylene-oxide was 79 : 20 : 1 (v/v/v), pH 6.64, TBA was 0.003 mol L^{-1}, good separation results were obtained (Fig. 1). The retention times of $(NH_4)_2CS_3$, $(NH_4)_2S$, NH_4SCN, and $(C_2H_5)_2NCS_2Na$

were 4.9, 11.6, 14.4, and 20.4 min, respectively. The maximum absorption wavelength of $(C_2H_5)_2NCS_2Na$ was 252 nm. To ensure its being detected at 220 nm, an excessive amount of $(C_2H_5)_2NCS_2Na$ was used in the analysis, which caused a tailed peak (20.4 min).

Figure 2 is the chromatograms of the sample, and the peak around 24 min is proposed to be $NH_2CS_2NH_4$ according to the retention time of $(C_2H_5)_2$-NCS_2Na. To verify the validity of this assumption, the effluent from 23 to 26 min was collected and enriched by freeze drying under vacuum. The MS analysis of the condensate under the condition of EI gave the m/z 110 and 44 (Fig. 3), which should correspond to $NH_2CS_2NH_4$ and C═S, respectively. Meanwhile, the retention time of the condensate equaled that of the effluent. All these testified that the peak of 24 min corresponded to $NH_2CS_2NH_4$.

The utility of the proposed method was verified by recovery experiments. Satisfactory recoveries of 95.7–103.0% showed that the method was useful in the analysis of the reaction mixture.

A series of samples were analyzed. The amount of $(NH_4)_2CS_3$, $(NH_4)_2S$, NH_4SCN, and $NH_2CS_2NH_4$ in 1 mL aqueous solution of the sample were calculated according to linear equations and Eq. (4). From the detection results (listed in Table 3), we could see that the contents of NH_4SCN and $NH_2CS_2NH_4$ toward different direction changed with the permittivity of solvents. NH_4SCN, $NH_2CS_2NH_4$ existed in the same reaction system, which

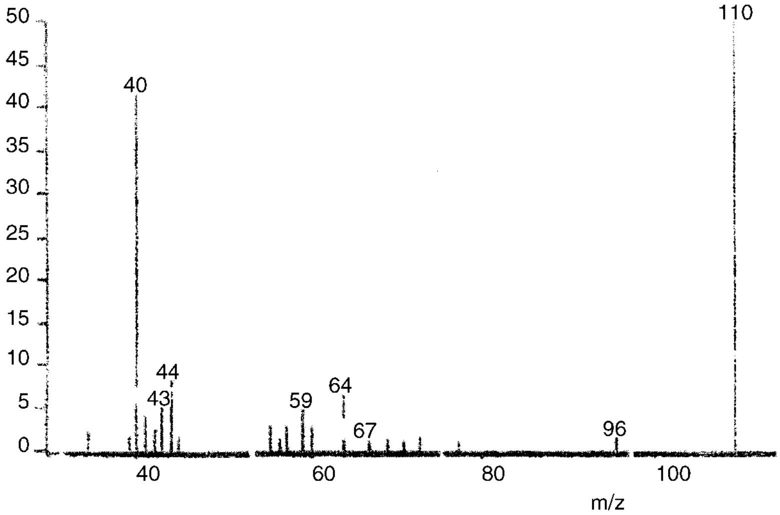

Figure 3. The MS analysis of condensate under the condition of EI.

Table 3. The detection results of $(NH_4)_2CS_3$, $(NH_4)_2S$, NH_4SCN, and $NH_2CS_2NH_4$ in samples.

	Mole ratio of components in sample (%)			
Sample	$(NH_4)_2CS_3$	$(NH_4)_2S$	NH_4SCN	$NH_2CS_2NH_4$
Cyclohexene	18.5	14.2	63.8	3.5
Ethyl ether	14.8	13.6	66.8	4.8
Alcohol	4.6	13.0	69.7	12.7
Nitrobenzene	18.2	14.2	52.3	15.3
Water	18.4	13.5	48.5	19.6
KNO_3–H_2O (7%)	11.2	13.8	52.5	22.5

provided important data for the influence of solvent on the reaction between CS_2 and NH_3.

CONCLUSIONS

In this research, the RPIPC method was suitable for the simultaneous separation of $(NH_4)_2CS_3$, $(NH_4)_2S$, NH_4SCN, and $NH_2CS_2NH_4$ within a short analysis time. The proposed method gives satisfactory analytical results. It provides a powerful means for the study of the mechanism.

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