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Short communication

Solvating gas chromatography using ammonia as mobile phase

Yufeng Shen, Milton L. Lee*

Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602-5700, USA

Abstract

In this study, the use of ammonia as the mobile phase in packed capillary column solvating gas chromatography (SGC) was investigated. Fused-silica capillary columns (0.9 m×250 μm I.D.) packed with 15 μm octadecyl bonded and polydimethylsiloxane encapsulated silica particles (300 Å) were evaluated under SGC conditions. Flame ionization detection was used for detection. Anilines, aliphatic (primary, secondary, and tertiary) amines, and aliphatic diamines were separated under SGC conditions. Although ammonia was converted from a liquid to a gas along the column, no significant loss in column efficiency was observed.   © 1998 Elsevier Science B.V.

Keywords: Mobile phase composition; Solvating gas chromatography; Ammonia; Amines

1. Introduction

Ammonia has unique properties, some of which are favorable and others unfavorable with respect to its use as a mobile phase in chromatography. The basicity and dipole moment of ammonia [1] result in advantageous interactions with solutes that facilitate the separation of polar, basic compounds.

In previous studies of open tubular column gas chromatography (GC) using ammonia as the mobile phase, flame ionization detection (FID) was used [2–5]. However, the detector background current slightly increased when adding ammonia to nitrogen carrier gas [2]. Columns coated with polar and nonpolar stationary phases were stable under GC conditions using ammonia [3,4]. In supercritical fluid chromatography (SFC), the solvating properties of ammonia have been studied [6,7]. High-molecular-mass polar compounds (e.g., Carbowax 4000) have greater solubility than nonpolar compounds (e.g., Apiezon L) in supercritical fluid ammonia [7]. FID could not be used in this situation [8]. Liquid ammonia has been little studied as a mobile phase in chromatography [9].

In packed column GC, the use of microparticles must be accompanied by a solvating mobile phase to achieve high column efficiency and short separation time, and the terminology ''solvating gas chromatography (SGC)'' has been used to describe this chromatographic variant [10–12]. In this study, the use of ammonia as the mobile phase in packed capillary column SGC was demonstrated.

2. Experimental

2.1. Materials and instrumentation

SFC grade NH_3 (Scott Specialty Gases, Plumsteadville, PA, USA) was used as the mobile phase in

*Corresponding author.

packed capillary SGC. Fused-silica capillary tubing (Polymicro, Phoenix, AZ, USA) was used to prepare the packed capillary columns. Spherical porous (300 Å) octadecyl bonded silica (ODS) particles having an average diameter of 15 μm (10–20 μm) and a pore size of 300 Å (YMC, Wilmington, NC, USA) were used as packing material. Polymer encapsulated particles were prepared by coating polydimethylsiloxane (United Chemical, Bristol, PA, USA) on the particle surface and then immobilizing the polymer layer using a free-radical reaction. Column connections were made using polyether ether ketone tubing and zero dead-volume unions (Valco, Houston, TX, USA). SFC grade CO_2 (Scott Specialty Gases) was used as a slurry solvent for the preparation of the packed capillary columns, and the packing itself was carried out using a Lee Scientific Model 600 SFC instrument (Dionex, Salt Lake Division, Salt Lake City, UT, USA). An HP-5890 gas chromatograph with FID (Hewlett–Packard, Little Falls, PA, USA) was used for SGC experiments. A μLC-500 microflow pump (ISCO, Lincoln, NE, USA) was used to deliver the liquid mobile phase. Other chemicals were purchased from Aldrich (Milwaukee, WI, USA).

2.2. Preparation of polymer encapsulated particles and packed capillary columns

A similar procedure as previously described [13] was used for preparation of polymer encapsulated silica particles. A CO_2 slurry packing method as previously described [10,14] was used to prepare the 0.9 m packed capillary columns containing 15 μm diameter particles.

2.3. SGC experiments

Similar instrumentation as previously described [10,11] was used for this study. A split at the outlet of the separation column was made using a stainless-steel tee connection (Valco). Two stainless-steel tubes (10 cm×200 μm I.D.) were connected to the arms of the tee to produce a split ratio of approximately 1:1. The FID temperature was set at 350°C.

3. Results and discussion

3.1. FID performance using ammonia as SGC mobile phase

When using a 0.9 m×250 μm I.D. capillary column packed with 15 μm diameter particles (300 Å pores) and SFC grade ammonia as mobile phase with 8 MPa column inlet pressure, greater than 2500 pA background level was observed in the FID. The baseline was not stable, and acceptable results could not be obtained. However, spiking was not seen in experiments, even though a high baseline was present. In order to reduce the FID response, a split at the column outlet was used (split ratio of approximately 1:1), and the signal was reduced to ~1500 pA. At this baseline level, 0.3 MPa fluctuation in ammonia pressure produced approximately 30 pA signal change. Even with this high detector background, a tolerable detection limit (ca. 20 μg of sample) was obtained. The background level in the FID limits the use of temperature or pressure programming since both temperature and pressure programming produce significant changes in the mass flow-rate of the mobile phase.

3.2. Pump considerations

When using ammonia and FID in SGC, pump fluctuations and leaks are critical to obtaining a stable baseline. A microflow pump was used in this study, however the seals needed to be changed after 2 months of use.

3.3. Column stability

When using high pressure ammonia as mobile phase, it was observed that for fused-silica capillary columns packed with ODS particles, the efficiency greatly decreased after 3 days' use of high pressure ammonia (>100% loss in column efficiency). In addition to column efficiency losses, column permeability also worsened. At any applied column inlet pressure, an approximate 60% reduction in average mobile phase linear velocity was observed.

Polydimethylsiloxanes were coated and immobilized on ODS particles. Experiments showed that

columns packed with these polymer encapsulated particles were stable under SGC conditions using high pressure ammonia as the mobile phase. After 5 weeks' use of these columns, no further column efficiency loss was observed.

3.4. Effect of ammonia liquid-to-gas phase transition on efficiency

In experiments, temperatures and pressures were studied from 120 to 150°C and from 8 to 11 MPa, respectively, which fall in ranges that lead to abrupt changes in physical properties [15]. Table 1 lists the column efficiencies and retention factors achieved at conditions below the critical, at the critical, and above the critical temperatures of ammonia. For aniline and N-methylaniline test solutes, the column efficiencies were almost the same at all three temperatures.

3.5. Separations of amines

Fig. 1 shows an SGC chromatogram of long-chain primary aliphatic amines. These compounds were eluted with some peak tailing. Fig. 2 shows an SGC chromatogram of primary, secondary, and

Table 1
Comparison of column efficiencies and retention factors (k) in SGC with ammonia as mobile phase at various temperatures[a]

Temp. (°C)	u[b] (cm s^{-1})	Solute	N (plates)	k
120	2.5	Aniline	11 500	1.5
		N-Methylaniline	9 100	4.7
		Hexylamine	8 283	3.1
		Octylamine	7 659	4.8
132	2.6	Aniline	12 500	1.2
		N-Methylaniline	10 200	3.8
		Hexylamine	15 200	2.7
		Octylamine	13 600	4.0
145	2.8	Aniline	12 300	1.1
		N-Methylaniline	9 300	3.1
		Hexylamine	15 900	2.1
		Octylamine	13 700	3.2

[a] Conditions: 0.9 m×250 μm I.D. fused-silica capillary column packed with 15 μm ODS-bonded and polydimethylsiloxane encapsulated particles, ammonia mobile phase, 8 MPa column inlet pressure, FID, CH$_4$ as unretained marker.
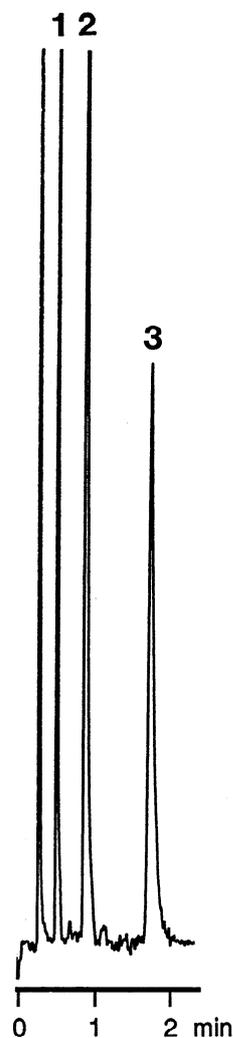[b] Mobile phase linear velocity.

Fig. 1. SGC chromatogram of primary aliphatic amines. Conditions: 0.9 m×250 μm I.D. fused-silica capillary column packed with 15 μm diameter ODS bonded and polydimethylsiloxane encapsulated particles, ammonia mobile phase, 14 MPa column inlet pressure, 150°C, mobile phase linear velocity of ~5 cm s^{-1}, FID. Peak identifications: (1) 1-hexylamine, (2) 1-octylamine, (3) 1-decylamine.

tertiary aliphatic amines. They eluted according to molecular weight. Long-chain aliphatic diamines were chromatographed, and tailing peaks were observed. In this study, we only modified the stationary phase by coating a polydimethylsiloxane film on the ODS particle surface. Optimization of suitable deactivation reactions and stationary phases is re-
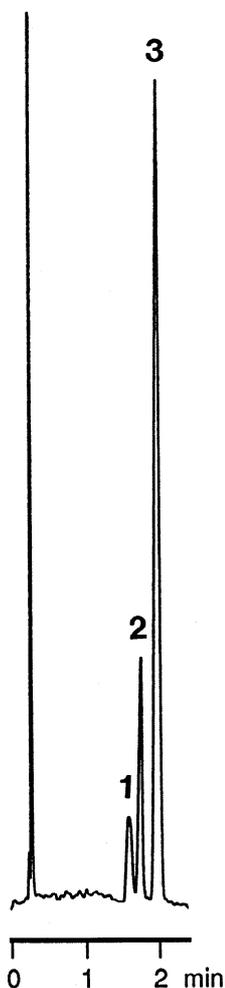
Fig. 2. SGC chromatogram of primary, secondary, and tertiary aliphatic amines. Conditions: 10 MPa column inlet pressure, 130°C, mobile phase linear velocity of ~4.5 cm s^{-1}, other conditions are the same as in Fig. 1. Peak identifications: (1) α-phenylethylamine, (2) N-methyl-α-phenylethylamine, (3) N,N-dimethy-α-phenylethylamine.

quired for separation of basic, strongly polar diamines.

Other more polar compounds including amine salts such as ethylenediamine dihydrochloride and amino acids such as valine were evaluated for analysis under SGC conditions using ammonia as the mobile phase. These compounds were not eluted from the column.

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