ELSEVIER

Journal of Chromatography A, 752 (1996) 287–290

JOURNAL OF CHROMATOGRAPHY A

Short communication

pH-Dependent elution behaviour of meleme in high-performance cation-exchange chromatography

Shin Ono[a], Yasuhiko Inoue[a], Naohiro Watanabe[a], Toshiaki Yoshimura[a], Hiroyuki Morita[a], Akihiro Shiroishi[b], Makoto Takakura[b], Choichiro Shimasaki[a,*]

[a]*Department of Chemical and Biochemical Engineering, Toyama University, Gofuku 3190, Toiyama 930, Japan*

[b]*Nissan Kagaku Kogyo Co. Ltd., Toyama Factory, Research & Development Center, Fuchu-machi, Nei-gun 939-27, Japan*

Received 15 March 1996; revised 13 May 1996; accepted 21 May 1996

Abstract

Meleme, one of thermal decomposition products of melamine, was analyzed satisfactorily by high-performance cation-exchange chromatography using 20 m*M* phosphate buffer as eluent. The elution behavior of meleme and melamine at various pH values (pH 2.0–6.0) was examined and the determination was accomplished simultaneously using photodiode array UV–Vis detection.

Keywords: pH effects; Meleme; Melamine; Amines

1. Introduction

Meleme is one of the de-ammonia condensation derivatives which are produced via melame during thermal decomposition of melamine. The structure of meleme has been proposed as shown in Fig. 1 [1,2]. Takimoto et al. [3,4] studied the synthesis, isolation and characterization of thermal decomposition derivatives of melamine, including meleme, about three decades ago.

According to their reports, these derivatives could be separated using cation-exchange chromatography (Amberlite IR-112, 20×0.8 cm I.D., 0.5 *M* hydrochloric acid). However, the elution of meleme in the system took 9–17 h and the determination was achieved after isolation [3]. Thus, no rapid and quantitative analysis has been reported so far due to their remarkably low solubility in various aqueous solutions and organic solvents. This disadvantage has made the fundamental study and the application of these derivatives difficult. In this paper, we report a method for the rapid and quantitative analysis of meleme using high-performance cation-exchange chromatography (HPCEC) with photodiode array UV–Vis detection, especially the influence of pH on the elution behavior.

2. Experimental

2.1. Chemicals

Phosphoric acid and sodium hydroxide were of

*Corresponding author.

0021-9673/96/$15.00
PII S0021-9673(96)00495-5

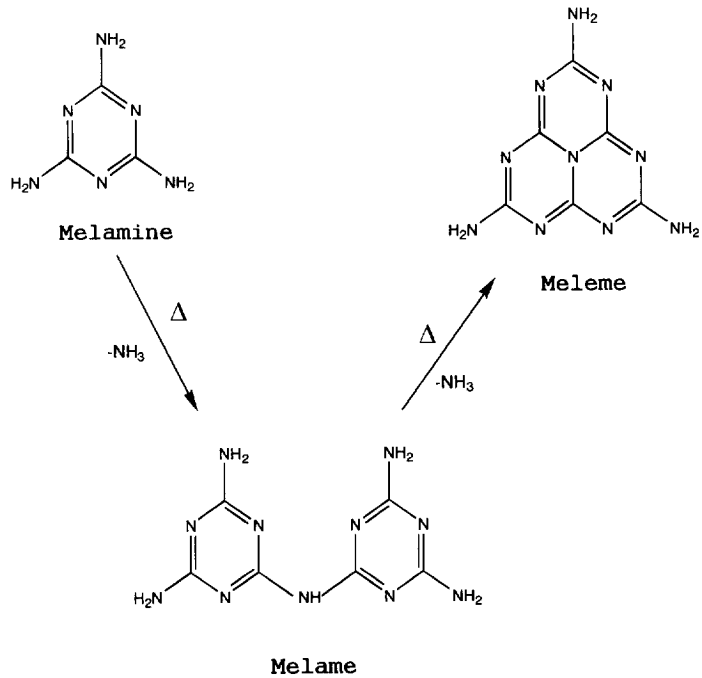

Fig. 1. Formation of meleme via melame during pyrolysis of melamine.

analytical-reagent grade (Wako). Water was distilled and filtered through a ultrapure water system (Advantec). The purified melamine and meleme were kindly supplied by Nissan Kagaku Kogyo.

2.2. Equipment

HPCEC analysis was carried out using a Shimadzu LC-6AD high-performance liquid chromatograph equipped with a photodiode array spectrometric detector (SPD-M6A), system controller (SCL-6B), column oven (CTO-6A), and SPD-6A data analysis system (M6PAC ver. 2.1). A Partisil-10 SCX analytical column (10 μm particle size, 250×4.6 mm I.D., GL Sciences), and guard column (10×4.0 mm I.D., GL Sciences) with the same material were used.

2.3. Preparation and procedure

As a sample solution, meleme and melamine were mixed according to the following procedure. Meleme (0.00434 g) was dissolved in 1.0 l of water and subsequently melamine (0.0166 g) was added to the solution. After stirring for 4 h, the solution saturated with these compounds was filtered through a 0.5-μm filter. The concentrations of meleme and melamine were determined by UV absorption (ϵ_{222}=52 400 M^{-1} cm^{-1} for meleme and ϵ_{217}=20 836 M^{-1} cm^{-1} for melamine).

Phosphate buffers (20 mM) at various pH values were prepared as mobile phases and filtered through a 0.5-μm filter. The flow-rate was 1.0 ml/min and the oven temperature was 40°C. A 20-μl volume of the sample solution containing meleme and melamine (0.0868 μg and 0.332 μg, respectively) was injected, and the elution was monitored at 283 nm and scanned between 200 and 300 nm by the photodiode array detector.

3. Results and discussion

In a preliminary experiment to seek an appropriate

eluent, phosphoric acid was found to be relatively suitable as solvent to dissolve cyclic cyanamide derivatives including meleme. Taking into account the harm to the apparatus and solid support caused by the eluent, 20 m*M* phosphate buffer (pH 2.0–6.0) was chosen in this work. Meleme showed higher solubility (20 mg/l) in 20 m*M* phosphate buffer (pH 2.7) than in diluted hydrochloric acid (3 mg/l at 25°C [4]). Melamine was also applied simultaneously to examine the separation ability of our system and its solubility in the same phosphate buffer was 130 mg/l.

The elution behavior of a mixture of meleme and melamine was examined at various pH values (pH 2.0–6.0) on our system (see in Section 2.3). The elution profiles for meleme and melamine as a function of pH were compared, as shown in Fig. 2.

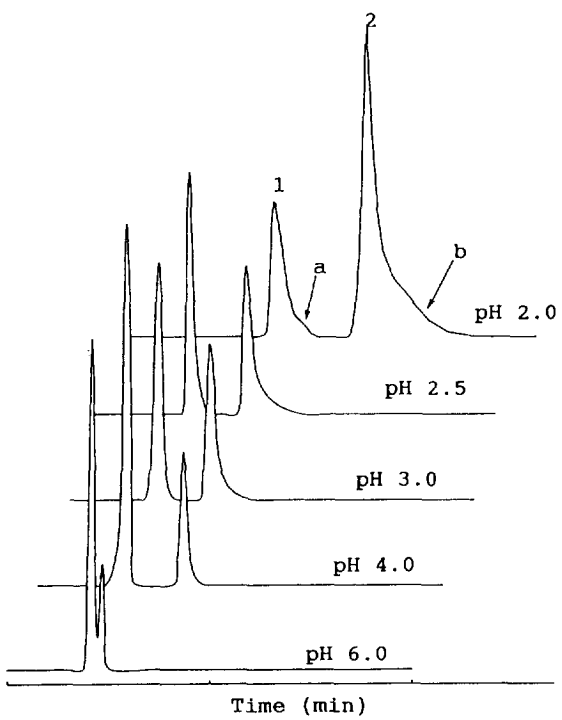

Fig. 2. pH-Dependent elution profiles of melamine and meleme in HPCEC. Peaks: 1=meleme and 2=melamine. The UV spectra were recorded at points a and b using photodiode array detection.

In the range of pH 2.0–4.0, meleme and melamine were separated satisfactorily but not at pH 6.0. Some tailing and broadening was observed in the profiles of meleme and melamine, especially at lower pH (Fig. 2). The UV spectrum measured at tailing points (a and b) at pH 2.0 by photodiode array detector (see Fig. 2) suggested that these tailings might not result from impurities (data not shown). In addition, linear calibration lines were obtained for meleme and melamine within the ranges 5.19–18.5 mg/l and 3.00–10.7 mg/l, respectively. The correlation coefficients were 0.9995 and 0.9999, respectively (data not shown).

Since significant changes in elution times were observed for both meleme and melamine in the pH range 2.0–3.0 (Fig. 2), the UV spectrum at the top of each peak was recorded by photodiode array detector. Noticeable pH-dependent changes in both absorption spectra were observed in the same pH range (data not shown). These findings indicate that changes in dissociation states of meleme and melamine occur in the pH range 2.0–3.0 as reported previously [4].

In our system using HPCEC, meleme was separated rapidly and determined satisfactorily depending on pH. Particularly, the use of photodiode array UV–Vis detection made the identification and estimation of purity for a microquantity of meleme possible. Therefore, our system should be suitable for studies on the reactivity and stability of meleme. Recently, the determination of cyclic cyanamide derivatives, isocyanuric acid, ammeline, ammelide and melamine, was achieved by using ion chromatography [5]. Our system was also applicable to the separation of ammelide and ammeline depending on pH (unpublished data). Moreover, the analysis of melame, an another thermal decomposition derivative of melamine (see Fig. 1), is in progress.

References

[1] C.E. Redemann and H.J. Lucas, J. Am. Chem. Soc., 61 (1939) 3420.

[2] C.E. Redemann and H.J. Lucas, J. Am. Chem. Soc., 62 (1940) 842.
[3] M. Takimoto, Kogyo Kagaku Zasshi (in Japanese), 64 (1961) 1452.
[4] M. Takimoto, T. Yokoyama, A. Sawada and M. Yamashita, Kogyo Kagaku Zasshi (in Japanese), 66 (1963) 793.
[5] J.K. Debowski and N.D. Wilde, J. Chromatogr., 639 (1993) 338.