Asian Journal of Chemistry Vol. 18, No. 2 (2006), 1085–1090

HPLC Determination of Chlorobenzene in Benzene Sulfonylchloride for Industrial use by High Performance Liquid Chromatography

CAI XIULAN, ZHU MEI, WEI YUNA and LIAN HONGZHEN*
Key Laboratory of Analytical Chemistry for Life Science, The Ministry of Education
Centre of Materials Analysis and Department of Chemistry, Nanjing University
22 Hankou Road, Nanjing 210 0093, China
Fax: (86)(25)83325180; Tel: (86)(25)83686075; E-mail: hzlian@nju.edu.cn

A reversed phase high performance liquid chromatographic method has been developed for the determination of chlorobenzene in industrial benzene sulfonylchloride. Analysis was accomplished in a Kromasil C_{18} column with methanol-water (65 : 35, v/v) or acetonitrile-water (60 : 40, v/v) as mobile phase and detection was performed by UV absorption at a wavelength of 215 nm. The chromatographic behaviour and separation performance of samples determined were compared under two elution conditions chosen. The method is rapid, accurate, reliable and has been successfully applied for the quality control analysis of benzene sulfonylchloride in the laboratories of some chemical plants.

Key Words: Chlorobenzene, Benzene sulfonylchloride, Methanol, HPLC, Acetonitrile.

INTRODUCTION

Benzene sulfonylchloride, a colourless or light yellow oily liquid, is an important fine chemical intermediate in areas of pesticide, medicine and dyestuff. It can be used to prepare ice dyes, sulfonamide drugs, etc. In industry, benzene sulfonylchloride is mostly manufactured through the reaction between benzene and superfluous chlorosulfonic acid[1]. During this process, small quantity of chlorobenzene is produced and mixed in the product. Because of its terrible toxicity and irritation, as well as the infection to later products, the content of residual chlorobenzene in fine chemicals is seriously limited by many countries[2].

In the past, the determination of chlorobenzene was mainly focussed on surface and drinking waters, waste and air, where it is referred to as a pollutant. Gas chromatograph (GC)[3–14] and high performance liquid chromatograph (HPLC)[15, 16] were the two most frequently employed methods. In recent years, the requirement of fine quality chemicals has been growing continuously. Therefore, it is necessary to control the content of chlorobenzene in many products, in which there may exist chlorobenzene as a relative impurity or a solvent residue. Mao[2] reported a GC method for the determination of chlorobenzene in *m*-phenoxy toluene for industrial use. Wang[17] and Zhou *et al.*[18] used HPLC to determine industrial diphenyl ether and cetirizine hydrochloride, an anti-allergic drug, respectively. In this paper, an HPLC method with UV detection was presented for determination of chlorobenzene residue in benzene sulfonylchloride for industrial use. This method has been proven to be applicable to the real samples.

EXPERIMENTAL

Reference substance of chlorobenzene (> 99.0%) was provided by Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, PRC). Methanol and acetonitrile were HPLC grade and purchased from Hanbang Science and Technology Co. Ltd. (Huaian, PRC) and Merck (Darmstadt, Germany), respectively. Wahaha purified water (Wahaha Group Ltd., Hangzhou, PRC) was used throughout the experiment.

Instrumentation for quantitative analysis included a Varian 5060 high performance liquid chromatograph (Varian, Walnut Creek, USA), a Rheodyne 7725i injector value equipped with a 10 μL loop (Rheodyne, Cotati, USA), a Waters 486 tunable UV absorbance detector (Waters, Milford, USA) operating at 215 nm. Data acquisition and processing was performed on a JS-3050 chromatographic working station (Dalian Johnsson Separation Science and Technology Corporation, Dalian, PRC) and a Yokogawa Hokushin Electric Type 3066 pen recorder (Sino-Japanese Sichuan Fourth Meter Factory, Chongquing, PRC).

The optimum UV wavelength of chlorobenzene was obtained by 2695 Separations Module equipped with a vacuum degasser, a quaternary pump and an auto-sampler and a 996 UV-Vis photodiode-array detector (PDA) (Waters, Milford, USA). The separation was controlled and the chromatograms were recorded by a Waters Millinium chromatography manager system.

HPLC separation and measurement were carried out on a 5 μm Kromasil C_{18} column with the dimensions of 150 × 4.6 mm (Hanbang Science and Technology Co. Ltd., Huaian, PRC) at 30°C. Two mobile phase systems were selected and compared: methanol-water (65 : 35, v/v) and acetonitrile-water (60 : 40, v/v). The flow rate was set at 1.0 mL/min.

Procedure: 25.00 mg of chlorobenzene reference substance was accurately weighed in a 25 mL volumetric flask and methanol was added to the volume. All other standard solutions of chlorobenzene were prepared from this stock solution by serial diluting with methanol in the further stages of the experiment. About 10 μL benzene sulfonylchloride sample was accurately weighed and transferred into a 10 mL volumetric flask. After being dissolved in methanol, methanol was added to the mark.

RESULTS AND DISCUSSION

Typical chromatograms of chlorobenzene standard solution and benzene sulfonylchloride sample solutions are shown in Fig. 1. The retention times for chlorobenzene were 9.1 min and 6.7 min, respectively, with methanol-water (65 : 35, v/v) and acetonitrile-water (60 : 40, v/v) as the mobile phase. Benzene sulfonylchloride showed multiple peaks under these chromatographic conditions and its shape changed with the increase of the solution standing duration, due to decomposition in aqueous or alcohol solution. However, the multiple peaks of benzene sulfonylchloride did not influence the determination of chlorobenzene, because the peaks of chlorobenzene and benzene sulfonylchloride had been well separated from each other.

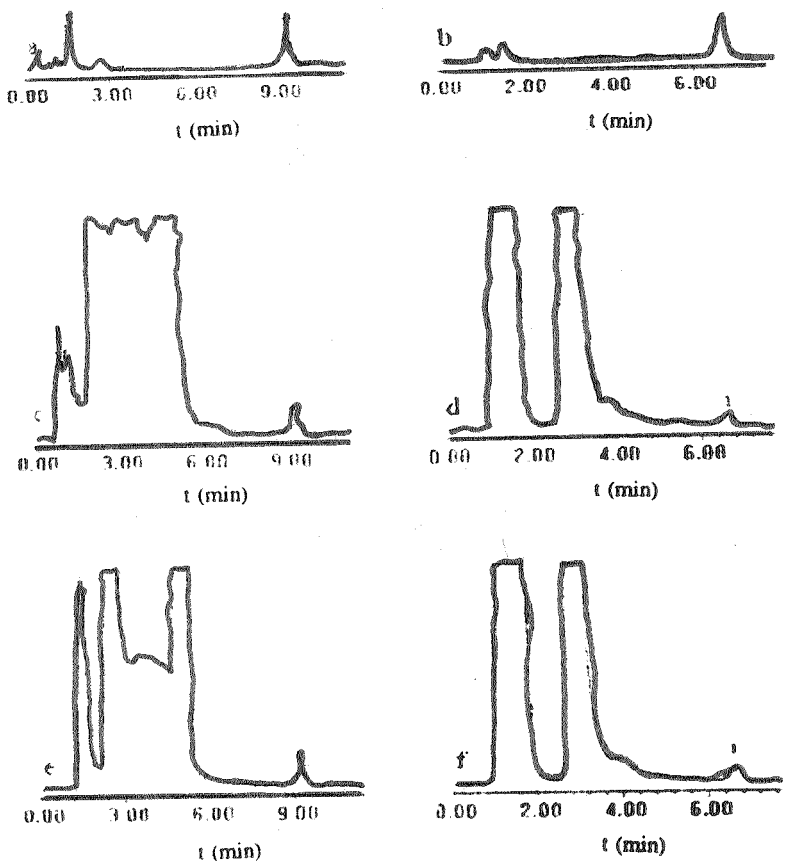

Fig. 1. Chromatograms of chlorobenzene standard and benzene sulfonylchloride sample solutions. Column: Kromasil C_{18}, 5 μm, 150 × 4.6 mm (I.D.); column temperature: 30°C; mobile phase: methanol-water (65 : 35, v/v) (a, c, e), acetonitrile-water (60 : 40, v/v) (b, d, f); flow rate: 1.0 mL/min; inject volume: 10 μL; detection wavelength: 215 nm; a, b: chlorobenzene standard; c, d benzene sulfonylchloride sample #1; e, f benzene sulfonylchloride sample #2; Peak: 1. chlorobenzene

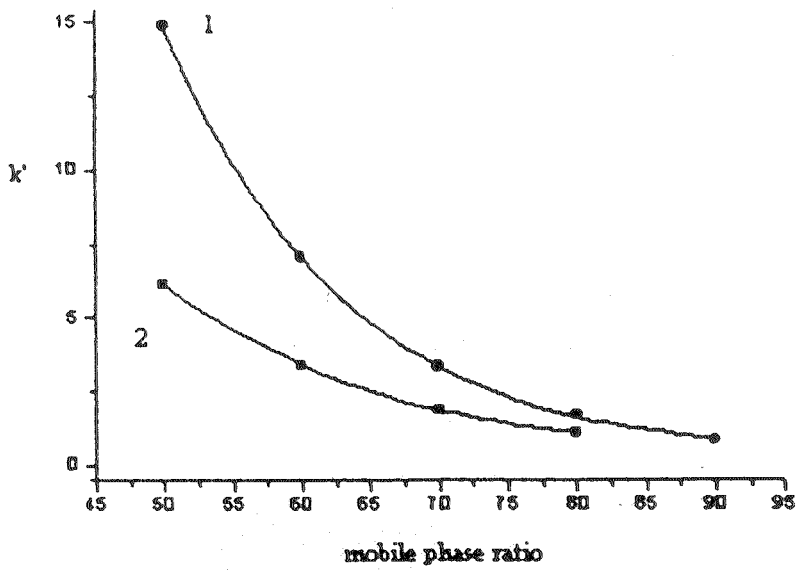

Fig. 2. Influences of organic modifier contents in mobile phase on retention of chlorobenzene. Other chromatographic conditions were same as in Fig. 1. 1. methanol-water; 2. acetonitrile-water

Linear Range and Detection Limit

A good linearity between peak areas *vs.* amounts of chlorobenzene ($r > 0.999$) was obtained in the concentration range of 0.0004–0.1 mg/mL and 0.00004–mg/mL, respectively, with methanol-water (65 : 35, v/v) and acetonitrile-water (60 : 40, v/v) as the mobile phase. The linear equations and correlation coefficients, as well as detection limits calculated at signal-to-noise ratio of 3 (S/N = 3) are shown in Table-1.

TABLE-1
THE REGRESSION EQUATIONS AND DETECTION LIMITS

Mobile phase	Regression equation	r	Detection limit (mg/mL)
Methanol-water (65 : 35, v/v)	A = –61573.04607 + 3.12495E8C	0.99989	1.00×10^{-4}
Acetonitrile-water (65 : 35, v/v)	A = –1773.19592 + 2.86843E8C	0.99998	6.25×10^{-6}

Sample Analysis

Two samples of benzene sulfonylchloride were analyzed for chlorobenzene content under two elution conditions, respectively. The determinations were based on the standard curves according to the peak areas. The contents of chlorobenzene (Table-2) were obtained from the triplicate analyses.

TABLE-2
DETERMINATION OF CHLOROBENZENE IN INDUSTRIAL BENZENE SULFONYLCHLORIDE SAMPLES (%, n = 3)

Sample No.	Methanol-water (65 : 35, v/v)			Acetonitrile-water (60 : 40, v/v)		
	Content	Average	RSD	Content	Average	RSD
1.	0.0335, 0.0329, 0.0350	0.0338	3.20	0.0314, 0.0314, 0.0314	0.0314	0.00
2.	0.0581, 0.0582, 0.0578	0.0580	0.36	0.0555, 0.0558, 0.0555	0.0556	0.31

The recovery was evaluated by adding known amounts of chlorobenzene to the samples taken and analyzed by the same HPLC method (Table-3). The recovery data are between 96.0–102.0% and 97.0–101.0%, respectively, with methanol-water (65 : 35, v/v) and acetonitrile-water (60 : 40, v/v) as the mobile phase.

Optimization of Chromatographic Conditions

Organic modifier in mobile phase: Various methanol or acetonitrile concentrations in mobile phase were adjusted to serve for optimum separation conditions. The retention time of chlorobenzene increased rapidly with the decrease of methanol content and, in contrast, slowly with the decrease of acetonitrile content. When more than 70% methanol as mobile phase was employed, the peak of chlorobenzene cannot separate from that of benzene sulfonylchloride. But the satisfactory separation was obtained when 65% methanol as mobile phase was used. For the same reason, 60% acetonitrile as another suitable mobile phase was selected.

TABLE-3
RECOVERIES OF CHLOROBENZENE (n = 3)

Mobile phase	Sample no.	Background	Added (mg/L)	Found	Recovery (%)	RSD (%)
Methanol-water	1	1.18	0.50	1.66	96.0	0.00
(65 : 35, v/v)		0.99	1.00	2.01	102.0	0.29
		1.01	2.00	3.02	100.5	0.17
		1.01	3.00	4.02	100.3	0.29
	2	1.69	0.50	2.18	98.0	0.00
		1.63	1.00	2.64	101.0	0.00
		1.63	2.00	3.62	99.5	0.00
		1.72	3.00	4.73	100.3	0.12
Acetonitrile-water	1	1.10	0.50	1.60	100.0	0.00
(60 : 40, v/v)		0.92	1.00	1.92	100.0	0.21
		0.93	2.00	2.95	101.0	0.35
		0.94	3.00	3.93	99.7	0.21
	2	1.62	0.50	2.11	98.0	0.00
		1.57	1.00	2.54	97.0	0.57
		1.56	2.00	3.57	100.5	0.21
		1.64	3.00	4.65	100.3	0.28

Detection wavelength: The strongest absorption peak can be found at 207.3 nm from UV-Vis PAD spectrum of chlorobenzene (Fig. 3). The wavelength of 215 nm was chosen because of the optimum signal-to-noise ratio.

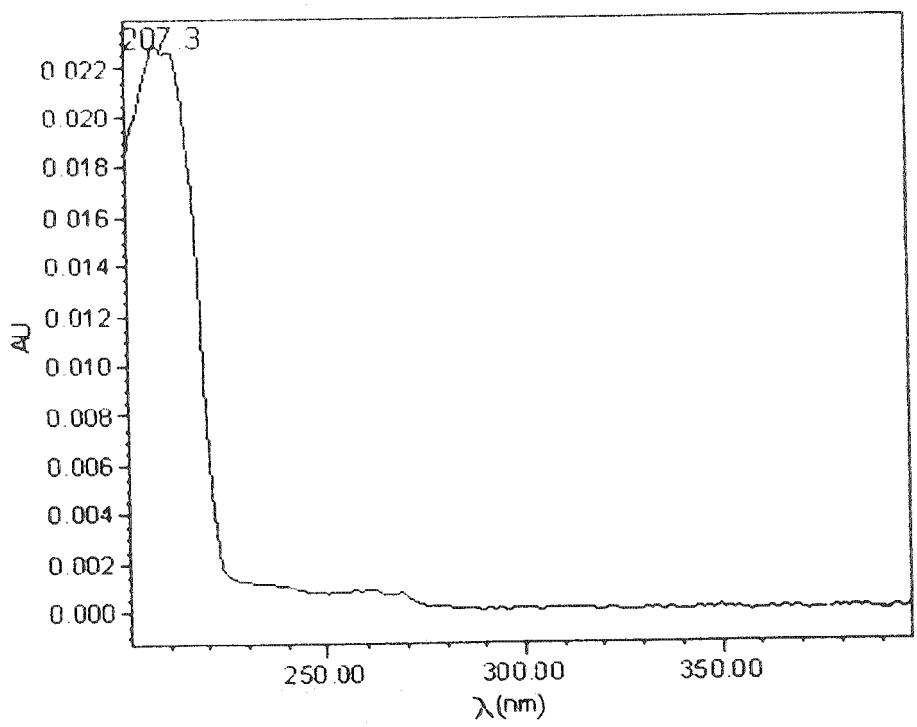

Fig. 3. PDA absorption spectrum of chlorobenzene. Chromatographic conditions were same as in Fig. 1

Conclusions

The content of chlorobenzene in benzene sulfonylchloride for industrial use was determined by reversed phase high performance liquid chromatography with two different elution systems. Detection was performed at 215 nm due to the UV-Vis spectrum of chlorobenzene. There are lower background absorbance, smoother baseline, lower detection limit and shorter equilibrium time with the mobile phase of acetonitrile-water. However, the price of acetonitrile is much higher than that of methanol and it is more economical to use methanol as the organic modifier. The result with methanol as the organic modifier is also satisfying for the department of quality inspection of a common factory, so long as the determination is achieved in the right way.

ACKNOWLEDGEMENT

This project was supported by the Analysis and Test Fund of Nanjing University.

REFERENCES

1. A.Y. Chen and Y.Z. Zhang, *Hebei Chemical Industry*, **2**, 27 (2001).
2. L. Mao, *Chinese J. Chromatogr.*, **16**, 456 (1998).
3. D.M. Ma, Y.Q. Xiao and G. Tian, *Admin. Tech. Environ. Monit.*, **13**, 34 (2001).
4. X.Y. Shen, N.B. Xu and B. Zhang, *Environ Pollut. Contr.*, **17**, 40 (1995).
5. R.K. Zhu, P. Chen, Y.H. Wang and D.Y. Hou, *Gansu Enrironmental Study and Monitoring*, **14**, 221, 245 (2001).
6. B.C. Zhu and X.M. Huang, *Anhui J. Preventive Med.*, **3**, 89 (1997).
7. S.J. Xiao and Y. Cheng, *Chinese J. Ind. Hygiene Occup. Dis.*, **11**, 106 (1993).
8. W.C. Lü, *Environ. Prot. Chem. Ind.*, **13**, 288 (1993).
9. P. Sun and Q.Y. Ma, *J. Ind. Health Occup. Dis.*, **22**, 182 (1996).
10. L.X. Yang, N. Song and Z.H. Liu, *China Public Health*, **18**, 614 (2002).
11. S.J. Xiao, W. Huang and Y.C. Yuan, *J. Ind. Health Occup. Dis.*, **20**, 313 (1994).
12. N.B. Xu, *Environ. Monitoring in China*, **12**, 16 (1996).
13. D. Gorlo, L. Wolska, B. Zygmunt and J. Namieśnik, *Talanta*, **44**, 1543 (1997).
14. Y. Wang and H.K. Lee, *J. Chromatogr. A*, **803**, 219 (1998).
15. Y.Z. Yan, X.Y. Li and L.Z. Hu, *Chemical World*, **32**, 24 (1991).
16. M.H. Xin, M.C. Li and J.R. Xu, *Environ. Eng.*, **21**, 53 (2003).
17. Y.A. Wang, *Liaoning Chemical Ind.*, **3**, 56 (1990).
18. J.C. Zhou, J.G. Zhang and H.W. Jin, *Chinese J. Hospital Pharm.*, **24**, 182 (2004).

(*Received*: 20 April 2005; *Accepted*: 12 December 2005) AJC-4536