*Journal of Chromatography*, 216 (1981) 399–401
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,135

## Note

# Separation of cyclic sulphur–nitrogen compounds by high-performance liquid chromatography. LXXVIII*

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(Received June 29th, 1981)

The cyclic sulphur imides of type $S_n(NH)_{8-n}$ with $n = 1, \ldots, 4$ as well as the related compounds $S_8$ and $S_4N_4$ are formed upon reaction of sulphur chlorides with ammonia as well as in other reactions[2]. Separation of the complex reaction mixtures by thin-layer and column chromatography on silica gel has been reported[2], but a quantitative determination of the components by weighing is difficult due to incomplete separation of some isomeric compounds on a preparative scale. Furthermore, the use of the toxic carbon disulphide as an eluent causes problems. We report here a rapid separation of several structurally related cyclic sulphur–nitrogen compounds by high-performance liquid chromatography (HPLC) using solvents of low toxicity.

## EXPERIMENTAL AND RESULTS

The compounds investigated were prepared by standard methods[2], and their purity checked by infrared and Raman spectra as well as by the melting points. A Varian 5020 liquid chromatograph equipped with a Waters UV detector (254 nm) and a Varian CDS-111 L data system and recorder was used. The sample volume was 10 $mm^3$ throughout (Valco loop injector). Waters Radial-Pak columns (10 cm × 8 mm I.D.) with $C_{18}$ and $SiO_2$, respectively, were employed (particle size 10 $\mu$m).

Table I and Fig. 1 show the compounds investigated. In most cases $SiO_2$ was superior to $C_{18}$ as a stationary phase, but sulphur-rich compounds like $S_{15}N_2$ and $S_{16}N_2$, due to their low solubility in polar solvents, could only be separated by reversed-phase chromatography (Table I). Even the ionic compound $NH_4[S_4N_5O]$[3] showed a considerable retention on $SiO_2$ on elution with pentane–methanol (75:25) (retention time, 3.7 min; flow-rate, 1 $cm^3$/min).

In general it can be said that cyclic SN compounds can easily be separated by HPLC. Because of the high absorbance at 254 nm caused by the sulphur atoms[4], a minute amount of substance is needed, and solvents of low cost and toxicity can be used. Small and polar molecules are separated best on $SiO_2$, while for larger and less polar substances $C_{18}$ columns are necessary. After appropriate calibration a quantitative analysis is possible[4]. HPLC thus provides a means to optimize preparative reaction conditions and to search for new compounds in complex reaction mixtures.

* For Part LXXVII, see ref. 1.

0021-9673/81/0000–0000/$02.50 

TABLE I

RETENTION TIMES ($t$) OF CYCLIC SULPHUR–NITROGEN COMPOUNDS UNDER VARIOUS CONDITIONS

| *Column and eluent* | *Compounds* | *t (min)* | *Flow-rate (cm³/min)* |
|---|---|---|---|
| $SiO_2$, pentane–methanol (90:10) | $S_8$ | 2.95 | 0–3.5 min: 1.0 |
| | $S_7NCH_3$ | 3.12 | 3.5–9.0 min: 1.0 → 2.0 |
| | $S_4N_4$ | 4.82 | 9.0–25 min: 2.0 |
| | $S_7NH$ | 5.47 | |
| Dead time | 1,3-$S_6(NH)_2$ | 8.62 | |
| *ca.* 2.2 min | 1,4-$S_6(NH)_2$ | 10.47 | |
| at flow-rate 1.0 $cm^3$/min | 1,5-$S_6(NH)_2$ | 10.86 | |
| | $S_4(NH)_4$ | 20.46 | |
| | (dissolved in eluent) | | |
| $C_{18}$, pentane–methanol (80:20) | $S_7NH$ | 2.4 | 1.0 |
| | $S_7NCOCH_3$ | 3.29 | |
| | $S_8$ | 3.79 | |
| | (dissolved in eluent) | | |
| $C_{18}$, pentane–methanol (30:70) | $S_{15}N_2$ | 10.40 | 1.0 |
| | $S_{16}N_2$ | 12.35 | |
| | (dissolved in $CS_2$) | | |

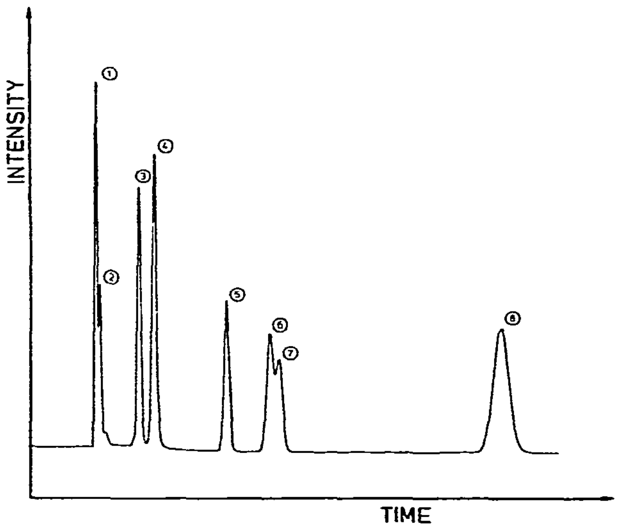


Fig. 1. Chromatogram of a mixture of $S_8$ and seven sulphur–nitrogen compounds using $SiO_2$ as a stationary phase and pentane–methanol as the eluent (see Table I, upper part). 1 = $S_8$; 2 = $S_7NCH_3$; 3 = $S_4N_4$; 4 = $S_7NH$; 5 = 1,3-$S_6(NH)_2$; 6 = 1,4-$S_6(NH)_2$; 7 = 1,5-$S_6(NH)_2$; 8 = $S_4(NH)_4$.

ACKNOWLEDGEMENTS

Support by the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie is gratefully acknowledged.

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