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Short communication

Normal-phase high-performance liquid chromatographic separation of halocyclophosphazenes

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Abstract

Lower members of the chlorocyclophosphazene homologous series $(NPCl_2)_n$, $n = 3–6$, were separated using normal-phase HPLC. Very good separation was achieved using Separon SGX (7 μm) silica gel column (250 × 4 mm I.D.) and *n*-heptane as the mobile phase. An addition of a more polar solvent (2-propanol) depressed the retention dramatically. The separated substances can be detected by spectrophotometry at a wavelength of *ca.* 220 nm, the detection limits varying the range *ca.* 30–1500 ng. The bromo derivative $(NPBr_2)_3$ exhibits a similar behaviour to the chloro derivatives.

1. Introduction

Cyclophosphazenes are inorganic cyclic compounds with staggered atoms of phosphorus and nitrogen. Their chloro derivatives, chlorocyclophosphazenes, having the general formula $(NPCl_2)_n$, were discovered about 160 years ago [1]. The greatest contributions to the chemistry of cyclophosphazenes were made by Stokes [2]. The chemistry of cyclophosphazenes is now a relatively widely developed field (see, e.g., reviews and monographs [3–7]) and the derivatives of cyclophosphazenes have been used in various branches of industry, agriculture and medicine (fertilizers, herbicides, fungicides, antioxidants, stabilizers for polymers, flame retardants, etc.) [8–11].

The separation of individual members of the homologous series of cyclophosphazenes is comparatively difficult. As far as chromatographic methods are concerned, gas chromatography [12–14], paper chromatography [15] and, most successfully, thin-layer chromatography (TLC) [16–18] have been applied. The objective of this work was to verify the viability of separating halocyclophosphazenes by liquid chromatography. The separation of the lower oligomers of cyclophosphazenes ($n = 3–6$) and the chromatographic behaviour of hexabromocyclotriphosphazene $(NPBr_2)_3$ were examined.

2. Experimental

The liquid chromatograph consisted of an HPP 5001 high-pressure pump, an LCI 30 injection valve with a 20-μl sampling loop, a TZ 4261 strip-chart recorder (all from Laboratorní

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přístroje, Prague, Czech Republic) and a Model 732780 UV–Vis spectrophotometric detector (Knauer, Berlin, Germany). Separation was effected on a 250 × 4 mm I.D. column packed with Separon SGX (7 μm) unmodified silica (Tessek, Prague, Czech Republic). *n*-Heptane (UV grade), alone or mixed with 2-propanol (analytical-reagent grade) (both supplied by Lachema, Brno, Czech Republic), served as the mobile phase. Prior to measurements the mobile phase was deaerated in an ultrasonic bath. The mobile phase flow-rate was 0.5 ml min^{-1}.

The chlorocyclophosphazenes were prepared by reaction of phosphorus pentachloride with ammonium chloride in tetrahydrofuran. Extraction, fractional distillation and fractional crystallization were applied for isolation and purification of the individual derivatives [19]. The purity of the preparations was checked by TLC [16,18].

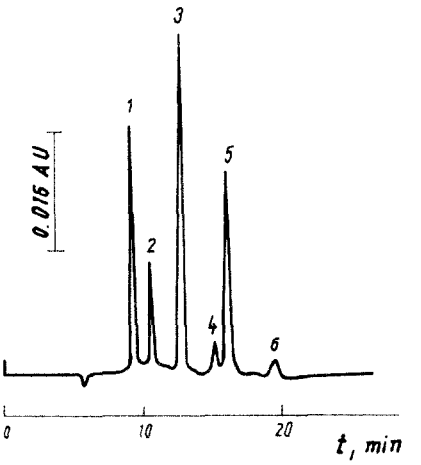

Fig. 1. Separation of a mixture of chlorocyclophosphazenes Column, 250 × 4 mm I.D. Separon SGX (7 μm); mobile phase, *n*-heptane; UV detection at 220 nm. Peaks: 1 = $(NPCl_2)_4$; 2 = $(NPCl_2)_5$; 3 = $(NPCl_2)_6$; 5 = $(NPCl_2)_3$; 4, 6 = unidentified (presumably higher derivatives).

3. Results and discussion

Halo derivatives of cyclophosphazenes are soluble in non-polar and low-polarity solvents and insoluble in water [19–22]. Consequently, chromatographic systems employing non-polar organic solvents as the mobile phases appear to be most convenient for their separation. It has been ascertained that the lower derivatives of chlorocyclophosphazenes (n = 3–6) can be readily separated on a silica column with *n*-heptane as the mobile phase (Fig. 1). The retention of analytes in a homologous series increases with increasing number of atoms in the ring, the exception being the lowest member, hexachlorocyclotriphosphazene, which is retained more strongly than the other derivatives examined. It was not possible to explain such a behaviour, but a similar anomaly was noticed during separation by TLC [16,17].

The retention of halocyclophosphazenes may be influenced by adding polar solvents to the mobile phase. The retention of analytes decreased steeply with increasing content of 2-propanol in *n*-heptane, the dependences of the capacity factors on 2-propanol concentration being almost linear (Fig. 2), which is inconsistent with both the common theoretical and empirical relationships for adsorption chromatography [23]. The limited number of experimental data,

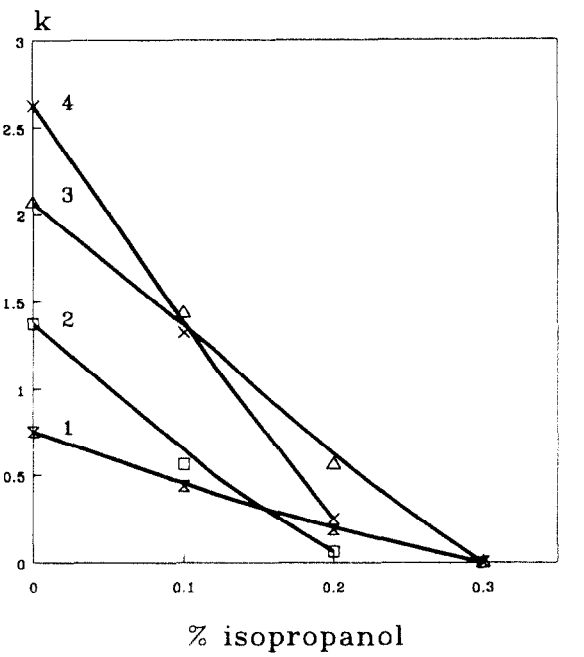

Fig. 2. Dependence of capacity factor on the content of 2-propanol in the mobile phase. 1 = $(NPCl_2)_4$; 2 = $(NPCl_2)_5$; 3 = $(NPCl_2)_3$; 4 = $(NPBr_2)_3$.

Table 1
Detection limits and parameters of calibration lines for the determination of halocyclophosphazenes

Substance	Detection limit (ng)	Slope (absorbance ng^{-1})	Intercept on the ordinate (absorbance)	Correlation coefficient ($n = 7$)
$(NPCl_2)_3$	86	$1.83 \cdot 10^{-6}$	$2.15 \cdot 10^{-2}$	0.9955
$(NPCl_2)_4$	31	$6.26 \cdot 10^{-6}$	$7.32 \cdot 10^{-2}$	0.9991
$(NPCl_2)_5$	54	$2.04 \cdot 10^{-6}$	$4.67 \cdot 10^{-2}$	0.9983
$(NPCl_2)_6$	72	$2.68 \cdot 10^{-6}$	$6.36 \cdot 10^{-2}$	0.9991
$(NPBr_2)_3$	1500	N.D.[a]	N.D.[a]	

[a] Not determined.

however, make it impossible to draw any more definite conclusions concerning the retention mechanism.

Direct spectrophotometric detection in the UV region was adopted for studying the separation of halocyclophosphazenes. Inconsistent data relating to the character of the spectra of halocyclophosphazenes in that region have been reported [24,25] and, therefore, the spectra of halocyclophosphazenes were measured in the mobile phase (Fig. 3). The shape of the spectrum is similar to that measured by Krause [24]. The highest sensitivity of detection was found at *ca.* 220 nm; at lower wavelengths the sensitivity was lower and additionally the baseline noise was higher. With increasing wavelength the sensitivity also decreased sharply, so that the most common UV detectors operating at 254 nm cannot be used for the detection of halocyclophosphazenes. Parameters of the calibration straight lines and the detection limits were measured at 220 nm (Table 1). It is obvious that for the chloro derivatives the detection limit is related to their retention (broadening of more strongly retained peaks).

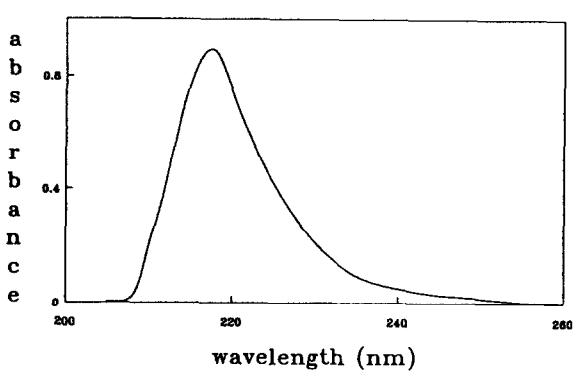

Fig. 3. UV spectrum of hexachlorocyclotriphosphazene in *n*-heptane. Spectra of other chlorocyclophosphazenes were very similar.

References

[1] J. Liebig and W. Woehler, *Justus Liebigs Ann. Chem.*, 11 (1834) 139.
[2] H.N. Stokes, *Am. Chem. J.*, 17 (1895) 275.
[3] I. Haiduc, *The Chemistry of Inorganic Ring Systems*, Part II, Wiley-Interscience, London, 1970.
[4] V.S. Matveev, *Khim. Volokna*, No. 4 (1992) 3.
[5] C.W. Allen, *Organophosphorus Chem.*, 24 (1993) 359.
[6] V. Chandrasekhar and K.R. Thomas, *Struct. Bonding (Berlin)*, 81 (1993) 41.
[7] C.W. Allen, *Coord. Chem. Rev.*, 130 (1994) 137.
[8] S.M. Zhivukhin and V.S. Tolstoguzov, *Plast. Massy*, 5 (1963) 24.
[9] C.W. Allen, *J. Fire Sci.*, 11 (1993) 320.
[10] H.R. Allock and M.L. Turner, *Macromolecules*, 26 (1993) 3.
[11] D. Kumar, A.D. Gupta and M. Khullar, *J. Polym. Sci., Part A*, 31 (1993) 707.
[12] L.G.R. Gimblett, *Chem. Ind. (London)*, (1958) 365.
[13] H. Rotzsche, R. Stahlberg and E. Steger, *J. Inorg. Nucl. Chem.*, 28 (1966) 687.
[14] K.S. Brenner, *J. Chromatogr.*, 57 (1971) 191.
[15] E. Uhlig and H. Eckert, *Z. Anorg. Allg. Chem.*, 204 (1969) 322.
[16] V. Novobilský, V. Kolský and W. Waněk, *Z. Anorg. Allg. Chem.*, 416 (1975) 187.
[17] V. Novobilský, V. Kolský and W. Waněk, *Z. Anorg. Allg. Chem.*, 423 (1976) 273.
[18] V. Novobilský, *Z. Anorg. Allg. Chem.*, 427 (1976) 189.
[19] J. Novák, *Ph.D. Thesis*, Purkyné University, Brno, 1970.

[20] M. Yokoyama and F. Yamada, *Kogakuin Daigaku Kenkyn Hokoku*, 6 (1958) 94; *Ref. Zh. Khim.*, 81 (1959) 507.
[21] N.L. Paddock and H.T. Searle, *Adv. Inorg. Chem. Radiochem.*, 1 (1959) 347.
[22] K. John and T. Moeller, *J. Inorg. Nucl. Chem.*, 22 (1961) 199.
[23] P. Jandera and J. Churáček, *J. Chromatogr.*, 91 (1974) 207.
[24] H.J. Krause, *Z. Elektrochem.*, 59 (1955) 1034.
[25] N.B. Jurinski, C.C. Thompson and P.A.D. DeMaine, *J. Inorg. Nucl. Chem.*, 27 (1965) 1571.