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The chromatographic separation of selenocyanate and thiocyanate*

A number of workers have studied the separation of sulphur- and selenoamino acids from each other in recent years. PETERSON AND BUTLER¹ noted that the seleno analogues of sulphur amino acids had the same R_F values in paper chromatography with butanol solvents and in DEAE-cellulose paper chromatography and small separation effects could only be observed in long paper electrophoretic runs. SCALA AND WILLIAMS² resorted to an oxidation reaction to distinguish between Se and S amino acids as no separation of analogues could be effected.

Separations were, however, obtained on Silica Gel G plates by MILLAR³ and on an ion exchange column by McCONNELL AND WABNITZ⁴.

The present study was prompted by the fact that no chromatographic separations of $CNSe^-$ and CNS^- have been recorded so far and an identification of $CNSe^-$ might be of interest especially in connection with qualitative ultimate analyses. Besides it was thought that the data obtained could give a useful lead for the separation of other pairs of seleno- and sulphur analogues.

All the chromatograms were performed in the usual manner at room temperature and the spots revealed by spraying with an acid solution of ferric nitrate.

Results

Partition chromatography. No separations could be obtained with isopropanol- NH_3 , butanol- NH_3 or amyl alcohol- NH_3 . Small R_F differences exist in butanol- NH_3 but the spots are elongated. Macherey, Nagel & Co. cellulose thin layers gave the same results as filter paper sheets.

The R_F values are shown in Table I.

TABLE I

R_F VALUES OF $KCNSe$ AND $KCNS$ IN PARTITION SOLVENTS ON WHATMAN 3MM PAPER AT ROOM TEMPERATURE

Solvent	$CNSe^-$	CNS^-
Isopropanol-1.5 N NH_4OH (95:5)	0.42	0.40
Isopropanol-1.5 N NH_4OH (90:10)	0.54	0.54
Isopropanol-1.5 N NH_4OH (80:20)	0.73	0.73
Butanol- NH_4OH-H_2O (100:10:90)	0.38	0.36
Amyl alcohol- NH_4OH-H_2O (100:10:90)	0.11	0.11

Adsorption on cellulose. In previous work on the adsorption of anions on cellulose paper⁵ a reasonably strong adsorption was observed from ammonium sulphate solutions and as shown in Table II not only do both the anions adsorb but there is also a good separation in 6 N and 8 N $(NH_4)_2SO_4$, thiocyanate moving ahead of the selenocyanate. See Fig. 1.

Ion exchange chromatography. Small R_F differences insufficient for separation were obtained on Macherey, Nagel & Co. quaternary ammonium anion exchange

* Dedicated to Professor E. LEDERER on the occasion of his 60th birthday.

TABLE II

R_F VALUES OF $KCNSe$ AND $KCNS$ WITH AQUEOUS SOLVENTS ON WHATMAN 3MM PAPER AT ROOM TEMPERATURE

Eluent: aqueous ammonium sulphate	$CNSe^-$	CNS^-
2 N	0.64 ± 0.02	0.68 ± 0.03
4 N	0.54 ± 0.02	0.58 ± 0.02
6 N	0.40 ± 0.02	0.45 ± 0.03
8 N	0.30 ± 0.03	0.35 ± 0.03

TABLE III

R_F VALUES OF $KCNSe$ AND $KCNS$ ON ANION EXCHANGE PAPERS AT ROOM TEMPERATURE

	$CNSe^-$	CNS^-
(i) <i>Macherey Nagel & Co. quaternary ammonium cellulose paper</i>		
Eluent: aqueous ammonium sulphate		
0.1 N	0.35	0.35
0.5 N	0.49	0.47
1 N	0.50	0.53
2 N	0.47	0.50
3 N	0.42	0.42
Eluent: aqueous lithium nitrate		
0.1 N	0.45	0.42
0.5 N	0.52	0.58
1 N	0.61	0.65
2 N	0.74	0.78
3 N	0.81	0.81
(ii) <i>Amberlite SB2 strong anion exchange resin paper</i>		
Eluent: aqueous lithium nitrate		
0.1 N	0.02	0.03
0.5 N	0.04	0.06
1 N	0.08	0.11
2 N	0.09	0.15
3 N	0.13	0.19
5 N	0.13	0.20
6 N	0.13	0.22
7 N	0.12	0.19
8 N	0.12	0.20

cellulose paper with ammonium sulphate or lithium nitrate as developing solvent. The spots were also elongated and not very compact.

By far the best separations were obtained with anion exchange resin paper (Amberlite SB2). While both anions are strongly absorbed around R_F 0 with ammo-

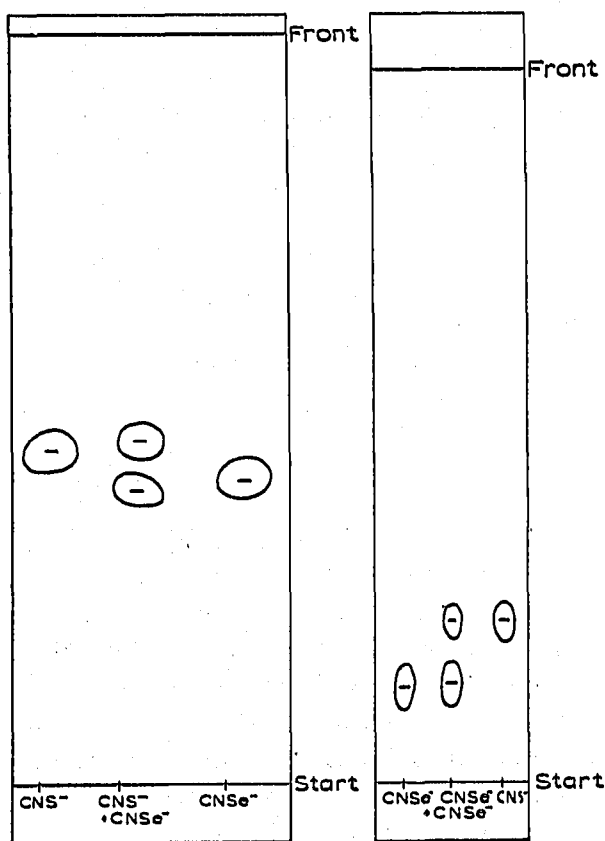


Fig. 1. (A) Separation of CNSe^- – CNS^- on Whatman 3MM paper with aqueous ammonium sulphate as eluant. (B) Separation of CNSe^- – CNS^- on Amberlite SB-2 paper with 6N LiNO_3 as eluant.

niium sulphate, they separate well with 6 N LiNO_3 , selenocyanate being more strongly retained than thiocyanate (Table III and Fig. 1).

Our findings seem to be identical to those with selenoamino acids, namely that pure partition systems (in butanol solvents) do not separate the seleno- from the sulphur analogue but that only when adsorption plays a part in the separation, *i.e.* on the resin matrix or by salting out on cellulose, separations can be effected.

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- 1 P. J. PETERSON AND G. W. BUTLER, *J. Chromatog.*, 8 (1962) 70.
- 2 J. SCALA AND H. H. WILLIAMS, *J. Chromatog.*, 15 (1964) 546.
- 3 K. R. MILLAR, *J. Chromatog.*, 21 (1965) 344.
- 4 K. P. MCCONNELL AND C. H. WABNITZ, *Biochim. Biophys. Acta*, 86 (1964) 182.
- 5 M. LEDERER AND L. OSSICINI, *J. Chromatog.*, 15 (1964) 514.

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