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A note on the chromatography of phosphorus anions

Many ion exchange separations of phosphorus anions have been reported[1] and their achievement is now quite routine. We report here some interesting correlations between structure and retention time.

Separations of various mixtures of phosphorus anions were performed using continuous elution with an approximately linearly increasing concentration of KCl in water buffered at pH 11.4. It was found that the retention times were, to a very good approximation: (a) proportional to the flowrate; (b) proportional to the gradient used; (c) when the gradient was not started from zero concentration of salt, decreased by a time equal to the time which would have been taken to reach the initial concentration if the elution had started from a zero concentration.

TABLE I

RETENTION TIMES FOR VARIOUS AMIDOTHIOORTHOPHOSPHATES UNDER VARIOUS CONDITIONS OF ELUTION
All at pH 11.4; linear gradients of 1 l into 1 l.

| Scheme | Gradient (g/l) | | Flow rate (ml/min) | Retention times (min) | | | |
	Reservoir	Initial		$PO_2(NH_2)_2^-$	$POS(NH_2)_2^-$	$PO_3NH_2^{2-}$	$PO_2SNH_2^{2-}$
1	30	0	1.01	40	150	250	400
2	30	5	1.01	0	0	60	140
3	50	0	1.01	20	110	165	250
4	50	5	1.01	0	0	40	80
5	100	0	1.01	10	55	90	125
6	100	0	1.33	10	40	60	90
7	150	0	1.01	10	35	55	85

Data for various flow rates, gradients and initial concentrations are given in Table I.

From the values in Table I the additivity of structural features may be seen. The series PO_4^{3-}; PO_3S^{3-}; $PO_2S_2^{3-}$; POS_3^{3-}; PS_4^{3-} occurs with equal time intervals between species (e.g. in row 6 they are 60–65 min apart). $POS(NH_2)_2^-$ elutes as far before $PO_2(NH_2)_2^-$ as $PO_2SNH_2^{2-}$ before $PO_3NH_2^{2-}$ but here the increment on exchanging an oxygen for a sulphur atom is only half that in the thiophosphate series. Why these different behaviours should be is not known.

Similarly with amidophosphates replacing oxygen by amide shortens the retention time by a constant (row 6:50 min).

That the additivity is a property of the fully ionized species is shown by a complete loss of such effect at pH 7.

The use of correlations such as these in predicting structures of unknown compounds is immediately obvious. For instance in reactions of P_4S_7 and aqueous Na_2S a strong peak at 540 min (scheme 6) was apparent. That this was the $P_2S_7^{4-}$ anion is likely from the retention time: $P_2O_7^{4-}$ 160 min; a PSP bridge should have little effect

not being a charged group; six terminal sulphur atoms should add 360–390 min, *i.e.* a total of 520–550 min. On isolation the compound proved in fact to be a $P_2S_7^{4-}$ salt.

Experimental

    An ion exchange column 6 cm long by 1.2 cm diameter was filled with Dowex 1X10 200–400 mesh anion-exchange resin. The linear gradient was constructed by connecting with a syphon tube two similar cylindrical bottles of 1 l capacity filled with KCl solutions (A.R. grade) buffered at pH 11.4 by 20 ml of 0.88 ammonia per l. The eluent was withdrawn from the bottle of lower concentration solution whence the more concentrated solution flowed in to maintain hydrostatic equilibrium, and was well mixed. Under conditions of equal density and perfect mixing the gradient may be shown to be linear[2]. Such conditions were approximately fulfilled here. The elution of phosphorus species was continuously monitored by a Technicon Auto Analyzer assembly[3]. Sample application was in a small volume of initial eluent solution to a

PO_4^{3-}	PO_3S^{3-}	$PO_2S_2^{3-}$	POS_3^{3-}	PS_4^{3-}	Ratio of ret. time with respect to No. 6		Displacement due to init. conc.	
					Calc.	*Exptl.*	*Calc.*	*Exptl.*
390	580	860	1100	1300	4.4	4.2 ± 1		
140	300	540	780	980	4.4	4.2 ± 1	330	320
240	365	550	710	840	2.7	2.6 ± 1		
80	190	350	510	640	2.7	2.6 ± 1	200	190
125	200	280	370	440	1.32	1.37 ± 0.03		
90	145	210	270	320	1.00	1.00		
85	135	200	250	300	0.88	0.92 ± 0.03		

column which had previously been equilibrated in the same solution for half an hour or so. Between runs the column was regenerated by running 4 N HCl through it for about one hour. Complete reproducibility was always found.

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