

PAPER CHROMATOGRAPHY OF INORGANIC IONS
XIX. THE CHROMATOGRAPHY OF POLONIUM
AND OTHER IONS ON ACETYLATED FILTER PAPER

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INTRODUCTION

Work with milligram amounts of polonium has shown that reduction of Po(IV) with SO₂ yields a pink solution of Po(II) (in dilute HCl) which is auto-oxidised to Po(IV) within a matter of minutes¹. It thus seemed of interest to us to attempt paper chromatographic experiments with Po(II) since here only tracer amounts are required and hence the behaviour of Po(II) in the absence of the auto-oxidation effect of its α -rays may be observed.

In the usual partition chromatography with butanol-HCl mixtures no differences in R_F values could be observed between chromatograms run in air and in SO₂, although this problem was investigated carefully². Furthermore no difference between Po(II) and Po(IV) was noted in adsorption paper chromatography with aqueous HCl solutions, where Po(IV) is strongly adsorbed³. It was, however, possible to distinguish between Po(IV) and lower valencies of Po by chromatography with organic solvents on acetylated cellulose paper, a technique which has not been used previously for inorganic ions.

This paper will describe the behaviour of a number of inorganic ions on acetylated paper and more specifically the differences obtained when polonium is chromatographed with air and with CO₂ and SO₂ as atmosphere and after mixing with reducing agents.

EXPERIMENTAL

(1) *Chromatography on acetylated paper*

Throughout this work either Binzer No. 202 acetylated paper with 43% acetylation or Schleicher and Schüll paper with 20-25% acetylation was employed. All the acetylated papers are hydrophobic so that development with aqueous solutions is impossible.

Solutions of ions to be chromatographed are best made in butanol-HCl mixtures since aqueous solutions do not wet the paper.

Table I shows the R_F values of several metal ions when developed with butanol-HCl mixtures on ordinary and acetylated papers.

(2) *The behaviour of Po(IV) on acetylated paper*

Solutions of Po(IV) in HCl were chromatographed in butanol-HCl mixtures on Schleicher and Schüll paper (20-25% acetylated). As shown in Fig. 1, Po(IV) is strongly retained on the acetylated paper, thus behaving like the chlorides of Au(III), Fe(III), Tl(III) and Sb(V) (which, incidentally, are also extracted into ether).

TABLE I
 R_F VALUES OF SOME CATIONS ON ACETYLATED FILTER PAPER

Cations	R_F values on	
	Whatman No. 1	Binzer (43% acetylated) paper
<i>Solvent I: butanol-conc. HCl (2:1)</i>		
Au (III)	1.0	0.20-0.28*
Bi (III)	0.53	0.58
Cd (II)	0.89	0.65
Cu (II)	0.62-0.59	0.55
Fe (III)	1.0	0.23
Hg (II)	0.86	0.63
Tl (III)	1.0	0.35
Sb (III)	0.76	0.41
Se (IV)	0.68	0.66
Ni (II)	0.14	0.18
Ga (III)	1.0	0.17
Sb (V)	1.0 comet to 0	0.15 forward comet
Al (III)	0.07	0.16
Co (II)	0.63	0.63
Mn (II)	0.15	0.28
<i>Solvent II: butanol-8 N HCl (2:1)</i>		
Au (III)	0.95	0.15
Cd (II)	0.89	0.83
Co (II)	0.24	0.38
Cu (II)	0.50	0.49
Fe (III)	1.0	0.44 comet to 0.04
Hg (II)	0.87	0.73
Ni (II)	0.19	0.37
<i>Solvent III: butanol-6 N HCl (2:1)</i>		
Au (III)	0.95	0.14
Cd (II)	0.97	0.94
Co (II)	0.24	0.40
Cu (II)	0.40	0.46
Fe (III)	1.0	0.38 comet to 0.08
Hg (II)	0.95	0.85
Ni (II)	0.21	0.34

* Figures in italics indicate a great difference between the two papers.

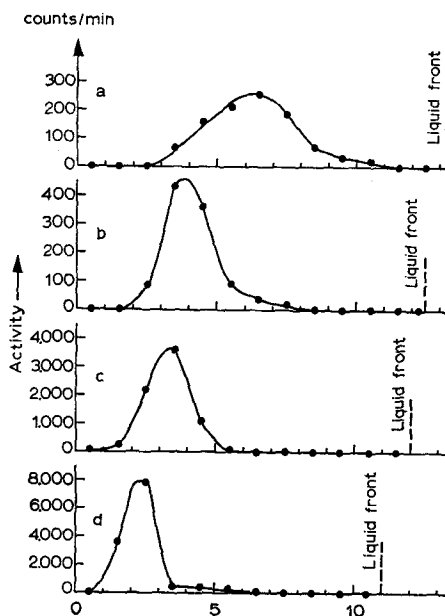


Fig. 1. Activity distribution on chromatograms of Po(IV) chromatographed in air (or CO_2) on Schleicher and Schüll 20–25% acetylated paper. Solvents and R_F values: (a) butanol–6 N HCl (2:1), R_F 0.47; (b) butanol–8 N HCl (2:1), R_F 0.31; (c) butanol–10 N HCl (2:1), R_F 0.28; (d) butanol–12 N HCl (2:1), R_F 0.21.

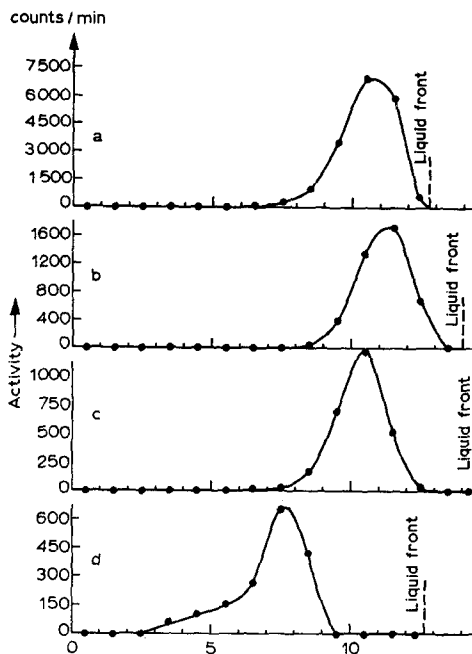


Fig. 2. Activity distribution on chromatograms of Po (originally as Po(IV)) chromatographed in an SO_2 atmosphere on Schleicher and Schüll 20–25% acetylated paper. Solvents and R_F values: (a) butanol–6 N HCl (2:1), R_F 0.84; (b) butanol–8 N HCl (2:1), R_F 0.80; (c) butanol–10 N HCl (2:1), R_F 0.72; (d) butanol–12 N HCl (2:1), R_F 0.61.

(3) *Experiments on the reduction of Po(IV) and chromatography in an inert or reducing atmosphere*

Po(IV) when chromatographed in an SO₂ atmosphere in the apparatus of SCHAMRAJ* moves close to the liquid front when developed with butanol-HCl mixtures as shown in Fig. 2. According to BAGNALL⁵ the species chromatographed was Po(II) and we have thus found a chromatographic system in which Po(IV) and Po(II) can be readily distinguished. We then proceeded to examine the influence of various reducing agents and of the atmosphere on this chromatographic system. When Po(IV) was mixed with cuprous chloride in HCl and chromatographed in a CO₂ atmosphere, usually two spots were obtained of which one corresponds to Po(IV) and the other moves faster than Po(IV) but slower than Po(II).

Typical results are shown in Fig. 3. The presence of Po(IV) indicated that the

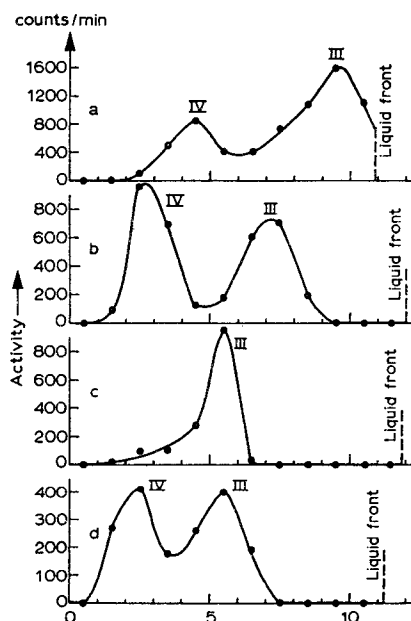


Fig. 3. Activity distribution on chromatograms of Po(IV) mixed with Cu(I) chromatographed in a CO₂ atmosphere on Schleicher and Schüll 20-25% acetylated paper. Solvents and R_F values: (a) butanol-6 N HCl (2:1), R_F 0.41 and 0.88; (b) butanol-8 N HCl (2:1), R_F 0.23 and 0.60; (c) butanol-10 N HCl (2:1), R_F 0.46; (d) butanol-12 N HCl (2:1), R_F 0.21 and 0.49.

reducing conditions led to a partial reduction and the intermediate spot should thus correspond to Po(III), a valency also observed in the auto-oxidation of macro-amounts of Po(II) by BAGNALL AND FREEMAN¹, but whose existence could not be confirmed by other methods.

The spot of intermediate R_F value was also obtained when Po(IV) was reduced with Fe(II), SO₂ or Ti(III) and chromatographed in an inert (CO₂) atmosphere. This

* An apparatus described in the handbook of HAIS AND MACEK⁴.

behaviour would be in agreement with the oxidation potential of about 0.74 V, which can be deduced from the results of BAGNALL AND FREEMAN¹. The behaviour of Po(II), Po(III) and Po(IV) is summarised in Fig. 4. On ordinary cellulose paper (*e.g.* Whatman No. 1) there is no difference between the movement of Po(III) and that of Po(IV) in butanol-HCl mixtures and, as has been observed previously², Po(II) also cannot be distinguished.

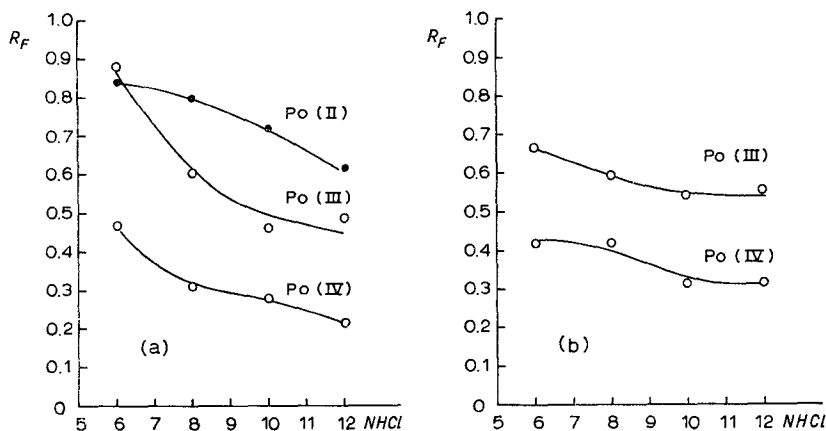


Fig. 4. Graphical representation of the change of R_F values with the concentration of HCl in butanol-HCl mixtures (ratio 2:1) for Po(IV), Po(III) and Po(II). (a) On Schleicher and Schüll 20-25% acetylated paper; (b) On Binzer 43% acetylated paper (for Po(IV) and Po(III) only).

DISCUSSION

Acetylated paper must be considered as similar to a stationary highly oxygenated liquid phase, which has little influence on the movement of cations and some complex anions, but extracts preferentially those halogen complexes which are soluble in ethyl ether and are also adsorbed on resin and cellulose surfaces. While in the usual partition chromatography little differentiation of these highly hydrophobic complexes may be made owing to their high R_F values, separations can be achieved by chromatography on acetylated papers with organic solvents. In the usual paper chromatography no differences can be observed between Po(IV) and the lower valencies of Po which all travel with the liquid front. On acetylated cellulose, three differently moving species could be observed in butanol-HCl mixtures: rather strongly adsorbed Po(IV), practically unadsorbed Po(II) which exists only in an atmosphere of SO_2 , and a species obtained by the addition of reducing agents to Po(IV) and chromatography in air or CO_2 , which has R_F values intermediate between Po(IV) and Po(II).

It is unlikely that this latter species is an equilibrium mixture of Po(II) and Po(IV), because both Po(IV) and this species may be separated from each other. A gradual oxidation of Po(II) to Po(IV) during the development should result in a trail and not a well-defined zone as is actually the case. As this species is formed under milder reducing conditions than Po(II) and is still stable in air, we consider it likely that it may be Po(III) which, according to the work of BAGNALL AND FREEMAN¹ should

be formed under these conditions. Our observations seem to constitute a confirmation of these results and the first chromatographic isolation of Po(III).

Previous evidence for the existence of Po(III) obtained by several workers by co-crystallisation experiments (for a summary see⁵) was considered doubtful by BAGNALL⁵; however, the stability of Po(III) in air as well as the ready reduction by Fe(II) in our solvent systems indicate that the presence of Po(III) in these experiments is not excluded.

SUMMARY

The chromatographic behaviour of metal ions on acetylated paper with butanol-HCl was investigated. The lower valencies of polonium may be differentiated in this system.

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