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The paper chromatography of inorganic ions at low temperatures

It was evident from several studies (*e.g.* the chromatography of Tc(V), the separation of diamminodihaloplatinum(II) complexes)[1,2] that reactions could be slowed down sufficiently at low temperatures to permit chromatographic separation where this was not possible at room temperature.

We therefore decided to investigate the conditions under which inorganic ions could be chromatographed at −30°. Argentation thin-layer chromatography at −30° is already a standard technique in the lipid field, but no data were available for the various partition, adsorption and ion-exchange systems employed in inorganic studies.

The key apparatus for this work proved to be the "Ignis" deep-freezer (made in Italy), internal dimensions 38 × 66 × 60 cm, with an opening lid (no doors). This freezer maintains a temperature of −30° throughout its volume (thermometers on bottom, near top and inside the chromatography jars) with variations not exceeding 1°. Furthermore this freezer is not more expensive than some of the usual chromatography containers on the market.

Experimental

The chromatography jars, 26 × 10 cm, used in this work were fitted with rubber stoppers which had glass hooks to hold the paper and to permit its insertion into the solvent while the jar was closed. The jars were placed into polythene bags both to ensure better insulation when opening the freezer and to avoid acid fumes escaping and condensing on the walls of the freezer.

The range of solvents which are liquid at −30°, as established with test tube experiments, is rather large and is shown in Table I.

TABLE I

SOLVENTS WHICH REMAIN LIQUID AT −30°

Methanol–water (1:1)	Isopropanol–water (9:1)
Methanol–water (8:2)	Isopropanol–water (8:2)
Ethanol–water (9:1)	Aqueous HCl above 4 *N*
Ethanol–water (1:1)	Butanol–6 *N* HCl (1:1)
Acetone–water (8:2)	Butanol–2 *N* HCl (1:1)
Acetone–water (1:1)	Butanol–1 *N* HCl (1:1)

One complication which we feared was that the stationary phase would be solid or altered to such an extent that equilibrium would not be established as at room temperature. However, this phenomenon was only observed in aqueous HCl from 4 to 6 *N*, while above 6 *N* chromatograms were obtained which developed and had spot shapes as those at room temperature.

Partition chromatography. Table II shows the R_F values of a number of metal ions in butanol–6 *N* HCl at room temperature and at −30°. Several complexed ions, *e.g.* Bi(III), yielded double spots or tails at −30° but not at room temperature. Ba(II) was completely insoluble at −30° and could not be placed on the paper.

TABLE II

R_F VALUES OF METAL IONS IN BUTANOL–6 N HCl (1:1) AT ROOM TEMPERATURE AND AT −30°
Paper: Whatman No. 3MM.

Metal ion	*20°*	*−30°*
Co(II)	0.43	0.32
Ni(II)	0.41	0.30
UO_2^{2+}	0.50	0.29
Hg(II)	1	0.68–0.89 (tail)
Cu(II)	0.53	0.29
Bi(III)	0.76	0.49 and 0.86
Cd(II)	0.96	0.66
Mn(II)	0.49	0.35
Al(III)	0.49	0.38
Mg(II)	0.47	0.36
Ca(II)	0.41	0.24
Sr(II)	0.34	0.24
Ba(II)	0.21	insoluble

In general the R_F values are lower at −30°, as expected from previous studies of temperature variations[3,4]. However, the overall picture is not altered much, and similar separations are possible at −30°.

Adsorption chromatography. Fig. 1 shows the R_F values of Au(III) and Ga(III) on Whatman No. 1 filter paper at 20° and at −30°. The differences observed at the two temperatures are surprisingly small.

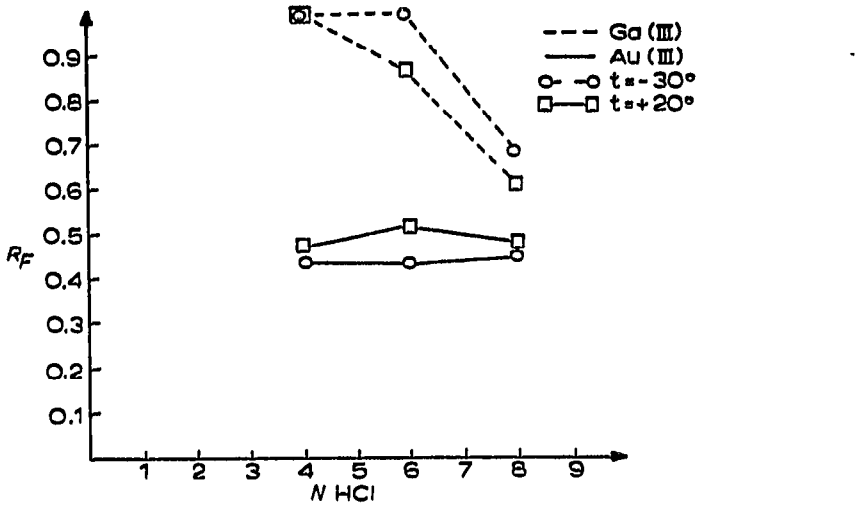

Fig. 1. R_F values of Au(III) and Ga(III) plotted against the concentration of HCl in the solvent. Whatman No. 1 paper was used.

Ion-exchange paper chromatography. Good results were obtained with aqueous HCl solutions above 5 N resin papers. The cellulose anion exchangers, however, become fragile above 7 N HCl and thus are limited to a small range of HCl concentrations.

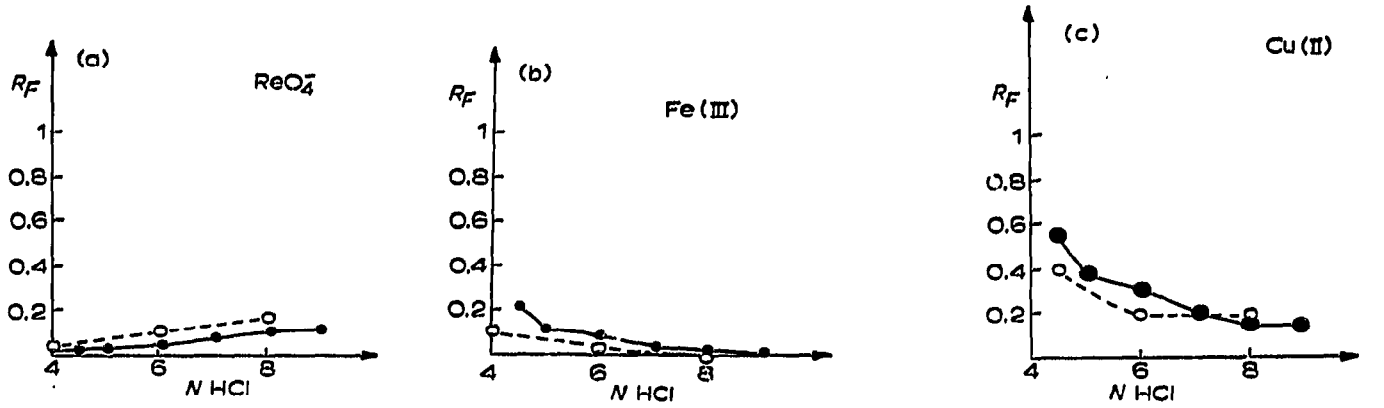

Fig. 2. R_F values of some ions plotted against the concentration of HCl in the solvent. The paper used was SB-2 strong anion-exchange resin paper. Continuous line, −30°; broken line, 20°.

Results obtained at room temperature and at −30° for some ions on the resin paper SB-2 (strongly anionic) are shown in Fig. 2.

In conclusion, there are no technical obstacles to the chromatography of inorganic ions at −30°; a good range of solvents and systems gives results similar to those obtained at room temperature.

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