PAPER CHROMATOGRAPHY OF INORGANIC ANIONS

A SYSTEM OF IDENTIFICATION USING PARTITION, ION EXCHANGE AND PAPER ELECTROPHORESIS

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INTRODUCTION

Paper chromatography has proved to be invaluable in the separation of inorganic anions such as polyphosphates, thionates and similar series; however, for the separation and identification of the common inorganic anions much less information has been recorded than for metal ions. The sequences in solvents such as butanol–ammonia, acetone–water, etc., are usually the same, since preferential complexation as employed for metal ions in solvents such as butanol–HBr cannot be employed for many inorganic anions.

Recently numerous organic compounds have been identified by means of so-called "R_F spectra", which are graphical representations of the R_F values in a number of solvents; these values taken together make it possible to distinguish one compound from others of the same type. This method of "R_F spectra" was also used by RITCHIE[1] for identifying a large number of metal ions, only four solvents being used: butanol–HBr, butanol–HCl–HF, ethanol–methanol–2 N HCl and acetone–HCl–HF.

In this paper an attempt to identify inorganic acids in the same way is described, namely by means of "R_F spectra" obtained with four different separation systems. Since partition systems yield essentially the same sequence we chose two partition solvents, one method involving ion-exchange paper and one electrophoretic separation. Except for the electrophoretic data[2], none of the results have been reported previously.

EXPERIMENTAL

(a) *Partition chromatography of inorganic anions in mixtures of isopropanol and aqueous ammonia*

No investigations of partition solvents containing varying amounts of water have so far been reported and hence we thought it would be interesting to study a solvent mixture in which the amount of water can be varied at will. Butanol is unsuitable since it is not miscible with aqueous ammonia and therefore isopropanol was chosen.

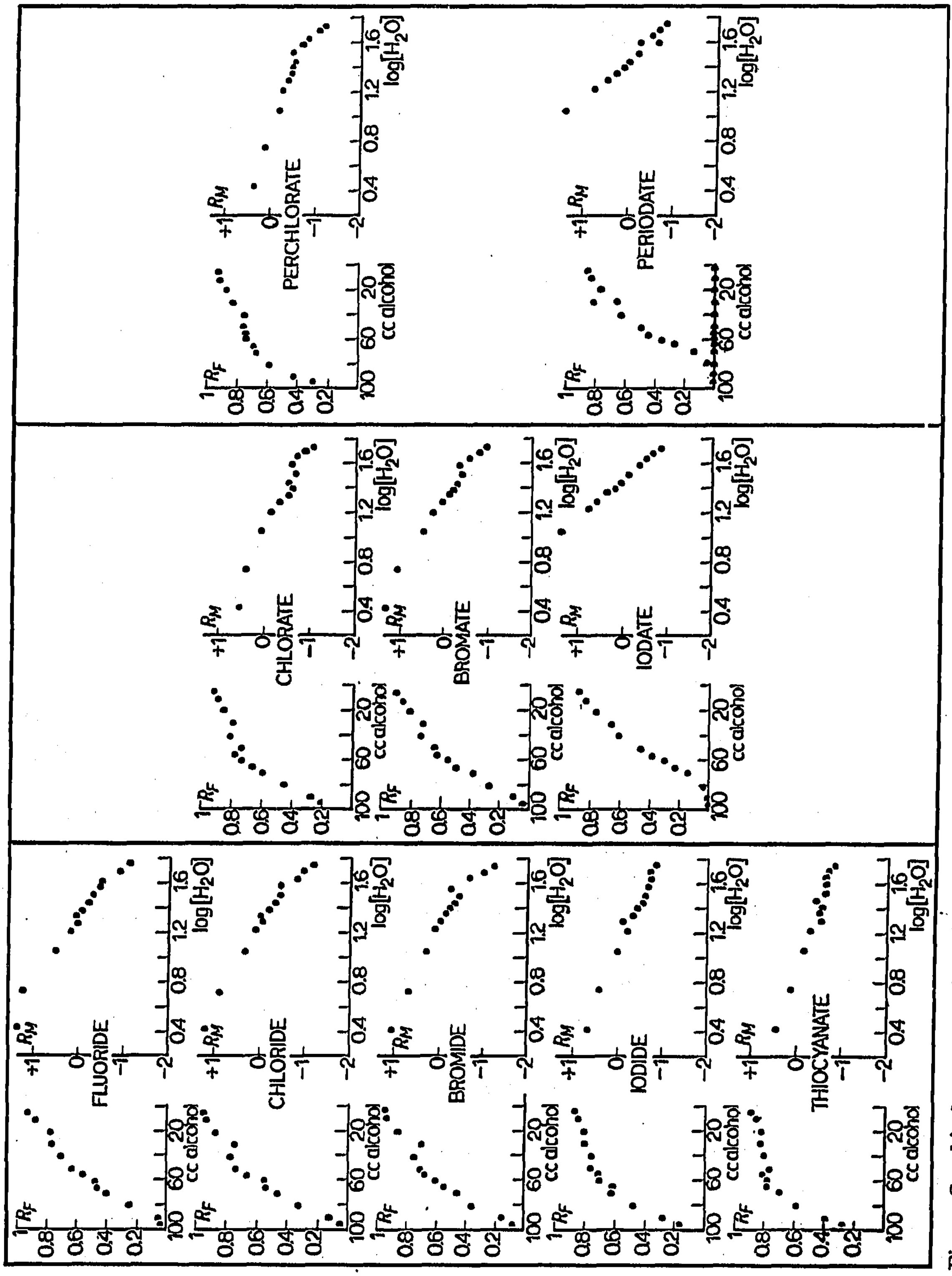

Fig. 1. Graphical representation of the alteration of the R_F value with the amount of water in the solvent and the alteration of the R_M value with log [H_2O], for all the anions examined (*continued on p. 353*)

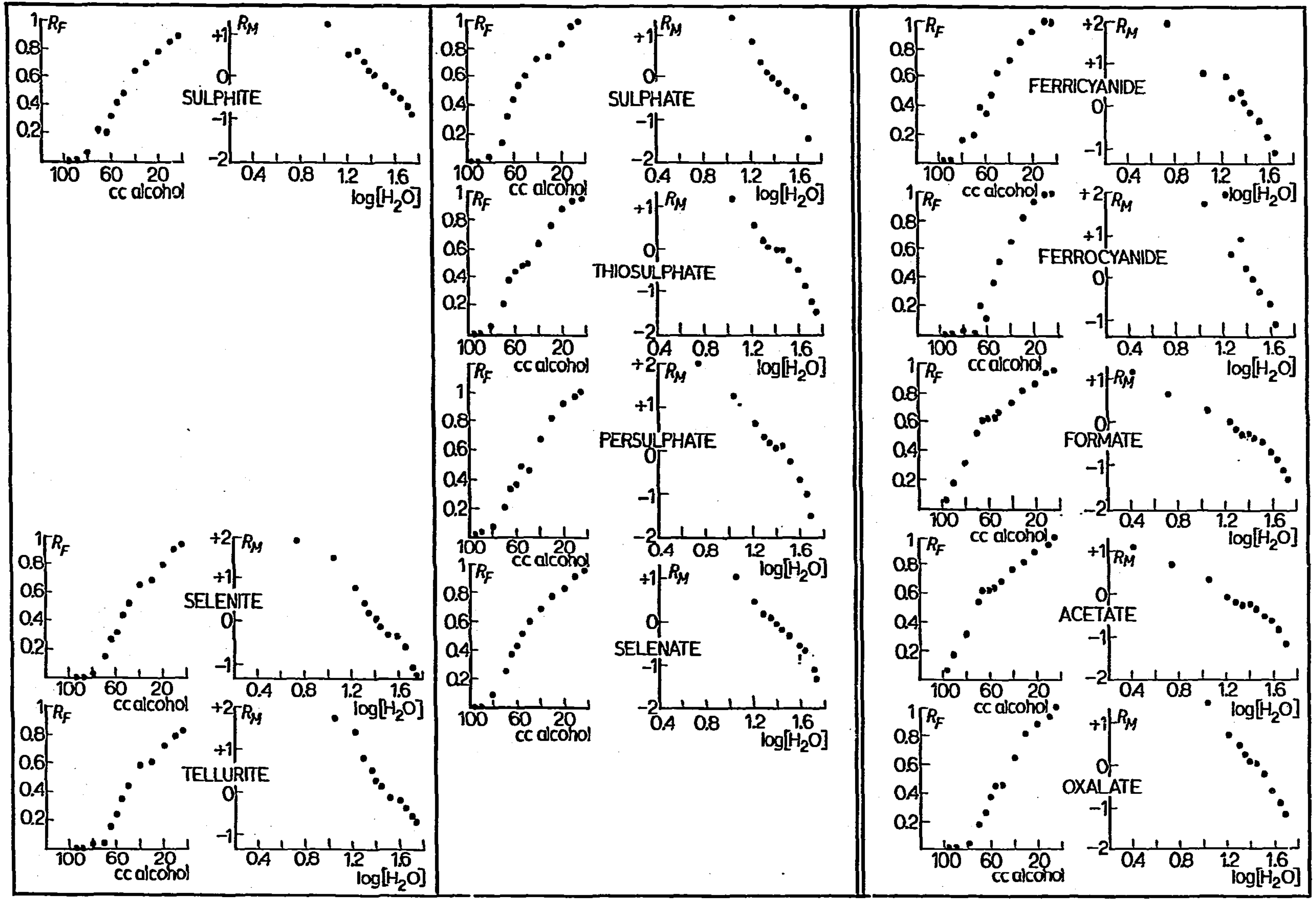

Fig. 1 (*continued*). Graphical representation of the alteration of the R_F value with the amount of water in the solvent and the alteration of the R_M value with log $[H_2O]$, for all the anions examined (*continued on p. 354*)

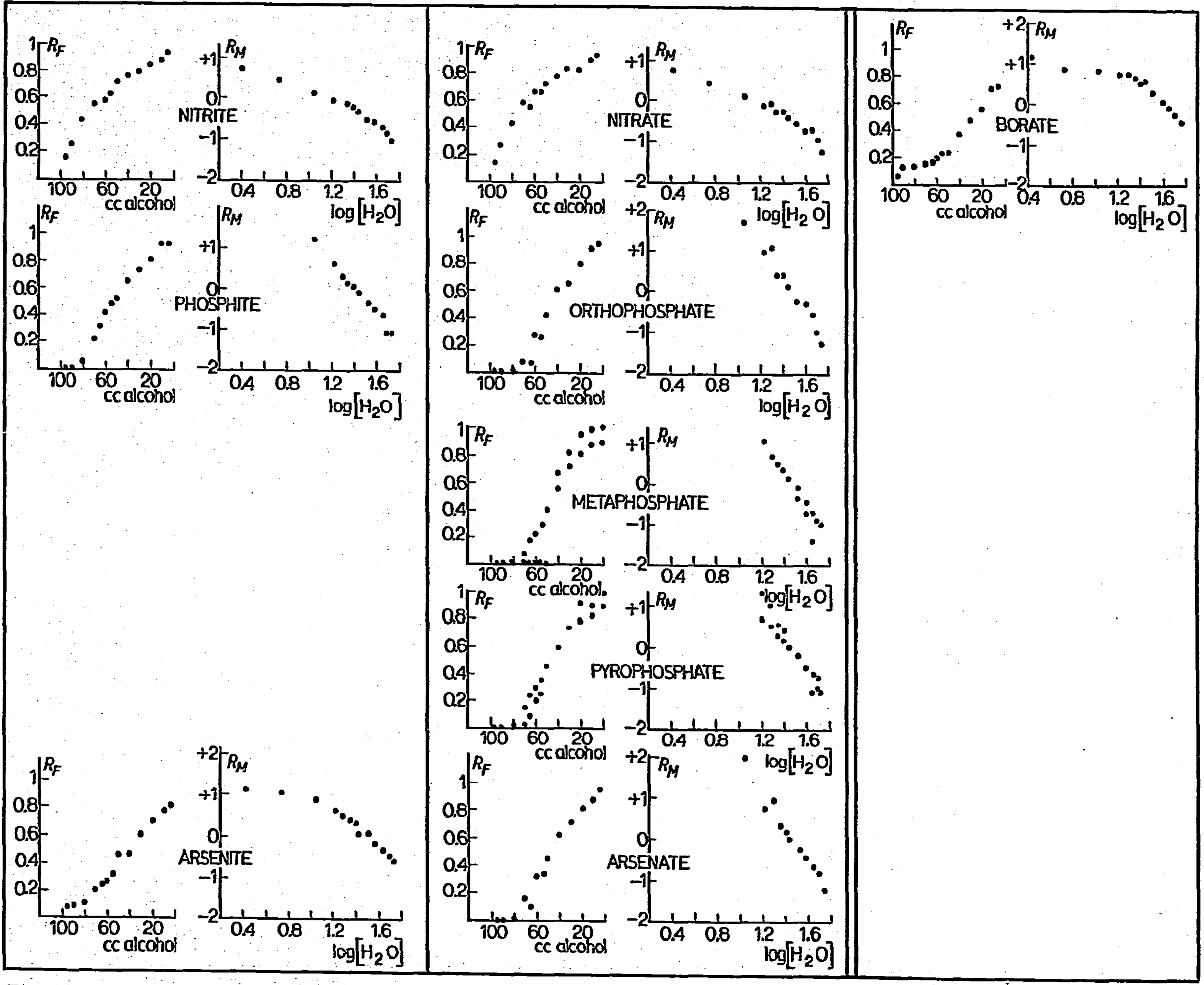

Fig. 1 (*continued*). Graphical representation of the alteration of the R_F value with the amount of water in the solvent and the alteration of the R_M value with log $[H_2O]$, for all the anions examined (*continued on p. 355*)

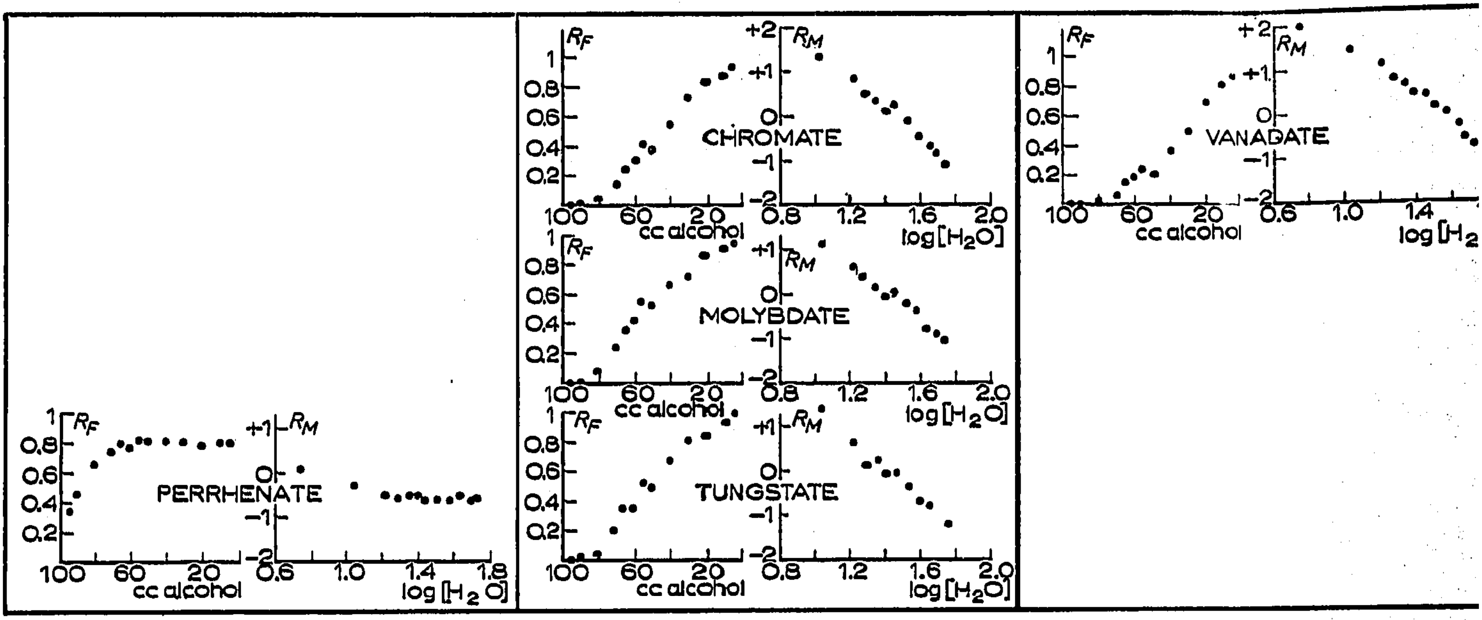

Fig. 1 (*continued*). Graphical representation of the alteration of the R_F value with the amount of water in the solvent and the alteration of the R_M value with log $[H_2O]$, for all the anions examined.

However, during the preliminary work some experimental difficulties were encountered. In the region of 50–50 mixtures of isopropanol–1.5 *N* ammonia variable R_F values were obtained with our conventional development jars which have a rather large volume. Satisfactory results were only obtained with jars (27 cm high and 14 cm diameter) fitted with tight-fitting lids with rubber gaskets. It seems that some critical factor of cellulose hydration or solvent volatility has a great influence on the development in these solvents.

In the first experiments we also noted that the cation sometimes has a retarding influence on the anion, producing comets. To avoid this, all the salts were converted to the ammonium salts when necessary by passing the solutions through a short column of Dowex–50 in the ammonium form.

The results obtained with forty-odd anions are presented in three different ways:

Fig. 1 shows the graphs of the R_F values *versus* water content and the R_M values *versus* log water content.

The actual R_F values measured, which cannot be read easily from either graph, are given in Table I.

It can be clearly seen that some separations are possible already in the water-poor region, for example that of Cl^-–Br^-–I^-–CNS^-, but many more separations can be achieved in the intermediate region where it seems that preferential hydration does play some role in the separation.

From the plots of R_M *versus* log $[H_2O]$ given in Fig. 1 it is evident that the change of the distribution coefficient is not always linear, but that for numerous anions there are distinct breaks in the lines. We believe that this can be attributed to effects other than partition, such as adsorption or complex formation (see especially borate). These effects are particularly strong in the region of very high water content and

TABLE I

R_F VALUES OF INORGANIC ANIONS (AS THE AMMONIUM SALTS) IN MIXTURES OF ISOPROPANOL–1.5 N AMMONIA

(Paper: Whatman No. 1)

	R_F in isopropanol-1.5 N ammonia												
	95:5	*90:10*	*80:20*	*70:30*	*65:35*	*60:40*	*55:45*	*50:50*	*40:60*	*30:70*	*20:80*	*10:90*	*5:95*
Fluoride	0.04	0.06	0.24	0.40	0.46	0.48	0.56	0.63	0.71	0.77	0.78	0.88	0.92
Chloride	0.06	0.13	0.32	0.47	0.55	0.56	0.68	0.74	0.77	0.76	0.88	0.94	0.96
Bromide	0.09	0.16	0.36	0.46	0.55	0.60	0.67	0.71	0.75	0.69	0.85	0.92	0.94
Iodide	0.18	0.28	0.48	0.62	0.60	0.70	0.71	0.76	0.77	0.80	0.81	0.85	0.87
Thiocyanate	0.26	0.39	0.59	0.68	0.77	0.77	0.79	0.76	0.80	0.81	0.81	0.85	0.88
Chlorate	0.21	0.28	0.47	0.60	0.67	0.74	0.77	0.74	0.81	0.80	0.85	0.89	0.92
Bromate	0.05	0.09	0.27	0.38	0.50	0.56	0.62	0.64	0.73	0.72	0.81	0.87	0.90
Iodate	0	0	0.04	0.14	0.23	0.30	0.39	0.47	0.60	0.65	0.76	0.83	0.86
Perchlorate	0.30	0.42	0.60	0.68	0.70	0.75	0.75	0.77	0.77	0.84	0.89	0.93	0.94
Periodate	0	0	0.04	0 0.14	0 0.26	0 0.36	0 0.45	0 0.49	0 0.62	0 0.65 0.82	0 0.77	0 0.83	0 0.86
Sulphite	0	0	0.05	0.21	0.20	0.32	0.40	0.47	0.63	0.70	0.77	0.85	0.89
Selenite	0	0.01	0.03	0.14	0.26	0.32	0.43	0.51	0.65	0.68	0.79	0.91	0.94
Tellurite	0	0	0.02	0.04	0.15	0.24	0.36	0.44	0.58	0.61	0.73	0.82	0.84
Sulphate	0	0	0.04	0.13	0.32	0.44	0.54	0.60	0.71	0.75	0.84	0.97	1
Selenate	0	0	0.08	0.26	0.38	0.44	0.51	0.60	0.68	0.78	0.84	0.93	0.96
Thiosulphate	0	0	0.06	0.21	0.37	0.44	0.48	0.50	0.64	0.77	0.90	0.95	0.97

Persulphate	0	0.01	0.07	0.20	0.33	0.38	0.49	0.46	0.67	0.80	0.91	0.97	1
Nitrite	0.16	0.26	0.43	0.55	0.69	0.59	0.62	0.71	0.76	0.79	0.85	0.88	0.93
Phosphite	0	0	0.05	0.21	0.32	0.42	0.48	0.52	0.65	0.74	0.80	0.92	0.92
Arsenite	0.07	0.08	0.11	0.20	0.25	0.28	0.33	0.47	0.46	0.60	0.70	0.77	0.80
Nitrate	0.16	0.27	0.45	0.59	0.56	0.67	0.67	0.72	0.78	0.84	0.83	0.90	0.95
Orthophosphate	0	0	0.02	0.10	0.09	0.29	0.29	0.43	0.63	0.66	0.80	0.91	0.96
Arsenate	0	0	0.01	0.16	0.10	0.33	0.34	0.48	0.62	0.72	0.83	0.89	0.96
Metaphosphate	0	0	0	0 0.08	0 0.17	0 0.22	0 0.30	0 0.41	0.57 0.68	0.72 0.82	0.82 0.96	0.87 1	0.90 1
Pyrophosphate	0	0	0	0.04 0.16	0.08 0.23	0.20 0.30	0.26 0.37	0.45	0.60	0.74	0.80 0.92	0.83 0.90	0.91 1
Perrhenate	0.30	0.45	0.67	0.76	0.80	0.78	0.82	0.82	0.81	0.81	0.79	0.81	0.80
Chromate	0	0	0.03	0.17	0.25	0.30	0.41	0.38	0.54	0.73	0.83	0.88	0.93
Molybdate	0	0	0.08	0.25	0.36	0.43	0.55	0.52	0.64	0.72	0.86	0.90	0.93
Tungstate	0	0	0.03	0.20	0.38	0.37	0.52	0.50	0.67	0.82	0.85	0.94	1
Vanadate	0	0.01	0.03	0.06	0.15	0.19	0.25	0.22	0.37	0.50	0.70	0.81	0.87
Borate	0.07	0.12	0.13	0.15	0.16	0.20	0.24	0.24	0.37	0.48	0.56	0.70	0.72
Ferricyanide	0	0.01	0.15	0.19	0.39	0.33	0.48	0.62	0.74 0.67	0.88 0.82	0.93	1	1
Ferrocyanide	0	0	0.02	0.01	0.20	0.11	0.37	0.51	0.66	0.82	0.94	1	1
Formate	0.06	0.17	0.31	0.53	0.61	0.63	0.63	0.67	0.73	0.82	0.88	0.94	0.96
Oxalate	0	0	0.03	0.17	0.26	0.36	0.44	0.45	0.65	0.82	0.89	0.94	1
Acetate	0.07	0.18	0.31	0.54	0.61	0.62	0.63	0.67	0.77	0.82	0.89	0.94	1

give some idea as to how much the partition of each anion is influenced by other processes.

(b) *Movement of inorganic anions on Whatman weak anion exchange resin paper*

Figs. 2 and 3 show the movement of inorganic anions (as K, Na or NH_4 salts) on Whatman weak anion exchange resin paper when developed with *N* KCl or *N* KNO_3. The latter is preferable because then Cl^- and Br^- can also be detected. Since the paper is originally in the chloride form it is repeatedly washed with KNO_3 and water and then air dried.

On this paper halides move rather slowly while phosphorus acids are hardly adsorbed. There seems to be thus little correlation with the charge of the anion, the main separatory effect being some sort of reversed phase adsorption.

The spot shape also seems to be quite specific, therefore we prefer the representation given in Figs. 2 and 3 to R_F tables.

(c) *The "R_F spectra of inorganic anions"*

We tried to find the minimum number of solvents or separation systems that would yield a maximum differentiation of the anions if R_F spectra were constructed.

We propose the following four systems:

1. Partition chromatography with isopropanol–1.5 *N* NH_4OH (90:10) on Whatman No. 1 paper.
2. Partition chromatography with isopropanol–1.5 *N* NH_4OH (55:45) on Whatman No. 1 paper.
3. Whatman weak anion exchange resin paper with *N* KNO_3 as solvent.
4. Paper electrophoresis in 0.1 *N* NaOH on Arches 302 paper. Most of the results obtained with system 4 have been published previously[2]. Some supplementary data are given in Table II.

TABLE II

ELECTROMIGRATION OF SOME ANIONS IN 0.1 *N* NaOH

Conditions as described previously[2].

Anion	*Distance moved (mm)*
Vanadate	56–59
Tungstate	65
Selenate	69–71
Pyrophosphate	52
Metaphosphate	48
Perrhenate	49

The R_F spectra are shown in Fig. 4. For some systems where elongated spots are formed a range of values has to be given. Also some anions, *e.g.* SO_3^{2-}, could not be detected in some systems. While it is, of course, not possible to identify all inorganic anions by means of the scheme proposed here, we believe that numerous anions can be identified unambiguously even when present as tracers. As the main purpose of

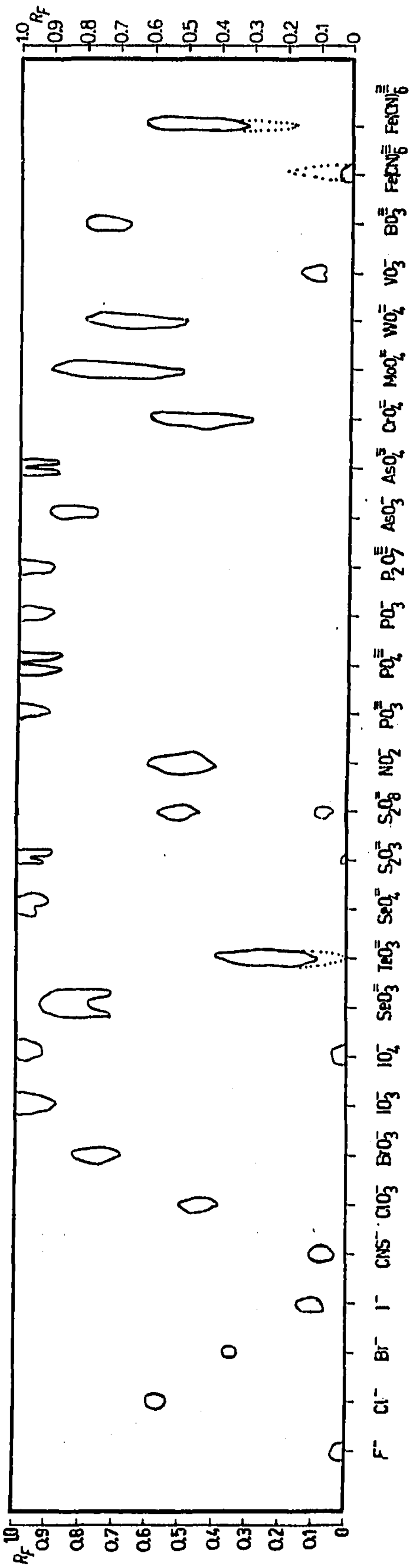

Fig. 2. Movement of inorganic anions on Whatman weak anion exchange resin paper with N KNO_3 as solvent.

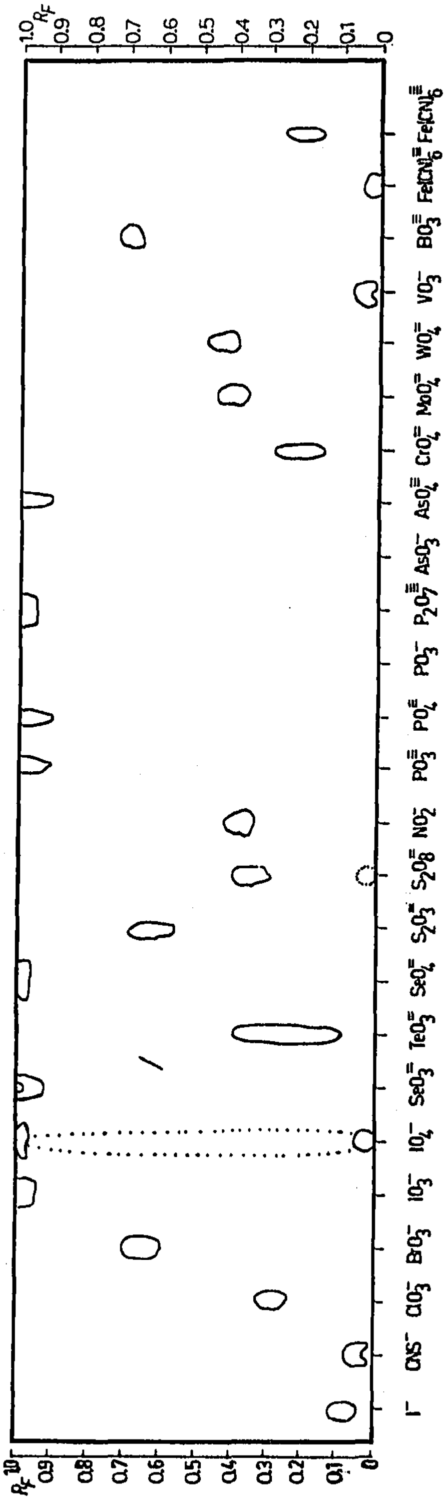

Fig. 3. Movement of inorganic anions on Whatman weak anion exchange resin paper with N KCl as solvent.

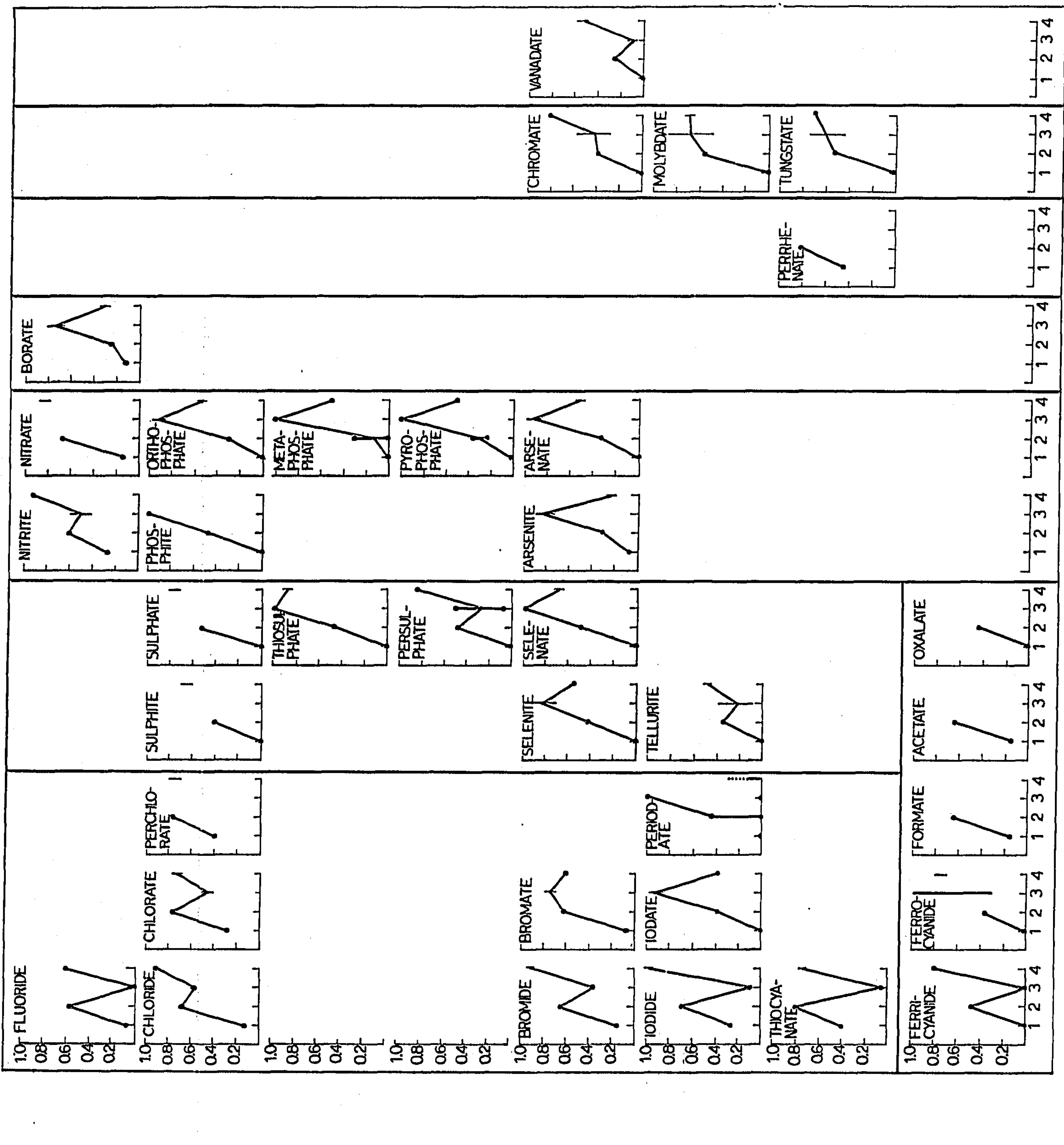

Fig. 4. "R_F spectra" of inorganic ions. System 1 — Isopropanol-1.5 N

this study was the identification of tracers we did not study the sensitivity of colour reagents, nor did we include condensed phosphates, thionates etc., which are of little interest in such problems.

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SUMMARY

The R_F values are given of about 40 inorganic anions in a number of isopropanol–1.5 *N* ammonia mixtures, as well as on anion exchange resin paper with *N* KCl or *N* KNO_3 as solvent. These data together with the electrophoretic mobilities in 0.1 *N* NaOH are used in a scheme of identification based on the principle of "R_F spectra".

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[2] G. GRASSINI AND M. LEDERER, *J. Chromatog.*, 2 (1959) 326.