

## THE USE OF THIOCYANIC ACID IN PAPER PARTITION CHROMATOGRAPHY

### PART II. THIOCYANIC ACID AND ORGANIC BASES USED IN CONJUNCTION AS CHROMATOGRAPHIC SOLVENTS

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#### INTRODUCTION

The formation of complexes with metallic ions of one or other of the three types, anionic, uncharged or cationic, has been the aim of much of the research in inorganic chromatography. To this end ligands of many types have been used including thiocyanate<sup>1</sup> ions and nitrogen bases<sup>2</sup> such as are discussed in this paper. The combination of thiocyanic acid and one or other of pyridine, quinoline and aniline in the same solution, however, gives a solvent which effectively buffers the chromatogram and favours the formation of complexes of the type  $MPy_n(SCN)_m$  which may have interesting properties.

To study the interplay of these solvents an analysis of variance was made on the results of the tests which comprised a series made using a noncomplexing ligand,  $ClO_4^-$  as perchloric acid, and a series containing only HSCN to supply the reaction group as well as the six series in which HSCN was used in conjunction with a nitrogen base.

#### EXPERIMENTAL

In the 38 solutions prepared for these tests, the following ions were present as nitrates: beryllium, magnesium, calcium, strontium, barium, cupric, silver, cadmium, zinc, mercuric, aluminium, lanthanum, cerous, zirconium, uranyl, thorium, gallium, indium, thallium, lead, bismuth, chromic, manganous, ferric, cobaltous and nickelous. Cerium was also used as ammonium hexanitratocerate (IV). The following ions: gold, stannous and ferrous were used as chlorides, the latter with some sulphurous acid in the solutions to prevent oxidation. Titanium as potassium titanyl oxalate, vanadium as vanadyl sulphate, arsenic as both arsenate and arsenite, antimony as potassium antimonyl tartrate, selenium as the dioxide, tellurium as telluric acid and molybdenum as ammonium molybdate made up the remainder. Acid was added

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where necessary to prevent hydrolysis. All solutions were 0.1 *M* except stannous chloride and mercurous nitrate, which were of indefinite strength, as they were stored over metallic tin and mercury respectively to prevent oxidation to the higher valency form.

#### *Preparation of thiocyanic acid solutions*

The thiocyanic acid was vacuum distilled from a concentrated solution of potassium thiocyanate acidified with 10 *N* sulphuric acid. The volatile thiocyanic acid was collected in a gas washing tower, packed with glass rings, and cooled in an ice and water bath. The washing tower contained 100 ml distilled water before distillation, and about 300 ml solution at the end of the operation. For the various distillations, this solutions ranged in strength from 2.6 *M* to 3.2 *M*. It was stored in a refrigerator to minimise its decomposition.

An alternative method, which proved useful for the production of a less pure thiocyanic acid solution, depended on the low solubility of potassium perchlorate to bring about the substantial completion of the reaction:



This was achieved by diluting a known quantity of 70–72%  $\text{HClO}_4$  to 18%  $\text{HClO}_4$ , chilling to 5° or lower, and adding the exact quantity of saturated KSCN solution, also at 5°, mixing thoroughly and standing the solution in a refrigerator overnight. The  $\text{KClO}_4$  and a certain amount of thiocyanogen were filtered off leaving a solution over 3 *M* in HSCN and containing about 1% of  $\text{KClO}_4$ . This solution was quite satisfactory for the solvents described below but was less stable than the acid produced by distillation.

#### *The solvents*

A preliminary test established the fact that a solution of thiocyanic acid in butanol and water, at a concentration greater than 0.5 *M* HSCN, would have no separate absorption front, and all solvents were based on this. In order to investigate the combined complexing effect of the thiocyanate ion and organic bases, six solutions were made incorporating one or other of pyridine, aniline and quinoline. This would

TABLE I  
SOLVENT PROPORTIONS BY VOLUME

Constituent	Solvent							
	1	2	3	4	5	6	7	8
<i>n</i> -Butanol	140	140	140	140	140	140	140	140
Thiocyanic acid	—	40	40	30	30	30	30	30
4 <i>N</i> Perchloric acid	40	—	—	—	—	—	—	—
Water	—	—	—	10	10	10	10	10
Base	—	—	5.3	8.8	6.3	10.3	7.9	13
pH	—	0.9	3.9	8.4	3.8	8.0	3.0	7.7

make a salt of the pyridinium thiocyanate type. Solutions were then made containing (a) a 30% excess of acid and (b) a 15% excess of base. The comparison solvent, containing perchlorate ions, was made from 4 *M* perchloric acid and *n*-butanol. (The precise compositions of all solvents are given in Table I.)

An alcohol-water ratio of approximately 0.5 mol. fraction of water was maintained throughout.

For making solvents 2 and 3, 2.63 *M* HSCN was used, and for solvents 4 to 8 the HSCN was 3.2 *M*. In all cases except No. 1, the HSCN concentration was adjusted to 0.53 *M* before the addition of the base. In solvents 3 and 4 pyridine was the base, 5 and 6 aniline and 7 and 8 quinoline.

#### *Preparation of chromatograms*

The chromatograms were made on Whatman's No. 41 paper cut into sheets approximately 19 cm by 28 cm. The metal ion spots were placed on the paper along a pencil line drawn parallel to and 3 cm from a major side. Eight spots were placed on each sheet, the first, 4 cm from one edge and then at 2.5 cm intervals. Each spot of about 0.02 ml was placed on the paper using a platinum wire loop such as that used for borax bead tests. The sheet of paper was then coiled into a cylinder, 8.5 cm diameter and 19 cm high, by overlapping the short edges by 2 cm and securing the outside end at top and bottom with white sewing cotton.

The spots were allowed to air dry before running the chromatogram and no period of humidification was allowed. The cylinder was then lowered into a petri dish containing the developing solvent which in turn was held in a development jar. The jar was of glass 15 cm diameter by 30 cm high, with the top edge ground flat and closed with a square of plate glass. In the bottom of the jar, and outside the petri dish, dry *n*-butanol was placed about 1 hour prior to the tests in order to saturate the atmosphere in the jar with the alcohol vapour.

The temperature remained at 24 to 28° for the series and the laboratory remained at 60 to 70% relative humidity during the course of the experiments. Each run took about 90 min and the liquid front rose approximately 15 cm.

#### *Location of spots*

Only two reagents ( $H_2S$  gas and 8-hydroxyquinoline) were used to find the position of the metal spots on the chromatograms.

The first was used for As, Sb, Bi, Pb, Hg, Cu, Cd, Ag, Sn, Au, Tl, Te. Chromatograms of these elements were exposed to  $H_2S$  gas in a jar, similar to the development jar, for from 5 to 30 min.

A solution of 8-hydroxyquinoline (0.5%) in 50% alcohol water<sup>3</sup> was used for the remaining metals. After being sprayed, the previously air-dried sheets were exposed to the vapour of 15 *N* aqueous  $NH_3$ , in a development jar covered with a glass plate. The exposure to ammonia vapour took 10-15 min, except in the case of the Group IIa metals which required a prolonged treatment to remove the pyridine, aniline or quinoline from the paper, before the characteristic fluorescence became apparent.

An Hanovia "Chromatolite" was used as the source of U.V. light. The  $R_F$  value was measured from the centre of greatest density of the spot to the centre of the original position, and referred to the distance of travel of the liquid front. Consequently all values were less than unity. All  $R_F$  values obtained are reported in Table II.

TABLE II

Ion used	$R_F$ values in solutions Nos. 1 to 8							
	1	2	3	4	5	6	7	8
Cu <sup>2+</sup>	0.14	0.54	0.24	0.28	0.72	0.78	0.72	0.67
Ag <sup>+</sup> *	—	0.76	0.80	0.86	0.80	0.86	0.88	0.64
AuCl <sub>4</sub> <sup>-</sup>	0.96	0.96	0.34		0.92	0.95	0.92	
Be <sup>2+</sup>	0.40	0.60	0.58	0.58	0.74	0.73	0.72	0.74
Mg <sup>2+</sup>	0.15	0.17	0.44	0.56	0.22	0.29	0.33	0.41
Ca <sup>2+</sup>	0.08	0.14	0.34	0.44	0.17	0.21	0.25	0.30
Sr <sup>2+</sup>	0.08	0.10	0.27	0.30	0.11	0.15	0.23	0.19
Ba <sup>2+</sup> *	—	0.08	0.24	0.26	0.10	—	0.15	0.14
Zn <sup>2+</sup>	0.12	0.94	0.91	0.83	0.95	0.94	0.91	0.91
Cd <sup>2+</sup>	0.17	0.73	0.67	0.60	0.84	0.83	0.72	0.75
Hg <sup>2+</sup>	0.26	0.94	0.89	0.62	0.92	0.86	0.88	0.79
Al <sup>3+</sup>	0.13	0.36	0.53	0.58	0.94	0.80	0.58	0.76
La <sup>3+</sup> *	—	0.06	0.12	0.10 **	0.07	—	0.10	0.04
Ce <sup>3+</sup> *	—	0.18	0.44	0.55	—	0.36	0.33	0.42
[Ce(NO <sub>3</sub> ) <sub>6</sub> ] <sup>2-</sup>	0.06	0.02	0.02	0.15	0.02	0.02	0.09	0.03
Ga <sup>3+</sup>	0.14	0.85	0.58	0.56	0.84	0.85	0.80	0.79
In <sup>3+</sup>	0.22	0.96	0.55	0.74	0.76	0.89	0.81	0.85
Tl <sup>3+</sup> *	—	0.30 **	0.30 **	0.30 **	0.35 **	0.30 **	0.30 **	0.30 **
[TiO(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] <sup>2-</sup> *	—	0.74	0.49	0.20 **	0.71	0.60 **	0.76	0.10 **
Zr <sup>4+</sup> *	—	0.10 **	0.50 **	0.20 **	0.90 **	nil	0.80 **	0.50 **
Th <sup>4+</sup>	0.08	0.40	0.52	0.50	0.56	0.32	0.60	0.56
Sn <sup>2+</sup>	0.73	0.69	0.67	0.64	0.80	0.84	0.74	0.74
Pb <sup>2+</sup> *	—	0.40 **	0.30 **	0.34	0.10 **	0.34	nil	0.39
VO <sup>2+</sup>	0.22	0.90	0.82	0.64	0.92	0.89	0.90	0.80
AsO <sub>3</sub> <sup>3-</sup>	0.45	0.45	0.45	0.50	0.55	0.57	0.56	0.58
AsO <sub>4</sub> <sup>3-</sup> *	—	0.50	0.52	0.35	—	—	0.65	0.56
SbO <sup>+</sup> *	—	0.14	0.08	0.34	0.11	0.25	0.30 **	0.10
Bi <sup>3+</sup> *	—	0.64	0.56	0.02	0.69	0.70 **	0.66	0.60 **
Cr <sup>3+</sup>	0.14	0.28	0.55	0.58	0.38	0.39	0.46	0.53
MoO <sub>4</sub> <sup>2-</sup> *	—	0.95	0.86	0.30 **	0.90	0.20 **	0.88	nil
UO <sub>2</sub> <sup>2+</sup>	0.28	0.88	0.80	0.64	0.90	0.88	0.90	0.79
SeO <sub>3</sub> <sup>2-</sup>	0.59	0.68	0.58	0.42	0.62	0.59	0.64	0.58
TeO <sub>4</sub> <sup>2-</sup>	0.12	0.08	0.14	0.19	0.08	0.12	0.12	0.11
Mn <sup>2+</sup>	0.14	0.42	0.56	0.53	0.61	0.65	0.67	0.73
Fe <sup>2+</sup>	0.17	0.65	0.54	0.65	0.70	0.74	0.73	0.33
Fe <sup>3+</sup>	0.20	0.98	0.92	0.56	0.55	0.67	0.46	0.70
Co <sup>2+</sup>	0.15	0.82	0.62	0.68	0.81	0.84	0.81	0.75
Ni <sup>2+</sup>	0.12	0.42	0.54	0.76	0.48	0.45	0.66	0.53

\* Omitted from statistical treatment.

\*\* Trailed from base line.

## DISCUSSION

The important difference between solvents No. 1 and No. 2 lies in the greater complexing power of the thiocyanate ion than the perchlorate ion. In large excess, as is the case in chromatography, the thiocyanate ion is known to form anionic complexes with

certain cations and, as PICKERING<sup>4</sup> has shown, this can lead to greatly increased  $R_F$  values for the metal ion complexes.

There is no direct proof that anionic complexes do form on chromatograms except in those cases where distinctively coloured complexes are observed. These cases are few, being limited to such possible examples as  $\text{VO}_2^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Bi}^{3+}$ . Nevertheless, on the basis of PICKERING'S findings and the large changes found between the  $R_F$  values obtained with solvents 1 and 2 in this work it is considered reasonable to suppose that formation of  $[\text{M}^{n+} \text{SCN}_x]^{n-x}$  complexes which are anionic do form in the cases given below.

Some of these complexes persist in the buffered atmosphere of solvents 3 to 8 while others form variants with the organic base and show significant changes in  $R_F$  value when compared with the results from solvent 2. A third group shows little change between solvent 2 and the others and in this case it is assumed that the ion remains as the complex thiocyanate.

It will be seen then that the zones between the salt front and acid front for solvents No. 3, 5 and 7 were acidic and similar to chromatograms made using solvent No. 2 while the zones between the salt and liquid fronts for solvents No. 4, 6 and 8 were basic, containing butanol, base and water. Reference to Table II, will show that many elements give spots clustered around these fronts. Thus they play an important role in such separations.

The conditions for obtaining a chromatogram, buffered over its whole length, would be satisfied if all adsorption fronts coincided with the liquid front, *i.e.* all had  $R_F$  values of unity.

#### *Statistical basis for discrimination of results*

An analysis of variance was carried out on some of the results from the above treatments. Silver gave two spots in both solvent No. 3 and No. 4, lanthanum, thallium (III), titanium, zirconium, lead, antimony (III), bismuth and molybdenum trailed in one or more of the solvents. Results for arsenic (III), barium and cerium were incomplete because of difficulties in locating the spot after the chromatogram was made. For these reasons 12 of the 38 sets of results were considered unsuitable and omitted from the statistical treatment. These have been marked with an asterisk in Table II.

The analysis gave a grand mean of 0.550. The test of significant variation between ions gave  $F = 16.2$  for 25 and 175 degrees of freedom compared with 2.4 required for the 0.001 level of significance. For the solutions, the results were  $F = 16.0$  for 7 and 175 degrees of freedom compared with 4.0 at the 0.001 level. The results for both ions and solutions could therefore be considered to differ significantly from a chance distribution.

The standard error (S.E.) of the treatment (solution) mean was 0.0275. It was therefore considered that variations between results for the same ion, in different solutions, which differed by more than  $t \times \text{S.E.} = 3.29 \times 0.0275 = 0.09$  could be taken as indicative of a chemical reaction occurring between solvent components and the ions, resulting in a new compound with different chromatographed characteristics.

This will be called the level of significant change. Table III shows the ions, chosen for statistical treatment, in the order of their change from the values obtained using solvent No. 1 and the extent of this change.

TABLE III

Group	Multiple of "Level of significant change"	Ions
A	Less than 1	Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup>
	1.1 to 2	Cr <sup>3+</sup>
	2.1 to 3	Al <sup>3+</sup> , Be <sup>2+</sup>
	3.1 to 4	Th <sup>4+</sup> , Mn <sup>2+</sup> , Ni <sup>2+</sup>
B	4.1 to 5	Cu <sup>2+</sup>
	5.1 to 7	UO <sub>2</sub> <sup>2+</sup> , Fe <sup>2+</sup> , Cd <sup>2+</sup>
	7.1 to 9	VO <sup>2+</sup> , Fe <sup>3+</sup> , Co <sup>2+</sup> , Zn <sup>2+</sup> , Hg <sup>2+</sup> , Ga <sup>3+</sup> , In <sup>3+</sup>

Four ion species showed less than  $\pm 0.09$  variation from their mean  $R_F$  for the eight solutions. They were arsenic (III), cerium (IV), tin (II) and tellurium. Two ions, gold and selenium, showed slightly greater variations in solution No. 4. It is clear that elements which had high  $R_F$  values in solvent No. 1 could show no great positive change. Such a case may have been Au<sup>3+</sup>. This ion, placed on the paper as AuCl<sub>4</sub><sup>-</sup> would presumably show little change if it travelled as [Au(SCN)<sub>4</sub>]<sup>-</sup>.

It is perhaps significant that the results fell into two groups. The first group, those which show a large deviation from the comparison  $R_F$  values was made up of the elements with complete, or nearly complete  $d$  orbitals and included two ions VO<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup> where near completion had been achieved with covalently bonded oxygen. This is the B group of Table III. The other group contained those elements where the  $d$  orbitals were far from complete with the one exception of nickel. This was called group A.

The area of discrimination between the two groups lay at about Group 8 of the Periodic Table.

Although Cr<sup>3+</sup>, Al<sup>3+</sup>, Th<sup>3+</sup>, Mn<sup>2+</sup> and Ni<sup>2+</sup> all form complexes of the type [M<sup>n</sup>+L<sub>x</sub>]<sup>n-x</sup> with halides or cyanides, there is little in the literature concerning the thiocyanates except for chromium. Here BJERRUM<sup>5</sup> has found that the reaction with thiocyanate is slow and it is unlikely that any significant quantity would form in the time of the chromatogram. Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Be<sup>2+</sup> apparently do not form complex thiocyanates. The behaviour of Ni<sup>2+</sup> may be explained if the nickel compounds of the formula K<sub>4</sub>Ni(SCN)<sub>6</sub> are double salts, as suggested in SIDGWICK<sup>6</sup>, and if the nickel actually moves as the [Ni(SCN)<sub>3</sub>]<sup>-</sup> ion. None of these ions had an  $R_F$  value exceeding 0.50 except Be<sup>2+</sup> though here the change was low by comparison with the others. It would seem that solubility effects alone were responsible for the variation in  $R_F$  values.

In the higher group, B, all except two are elements with completed  $d$  orbitals. The exceptions are VO<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup>. Of these, VO<sup>2+</sup> is known readily to form complexes of the anionic type. The intense orange colour developed by UO<sub>2</sub><sup>2+</sup> ions in the

presence of  $\text{SCN}^-$  ions indicated the formation of a complex salt possibly of the type being discussed. This opinion is supported by AHLAND's work<sup>7</sup>. Of the remainder,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Hg}^{2+}$  thiocyanate complexes are well known, but there are few references to complexes of the other metals.

The sensitivity of the reagents used to locate the spots after chromatographing the ions is probably not sufficiently high to react with very low concentrations of metal ions or with those which are already very strongly complexed. However, those spots which were found, appeared by their area to constitute at least 90% of the quantity of metal ion originally taken.

#### *Solvents with added bases*

Those solvents containing nitrogen bases, Nos. 3 to 8 ranged in pH from 3.0 to 8.7 (Table I). This resulted in the trailing of certain ions which form easily hydrolysed salts at the higher pH range. This group comprised  $\text{La}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Zn}^{4+}$ ,  $\text{Bi}^{3+}$ , and  $\text{MoO}_4^{2-}$ . While  $\text{Pb}^{2+}$  showed the same phenomena in the acid solutions, where the acidity was less than pH 7, it travelled as a discrete spot probably due to the formation of a complex with the base. The overall picture associated with this group of solvents is too complex to interpret on the above data alone and a more extensive statistical treatment and investigation is planned for this purpose.

#### *R<sub>A</sub> values*

POLLARD'S  $R_P$  value<sup>8</sup> indicates the position of the adsorption front but only in relation to the surface of the solvent pool. This may be related to what may be called the  $R_A$  value, the ratio of the distance travelled by the liquid front, both measured from the starting point of the metal ions. The  $R_A$  value has no theoretical significance as does the  $R_P$  value, but its use is convenient when comparisons between ions are being

TABLE IV  
 $R_A$  AND  $R_P$  VALUES OF SOLVENTS

	Solvent							
	1	2	3	4	5	6	7	8
$R_P$ (acid)	0.95	1.0	0.92	—	0.92	—	0.91	—
$R_A$ (acid)	0.94	1.0	0.91	—	0.91	—	0.90	—
$R_P$ (salt)	—	—	0.57	0.64	0.83	0.86	0.75	0.76
$R_A$ (salt)	—	—	0.51	0.59	0.81	0.84	0.72	0.73

made or when considering the atmosphere in which an ion is submerged on a chromatogram.  $R_A$  may be calculated from  $R_P$  by the formula  $R_A = R_P - x(1 - R_P)/d$  where  $x$  is the height of the starting line above the level of the solvent pool and  $d$  is the distance the liquid front passes beyond the starting line. The values for the solvents used in this investigation are given in Table IV.

## SUMMARY

The chromatographic properties of eight solvents have been determined. The solvents were *n*-butanol–water–perchloric acid, which was non-complexing, and seven complexing solvents based on *n*-butanol–water–thiocyanic acid. The addition of one or other of pyridine, aniline or quinoline to the thiocyanic acid solution resulted in solvents which were buffered in the range pH 3 to pH 8. An analysis of variance carried out on the results enabled criteria of complexing properties to be established. It was found that these properties for the 38 ions tested were related to their electronic structure.

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