

METALLIC NITRATES IN PAPER CHROMATOGRAPHY

V. SYSTEMS CONTAINING AMMONIUM THIOCYANATE

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In previous papers the chromatographic behaviour of a large number of metallic nitrates was reported: in mixtures of nitric acid and methyl isobutyl ketone¹; in these same mixtures with the addition of lithium nitrate as a salting-out agent²; in the system di-isopropyl ether-nitric acid-water³; and finally in the system isoamyl alcohol-nitric acid-water⁴.

In all the above reports the extent to which nitric acid (and lithium nitrate) are distributed between the aqueous and organic phases was determined. The effects were considered which this distribution had on the R_F values of metallic nitrates in each of these systems.

We believe that, up to the present, no attention has been paid to the exact composition of the eluants used in paper chromatography. A study of the distribution of the acid and the salting-out agent between the initial aqueous solution and the organic layers, and the corresponding R_F values, permitted a more fundamental interpretation of the R_F values obtained and served as a basis for some theoretical considerations.

Apart from being employed for numerous useful separations, partition chromatography on paper also yields results which may to a certain extent be related to the distribution coefficients of the same cations, in the same solvent system, obtainable by the extraction technique. Thus, a chromatographic study may serve as a preliminary to an investigation of the possibilities of separating larger quantities by extraction. It is important for this purpose to know the R_F values of as many ions as possible in the given solvent system.

With this aim in mind we undertook a comprehensive study of a large number of metallic nitrates in systems containing an inorganic complexing agent: ammonium thiocyanate. Chromatograms were run in: (1) methyl isobutyl ketone (MIBK), (2) di-isopropyl ether (DIPE), and (3) isoamyl alcohol (IAA), equilibrated with aqueous solutions containing various concentrations of the complexing agent both with and without nitric acid (approximately 0.1 *M*).

Useful R_F values were only obtained with the three following systems:

1. MIBK-HNO₃-NH₄CNS-H₂O
2. IAA-HNO₃-NH₄CNS-H₂O
3. IAA-NH₄CNS-H₂O

For the other three systems:

1. MIBK-NH₄CNS-H₂O
2. DIPE-HNO₃-NH₄CNS-H₂O
3. DIPE-NH₄CNS-H₂O

the R_F values of nearly all the cations tested were equal, or approximately equal, to zero.

The first three valuable solvent systems were then systematically studied by determining the distribution of the thiocyanate and nitric acid between the aqueous and organic layers. The distribution coefficients were then used to interpret the results obtained in the paper-chromatographic experiments.

Ammonium thiocyanate, owing to its great tendency to form complexes, has been widely used for the separation of cations by the extraction technique⁵. In paper-chromatographic separations advantage has also been taken of this tendency, and in recent years numerous procedures have been suggested⁶. LEDERER⁷ studied extensively the possibilities of separating the rare earths by paper chromatography, using butanol saturated with thiocyanate as the eluant.

This distribution study describes the chromatographic behaviour of various elements under different experimental conditions. Although the results are not presented as established analytical procedures, they should be of considerable help in further development of analytical separations.

EXPERIMENTAL

The organic solvents, methyl isobutyl ketone, di-isopropyl ether and isoamyl alcohol were purified as previously described^{2, 3, 4}. The initial aqueous solutions of ammonium thiocyanate were prepared by diluting a stock solution of Baker's Analyzed C.P. grade thiocyanate; for the solutions containing nitric acid non-fuming nitric acid was used. Solutions of the radioisotopes ¹⁴⁴Ce, ¹⁵⁴Eu, ¹⁵³Gd, ¹⁷⁰Tm and ¹⁰⁰Ru in dilute nitric acid, and ⁹⁹Tc were obtained from Harwell.

The distribution of the solutes in both aqueous and organic layers was followed potentiometrically for nitric acid as described in previous papers¹⁻⁴ and colorimetrically for thiocyanate using the ferric iron reaction.* The sum of the masses in both layers showed a maximum variation of $\pm 1\%$ for nitric acid and $\pm 3\%$ for thiocyanate. Good reproducibilities were obtained in the determination of the volume changes of the aqueous and organic phases after equilibration by the method previously given^{3, 4}. The distribution of the solutes is presented as their normalities in both layers, as their concentration distribution coefficient α and as their mass distribution coefficient μ . The relation between these two coefficients is given by $\mu = (V_o/V_w) \cdot \alpha$, where V_o and V_w represent the volumes of the organic and aqueous layers after equilibration.

The technique and procedure for the chromatographic experiments, as well as the reagents and methods for detection of the spots have been described in previous

* The determinations were made in fresh solutions in order to eliminate the errors caused by the reaction between the nitric acid and the thiocyanate. However, no marked influence of this reaction upon the R_F values was observed.

papers^{4,8}. Radioisotopes were detected using either a Victoreen 1B85 thyrode counter tube with thin metal wall or a Nuclear Instrument, model D 34 mica end-window tube, employing the technique previously used⁹.

The chromatographic experiments were carried out with the following solutions spotted on filter paper:

KNO ₃	Ce(NO ₃) ₃	ZrO(NO ₃) ₂	TaF ₅
RbNO ₃	Pr(NO ₃) ₃	Pb(NO ₃) ₂	AsCl ₃
CsNO ₃	Nd(NO ₃) ₃	Bi(NO ₃) ₃	SbCl ₃
Be(NO ₃) ₂	Sm(NO ₃) ₃	Cr(NO ₃) ₃	NH ₄ MoO ₄
Mg(NO ₃) ₂	Eu(NO ₃) ₃	Mn(NO ₃) ₂	Na ₂ WO ₄
Ca(NO ₃) ₂	Gd(NO ₃) ₃	Fe(NO ₃) ₃	Na ₂ ScO ₃
Sr(NO ₃) ₂	Er(NO ₃) ₃	Co(NO ₃) ₂	Na ₂ TeO ₃
Ba(NO ₃) ₂	Tm(NO ₃) ₃	Ni(NO ₃) ₂	NH ₄ TcO ₄
Cu(NO ₃) ₂	Th(NO ₃) ₄	Ru(NO ₃) ₃	KReO ₄
AgNO ₃	UO ₂ (NO ₃) ₂	AuCl ₃	NaI
Zn(NO ₃) ₂	Al(NO ₃) ₃	TiCl ₃	OsO ₄
Cd(NO ₃) ₂	Ga(NO ₃) ₃	GeO ₂	RhCl ₃
Hg(NO ₃) ₂	In(NO ₃) ₃	SnCl ₂	PdCl ₂
Y(NO ₃) ₃	TlNO ₃	VCl ₃	H ₂ PtCl ₄
La(NO ₃) ₃	Tl(NO ₃) ₃	NbF ₅	

RESULTS AND DISCUSSION

Systems with isoamyl alcohol

Table I shows the normality of ammonium thiocyanate both in the initial aqueous solution, and in the aqueous and organic phases after equilibration, as well as the calculated distribution coefficients. Table II shows parallel results for the thiocyanate partition and the distribution of acid for the system containing 0.1 *M* nitric acid and various amounts of ammonium thiocyanate. As can be seen from Table I, the distribution coefficient α remains practically unchanged and is independent of the initial concentration of the thiocyanate for ammonium thiocyanate concentrations up to approximately 2 *M*. For higher initial concentrations a slight increase in α is observed. Table II shows results that are very similar. The distribution coefficient of

TABLE I
THE DISTRIBUTION OF AMMONIUM THIOCYANATE BETWEEN WATER
AND ISOAMYL ALCOHOL

No. of soln.	Normality of NH ₄ CNS			V _o /V _w	α	μ
	initial soln.	aqueous phase	organic phase			
1	2	3	4	5	6	7
1	0.045	0.045	0.0031	1.12	0.069	0.077
2	0.090	0.091	0.0056	1.12	0.062	0.069
3	0.180	0.181	0.012	1.12	0.066	0.074
4	0.27	0.27	0.02	1.10	0.074	0.081
5	0.45	0.43	0.03	1.11	0.070	0.077
6	0.90	0.86	0.06	1.11	0.070	0.077
7	1.90	1.80	0.21	1.14	0.117	0.133
8	2.85	2.75	0.38	1.20	0.138	0.166
9	3.80	3.60	0.58	1.26	0.161	0.203
10	4.75	4.55	0.83	1.36	0.183	0.249

TABLE II
THE DISTRIBUTION OF AMMONIUM THIOCYANATE AND NITRIC ACID
BETWEEN WATER AND ISOAMYL ALCOHOL

No. of soln.	Normality in the initial solution		Normality in the aqueous phase		Normality in the organic phase		V_o/V_w	Distribution coefficients of			
	HNO_3	NH_4CNS	HNO_3	NH_4CNS	HNO_3	NH_4CNS		HNO_3		NH_4CNS	
								α	μ	α	μ
1	2	3	4	5	6	7	8	9	10	11	12
1	0.098	0.00	0.096	0.00	0.005	0.00	1.08	0.06	0.065	—	—
2	0.097	0.45	0.038	0.39	0.059	0.072	1.09	1.55	1.70	0.187	0.204
3	0.097	0.90	0.024	0.82	0.072	0.12	1.14	3.00	3.42	0.145	0.165
4	0.097	1.90	0.011	1.70	0.081	0.26	1.17	7.36	8.64	0.153	0.179
5	0.097	2.85	0.009	2.61	0.081	0.44	1.21	9.00	10.90	0.166	0.202
6	0.097	3.80	0.006	3.59	0.081	0.63	1.29	13.50	17.50	0.175	0.228
7	0.097	4.75	0.005	4.35	0.082	0.79	1.31	16.40	21.50	0.181	0.237

the thiocyanate is only slightly influenced by a tenfold increase of the thiocyanate concentration in the initial aqueous solution. Furthermore, the presence of 0.1 *M* nitric acid has practically no influence on the passage of the thiocyanate from the aqueous solution into the alcohol.

As regards the distribution coefficient of the hydrogen ion, the opposite behaviour is observed. When no thiocyanate is present in the solution, only traces of the acid pass into the alcoholic phase, but a very small amount of thiocyanate increases the acid distribution 25-fold. To obtain further information regarding the acidic species extracted by the alcohol, we plotted the logarithm of $\alpha_{[H^+]}$ against the logarithm of

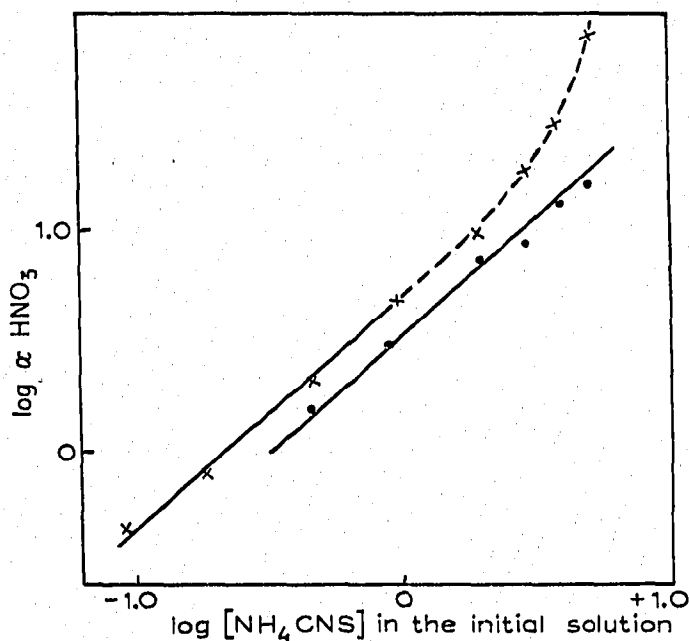


Fig. 1. The distribution coefficient of nitric acid (α_{HNO_3}) as a function of ammonium thiocyanate concentration in the initial aqueous solution. ● in the system IAA- $NH_4CNS-HNO_3-H_2O$. × in the system MIBK- $NH_4CNS-HNO_3-H_2O$.

the thiocyanate concentration in the initial aqueous solution (Fig. 1). A straight line was obtained with a slope = 1, indicating that each hydrogen ion of the nitric acid is attached to one thiocyanate. The extracted species, therefore, probably consist of free thiocyanic acid in addition to ammonium thiocyanate molecules.

The results obtained in paper-chromatographic experiments are presented in Table III. The ions not mentioned in the table gave R_F values equal to, or approximately equal to, zero in all the systems tested, except in the cases of molybdenum, vanadium and titanium. These cations show "multi-spot" phenomena, so that exact R_F values could not be given. The behaviour of these cations is complicated by the fact that they co-exist in two or more chemical forms, with widely different chromatographic behaviour, in a given solvent system. In addition to the "multi-spots" shown by these cations, a tailing was observed, due probably to a relatively slow rate of transition from one chemical form to another. Such phenomena are quite commonly observed in paper chromatography of these cations. The cations with R_F values of zero form either thiocyanates that are insoluble in water and alcohol, e.g. silver, thallium and lead, or thiocyanates or nitrates that are inextractable by alcohol, e.g. alkali and alkaline earth metals.

As regards the cations listed in Table III, the effect of increasing the thiocyanate concentration in the initial aqueous solution has first to be considered. In the systems without nitric acid all the cations, with the exception of arsenic, antimony, gold and palladium, show zero or nearly zero R_F values for concentrations of thiocyanate in the initial solution up to approximately 2 M. Higher R_F values in more concentrated solutions are connected with the appearance of the "water-front" on the chromatograms, the cations moving with the water-front. The appearance of the water-front must be due to a higher solubility of water in the alcohol, as can be seen from the volume ratios of the two separated phases (Table I, column 5). For concentrations up to 1.9 M thiocyanate in the initial aqueous solution, the ratio V_o/V_w is practically constant ($\pm 1\%$); for higher initial concentrations, this ratio increases due to the swelling of the organic phase by its greater water content. The increase in the $\alpha_{\text{NH}_4\text{CNS}}$ coincides with the increase in the ratio V_o/V_w , as pointed out above.

Most of the cations listed in Table III readily form complex compounds with the thiocyanate, but it seems that they are only sparingly soluble in the alcohol. For a higher solubility (higher R_F values) a higher polarity of the solvent is needed. Greater polarity is achieved by increasing the water content of the solvent, i.e. by equilibrating it with a more concentrated aqueous solution of ammonium thiocyanate.

The above conclusions concerning the effect of initial thiocyanate concentration upon the R_F values obtained, seem to be completely valid for the parallel systems containing nitric acid. The "break" in the chromatographic behaviour of cations at the initial thiocyanate concentration of about 2 M, could be observed to a lesser degree, due to fewer experimental data being presented for lower thiocyanate concentrations.

The main aim of these experiments was to study the effect of the acid upon the R_F values in systems containing various concentrations of thiocyanate. Comparing the R_F values for the cations in the two sets of experiments, in the presence and

TABLE III

R_F VALUES OF IONS OBTAINED IN ISOAMYL ALCOHOL SATURATED WITH VARIOUS CONCENTRATIONS OF AQUEOUS AMMONIUM THIOCYANATE SOLUTION IN THE PRESENCE AND IN THE ABSENCE OF NITRIC ACID

M	n																		
	0	0.097	0	0.097	0	0.097	0	0.097	0	0.097	0	0.097	0	0.097	0	0.097	0	0.097	
M	0.00	0.09	0.18	0.45	0.90	1.90	2.85	3.80	4.75	0.00	0.45	0.90	1.35	1.80	2.25	2.70	3.15	3.60	4.05
I	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
$Cu(NO_3)_2$	0.01	0.01	0.01	0.01	0.01	0.03	0.08 t	0.16	0.12	0.00	0.09	0.04	0.06	0.10	0.12	0.09			
$AuCl_3$	0.49	0.12 t	0.12 t	0.13 t	0.11 t	0.22	0.26	0.29	0.32	0.23	0.64	0.66	0.73	0.77	0.82	0.84			
$Be(NO_3)_2$	0.06	0.04	0.06	0.06	0.06	0.16	0.21	0.21	0.22	0.04 t	0.27 t	0.30 t	0.33 t	0.39 t	0.51	0.49			
$Mg(NO_3)_2$	0.01	0.01	0.00	0.02	0.03	0.18	0.28	0.27	0.28	0.00	0.01	0.06	0.14	0.22	0.26	0.33			
$Zn(NO_3)_2$	0.00	0.00	0.00	0.02	0.07	0.39	0.41	0.41	0.43	0.00	0.48 t	0.57 t	0.56 t	0.61 t	0.77	0.77			
$Cd(NO_3)_2$	0.01	0.01	0.01	0.01	0.02	0.15	0.21	0.25	0.30	0.00	0.22	0.26	0.27	0.26	0.29	0.32			
$Hg(NO_3)_2$	0.00	0.00	0.00	0.01	0.01	0.20	0.28	0.42	0.34	0.00	0.59	0.60	0.62	0.68	0.67	0.64			
$Al(NO_3)_3$	0.00	0.00	0.00	0.00	0.01	0.09	0.13	0.10	0.05	0.03	0.08	0.10	0.21	0.27	0.38	0.41			
$Ga(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.16	0.38	0.29	0.30	0.00	0.02	0.03	0.16	0.22	0.28	0.26			
$In(NO_3)_3$	0.00	0.03	0.00	0.01	0.03	0.27	0.18	0.21	0.27	0.00	0.58 t	0.59 t	0.67 t	0.71 t	0.82 t	0.82 t			
$Y(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.10	0.18	0.21	0.27	0.00	0.00	0.02	0.14	0.23	0.26	0.28			
$La(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.10	0.17	0.27	0.21	0.00	0.00	0.01	0.13	0.21	0.26	0.28			
$Ce(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.14	0.21	0.26	0.30	0.00	0.00	0.03	0.15	0.23	0.27	0.27			
$Pr(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.07	0.16	0.19	0.24	0.00	0.01	0.04	0.15	0.23	0.27	0.28			
$Nd(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.15	0.21	0.29	0.26	0.00	0.00	0.03	0.15	0.23	0.27	0.27			
$Sm(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.08	0.08	0.00	0.00	0.04	0.16	0.22	0.27	0.25			
$Eu(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.15	0.22	0.27	0.26	0.00	0.00	0.03	0.13	0.21	0.26	0.28			
$Gd(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.10	0.18	0.20	0.23	0.00	0.03	0.01	0.15	0.23	0.25	0.26			
$Er(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.07	0.08	0.14	0.12	0.00	0.08	0.09	0.19	0.26	0.29	0.27			
$Tm(NO_3)_3$	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.05	0.09	0.18	0.21	0.31	0.32			
$Th(NO_3)_4$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.08	0.09	0.09	0.12	0.15	0.18			
GeO_2	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.08	0.09	0.12	0.15	0.18			
$SnCl_2$	0.41	0.40	0.42	0.40	0.30	0.41	0.33	0.46	0.40	0.39	0.55	0.45	0.40	0.44	0.48	0.44			
$AsCl_3$	0.41	0.24	0.23	0.26	0.25	0.33	0.33	0.30	0.26	0.41	0.40	0.40	0.40	0.40	0.40	0.40			
$SbCl_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.37	0.37	0.37	0.37	0.37	0.37			
$Bi(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.10	0.16	0.23	0.25	0.26			
$Cr(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.15	0.22	0.46	0.30			
$UO_2(NO_3)_2$	0.02	0.04	0.03	0.03	0.03	0.24	0.28	0.23	0.25	0.04	0.46 t	0.56 t	0.64	0.65	0.65	0.82			
Na_2SeO_3	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.03	0.06	0.00	0.42	0.49	0.46	0.54	0.51	0.48			
$Mn(NO_3)_2$	0.00	0.01	0.00	0.00	0.05	0.20	0.23	0.28	0.28	0.00	0.12	0.12	0.16	0.23	0.30	0.32			
NH_4TCO_4	0.07	0.07	0.07	0.07	0.04	0.11	0.15	0.15	0.20	0.08	0.35	0.33	0.35	0.36	0.27	0.29			
$KReO_4$	0.01	0.04	0.04	0.03	0.04	0.11	0.16	0.19	0.21	0.07	0.34	0.36	0.42	0.39	0.39	0.39			
NaI	0.02	0.01	0.01	0.01	0.03	0.03	0.06	0.06	0.09	0.07	0.30	0.28	0.33	0.50	0.50	0.37			
$Fe(NO_3)_3$	0.00	0.00	0.00	0.00	0.00	0.06 t	0.10 t	0.06 t	0.08 t	0.00	0.37 t	0.42 t	0.45 t	0.54 t	0.56 t	0.57 t			
$Co(NO_3)_2$	0.00	0.01	0.01	0.01	0.01	0.14	0.23	0.28	0.31	0.00	0.16	0.20	0.21	0.29	0.40	0.33			
$Ni(NO_3)_2$	0.00	0.01	0.02	0.01	0.02	0.17	0.26	0.31	0.39	0.00	0.12	0.15	0.20	0.26	0.28	0.31			
$PdCl_2$	0.39	0.23 t	0.21 t	0.24 t	0.19 t	0.18 t	0.23	0.27	0.29	0.03	0.46	0.43	0.52	0.50	0.49	0.49			
H_2PtCl_4	0.00	0.00	0.00	0.00	0.00	0.12	0.19	0.25	0.26	0.10	0.43	0.44	0.53	0.47	0.54	0.57			

absence of nitric acid, one can see that, in the presence of acid, the values are either the same or higher.

Cations showing equal R_F values in both systems are those forming water- and/or alcohol-insoluble compounds ($R_F = 0$), and those forming relatively stable undissociated thiocyanate complexes (whose extractability is not influenced by the acid present in the eluant), such as copper, cobalt, nickel, manganese, cadmium, yttrium and the rare earths. It must here be recalled that all the cations belonging to this group, *i.e.* those that have equal R_F values in both systems, showed R_F values of zero or approximately zero in the previously studied systems containing isoamyl alcohol and various concentrations of nitric acid⁴.

The effect of the nitric acid can possibly be explained either by the inhibition of hydrolysis and the formation of more extractable acid thiocyanate complexes, as in the case of iron, zinc, mercury and uranyl, or by the inhibition of hydrolysis preventing the formation of insoluble compounds of more or less amphoteric covalent species, such as those of aluminium, beryllium, indium and gallium.*

Systems with methyl isobutyl ketone

It was our intention to carry out experiments with methyl isobutyl ketone parallel to those with isoamyl alcohol. However, the preliminary chromatographic experiments showed that, when the eluant used was methyl isobutyl ketone saturated with ammonium thiocyanate (without nitric acid), practically all the cations listed in the experimental part gave R_F values of zero. In the presence of nitric acid, however, a number of cations showed R_F values other than zero. In view of the negative chromatographic results obtained in the system MIBK-NH₄CNS-H₂O, only the second system MIBK-NH₄CNS-HNO₃-H₂O was thoroughly investigated. The distribution of the two solutes, the thiocyanate and the acid, between water and the ketone, is presented in Table IV. The amounts of thiocyanate extracted by the ketone are very small, and its distribution coefficient decreases with increasing concentrations of thiocyanate in the initial aqueous solution, but at high initial thiocyanate concentrations the distribution coefficient remains practically constant. This low solubility of the thiocyanate in the ketone is further indicated by the unchanged volume ratios of organic and aqueous layers after equilibration, as shown in column 8.

Comparing the numerical values of the normalities of the thiocyanate with those of the acid in the organic phase (columns 6 and 7), it can be seen that equinormal amounts of both are extracted by the ketone, using concentrations up to approximately 2 *M* of thiocyanate in the initial aqueous solution. A further indication of the composition of the species extracted by MIBK can be derived from the results presented in Fig. 1. The slope of the straight line obtained by plotting $\log \alpha_{[H^+]}$ versus the logarithm of the thiocyanate concentrations in the initial aqueous solution, is equal to one, which is similar to the results obtained with the isoamyl alcoholic

* Note added in proof: The authors are much indebted to Dr. LEDERER, Editor of this Journal, for kindly suggesting the dismutation of Fe(CNS)₃ to Fe⁺⁺ and (CNS)₂ as a plausible explanation for the tailing of iron on the chromatograms.

TABLE IV
THE DISTRIBUTION OF AMMONIUM THIOCYANATE AND NITRIC ACID BETWEEN
WATER AND METHYL ISOBUTYL KETONE

No. of soln.	Normality in the initial solution		Normality in the aqueous phase		Normality in the organic phase		V_o/V_w	Distribution coefficients of			
								HNO ₃		NH ₄ CNS	
	HNO ₃	NH ₄ CNS	HNO ₃	NH ₄ CNS	HNO ₃	NH ₄ CNS		α	μ	α	μ
1	2	3	4	5	6	7	8	9	10	11	12
1	0.097	0.00	0.095	0.00	0.002*	0.00	1.00	—	—	—	—
2	0.097	0.09	0.067	0.063	0.030*	0.027*	1.00	0.45	0.45	0.43	0.43
3	0.097	0.18	0.054	0.135	0.043*	0.040	1.00	0.79	0.79	0.30	0.30
4	0.097	0.45	0.032	0.39	0.065*	0.060	1.00	2.04	2.04	0.15	0.15
5	0.097	0.92	0.017	0.83	0.081	0.084	1.00	4.77	4.77	0.10	0.10
6	0.097	1.84	0.009	1.75	0.088	0.091	1.00	9.78	9.78	0.052	0.052
7	0.097	2.76	0.005	2.58	0.093	0.10	1.00	18.5	18.5	0.039	0.039
8	0.097	3.68	0.003	3.48	0.094*	0.12	1.00	31.4	31.4	0.034	0.034
9	0.097	5.52	0.0012	5.18	0.096*	0.25	1.00	79.8	79.8	0.048	0.048

* Calculated from the differences.

systems described above. This slope indicates that each hydrogen ion is attached to one thiocyanate ion. A change in the slope occurs when the initial thiocyanate concentration exceeds 2 *M*, coincidental with non-equinormal amounts of hydrogen and thiocyanate ions extracted by the ketone.

Chromatograms of the ions listed in the experimental part were run in methyl isobutyl ketone saturated with aqueous ammonium thiocyanate solutions of varying concentrations (0.1–5.5 *M*). With the exception of covalent chloride compounds, compounds of arsenic, antimony and tin, all the cations gave zero R_F values. The high extractability of these three covalent chlorides by methyl isobutyl ketone has already been observed^{1,2}. No thiocyanate compounds, either complexes or salt-like, are known for these cations. On the other hand, the addition of nitric acid to the thiocyanate solution resulted in R_F values other than zero, as shown in Table V. Almost all the cations moved on the paper with tailing. This tailing is generally

TABLE V
 R_F VALUES OF IONS IN METHYL ISOBUTYL KETONE EQUILIBRATED WITH AQUEOUS SOLUTIONS
CONTAINING NITRIC ACID AND AMMONIUM THIOCYANATE OF VARIOUS CONCENTRATIONS

<i>M</i> HNO ₃	0.097									
<i>M</i> NH ₄ CNS	0	0.09	0.18	0.45	0.92	1.84	2.76	3.68	5.52	
Be(NO ₃) ₂	0.00	0.18 t	0.25 t	0.24 t	0.28 t	0.26 t	0.30 t	0.36 t	0.42 t	
Zn(NO ₃) ₂	0.00	0.32 t	0.41 t	0.40 t	0.45 t	0.46 t	0.44 t	0.48 t	0.50 t	
In(NO ₃) ₃	0.00	0.35	0.39	0.48	0.56 t	0.55 t	0.60 t	0.60 t	0.57 t	
SbCl ₃	0.17	0.15	0.14	0.19	0.21	0.19	0.16	0.15	0.15	
UO ₂ (NO ₃) ₂	0.08	0.26 t	0.31 t	0.31 t	0.36 t	0.40 t	0.37 t	0.40 t	0.43 t	
Mn(NO ₃) ₂	0.00	0.25 t	0.28 t	0.32 t	0.41 t	0.35 t	0.37 t	0.38 t	0.37 t	
Fe(NO ₃) ₃	0.00	0.22 t	0.29 t	0.33 t	0.36 t	0.37 t	0.13 t	0.12 t	0.12 t	
Co(NO ₃) ₂	0.00	0.05 t	0.10 t	0.08 t	0.12 t	0.30 t	0.30 t	0.30 t	0.37 t	
PdCl ₂	0.00	0.11 t	0.08 t	0.10 t	0.08 t	0.08 t	0.10 t	0.13 t	0.08 t	

caused by the very slow rate of hydrolysis of the compounds in question. Uncharged species, the only ones that could be extracted by a non-polar organic solvent (such as methyl isobutyl ketone), were probably formed as products of a slow and irreversible hydrolysis of the metal species. The usefulness of chromatographic separations in the above systems is therefore very limited. The effect of increasing the thiocyanate concentration could only be observed in the cases of cobalt and beryllium. The phenomenon is clearly a consequence of the limited solubility of the complexant itself in the organic phase, as pointed out above.

Only the presence of acid in the eluant affected the mobility of the listed cations. The influence of the acid must be similar to its influence in the systems with isoamyl alcohol, *i.e.* promoting the formation of uncharged thiocyanate complexes as in the case of ferric iron, cobalt, manganese and uranium, or inhibiting hydrolysis as in the case of amphoteric beryllium and indium. The R_F values of covalent antimony chloride are not influenced by the presence of acid.

Systems with di-isopropyl ether

Since one of the main aims of this research was to make a comparative study of the chromatographic behaviour of metallic nitrates in systems containing an alcohol, a ketone or an ether, we intended to carry out experiments parallel to those given above, using di-isopropyl ether as the representative of the ethers. Chromatographic experiments with systems containing various concentrations of ammonium thiocyanate with and without 0.1 *M* nitric acid, showed R_F values of zero irrespective of the thiocyanate concentration and the presence of nitric acid. The only exceptions were the cations, such as antimony, which owing to their covalent bonds, are readily soluble in ether. In view of the negative chromatographic results we did not find it worthwhile to undertake a comprehensive study of the distribution of the thiocyanate and the acid between water and the ether.

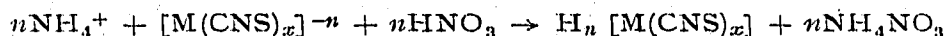
CONCLUSION

Ammonium thiocyanate is readily soluble in isoamyl alcohol, only very sparingly soluble in methyl isobutyl ketone and probably completely insoluble in di-isopropyl ether. Thiocyanic acid is easily extractable by the first two solvents and probably inextractable by the ether. The extractability of ammonium thiocyanate from an aqueous solution by an organic solvent seems to be connected with an appreciable swelling of the organic phase. This means that the extracted ammonium thiocyanate molecule must be readily hydrated. On the other hand, the extraction of thiocyanic acid does not seem to cause a swelling of the organic phase, which suggests that the extracted species is unhydrated.

The moving of cationic species on the paper depends mainly on the charge of the species and on the polarity of the organic solvent: non-polar organic solvents can extract only uncharged species. Since the thiocyanate metallic species formed during these chromatographic experiments were inextractable by the three non-polar

organic solvents, saturated with aqueous solutions of ammonium thiocyanate, it follows that these species must be either cationic or anionic but not uncharged. Increased water content in the non-polar isoamyl alcohol (dielectric constant 5.7) increases the polarity of the water-alcohol mixture and enables even the charged thiocyanate species to move on the paper.

The presence of free thiocyanic acid in the organic solvent, apart from its effect of inhibiting hydrolysis, promotes the formation of less dissociated thiocyanate complex species, according to the reaction:



The hydrogen ion here plays the role of the cation. The acid-complex species are more extractable by non-polar organic solvents than the corresponding ammonium salts, and therefore higher R_F values were obtained in systems containing nitric acid.

SUMMARY

Data are presented for the partition of nitric acid and/or ammonium thiocyanate between (1) water and isoamyl alcohol, (2) water and methyl isobutyl ketone. The R_F values of about sixty ions have been measured in isoamyl alcohol, methyl isobutyl and di-isopropyl ether, saturated with aqueous solutions containing varying amounts of ammonium thiocyanate and nitric acid. The effects of the solutes on the extractability of metallic species from aqueous solution by alcohol, ketone and ether, have been discussed and compared.

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