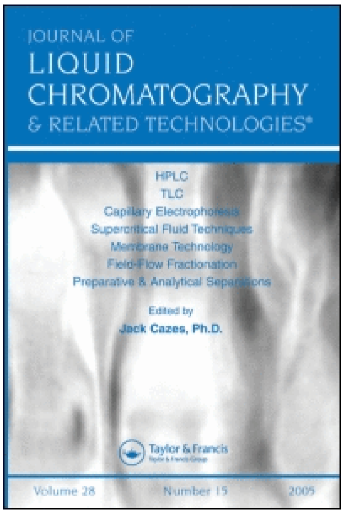

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INVESTIGATIONS OF THIOCYANATE COMPLEXES OF RHENIUM, MOLYBDENUM, VANADIUM AND TUNGSTEN BY ION-EXCHANGE CHROMATOGRAPHY METHOD

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ABSTRACT

The main purpose of this paper is examination of complexe formation between thiocyanate ions and rhenium, molybdenum, vanadiun and tungsten under identical detailed analysis of the chromatographic conditions of complex separation, definition of relative stability of the complexes, in order to determine the separation method of complex mixture of these ions.

INTRODUCTION

During technological processing of ores and minerals, such elements as: molybdenum, vanadium, rhenium and tungsten, go into solution and exist in the form of molybdate, vanadate, perrhenate and tungstate anions which are characterized by very similar analytical properties. This fact makes determination of these anions in their mixtures considerably difficult. In this connection, a preliminary separation before their determination is necessary. For separation of the ions of similar properties such methods as liquid chromatography, ion-exchange chromatography, thin-layer chromatography and eloctrochromatography are often used.

Recently, the methods consisting in the separation of metal ions in the solutions containing the ligands capable of forming the complexes with molybdenum, vanadium, rhenium and tungsten have often been used. The complexes formed have different composition and stability which leads to significant differentation of the metal properties.

Thiocyanate ions contain nitrogen and sulphur atoms capable of forming coordination bonds with the ions of many elements which leads to formation of the complexes of different stability and is often utilized in separation of these elements. The investigations of thiocyanate complexes of rhenium, molybdenum, vanadium and tungsten are described in numerous papers (1 - 14). These investigations have shown relatively complex nature of the equilibria in Me - SCN - HCl - Sn(II) systems, were Me = Re, Mo, V, W, determined by acidity of the medium and by thiocyanate and $SnCl_2$ concentration. Unfortunately, conclusions included in the papers relating to complex composition (1 - 3), complex charge (4 - 6)and optimal conditions of complex formation (7 - 14) are often incompatible.

It appears that the composition and charge of the complex formad as well as optimal conditions of their formation depend mainly on the concentration of hydrogen thiocyanate and $SnCl_2$ and discrepancies between the results published by different authors may be explained by different conditions of complexation reactions.

The main purpose of this paper is examination of complex formation between thiocyanate ions and rhenium, molybdenum, vanadium and tungsten under identical conditions, detailed analysis of the chromatographic conditions of complex separation, definition of relative stability of complexes, in order to determine the separation method of complex mixture of these ions.

MATERIALS AND METHODS

In order to determine preliminarily optimal conditions of the sorption of Re (VII), Mo (VI), V (V), W (VI) on the ion-exchanger, the procedure is described in detail in paper (15).

In the ion-exchange chromatography the strongly basic anion-exchanger AW-17 in the form of the salts of hydrochloric and thiocyanic acids and strongly acidic cation-exchanger KU-2 in the hydrogen form were employed. Preliminary purification of ion-exchangers 0.25-0.50 mm fraction from iron was carried out in the separatory funnel. Ion-exchanger in the separatory funnel was washed several times with hydrochloric acid solution and then with water for neutralizytion.

Standard solutions of Re (VII), Mo (VI), V(V) and W (VI) were prepared by dissolution of precisely weighed samples of recrystallized sodium or ammonium salts of these metals. Final concentration of each element investigated was equal to 1 mg/ml. Hydrochloric acid solutions of varying concentrations containing different amounts of thiocyanate in the presence or in the absence of $SnCl_2$ were used as the medium or a mobile phase.

RESULTS AND DISCUSSION

The data relating to described static measurements of the sorption of Re (VII), Mo (VI), V(V), W (VI) on AW-17 anion-exchanger used in the chloride form at different concentrations of thiocyanate ions are listed in Table 1.

Table 1.

Sorption of Mo, V, W and Re from thiocyanate solutions on the chloride form of AW-17 anion exchanger

c_{HCl} mole/l	c_{NH_4SCN} mole/l	sorption %			
		Mo	V	W	Re
$1x10^{-5}$	0	97	98	99	98
	0.01	95	41	99	98
	0.10	93	27	98	98
	1.00	48	x	63	76
	5.00	28	x	17[xx]	94[xx]
$1x10^{-3}$	0	97	97	99	98
	0.01	94	31	99	98
	0.10	91	16	99	97
	1.00	71	x	81	81
	5.00	66	x	52[xx]	97
$5x10^{-3}$	0	97	97	99	98
	0.01	93	17	99	98
	0.1	91	18	98	97
	1.00	90	x	88	85
	5.0	74	x	74[xx]	73[xx]
$1x10^{-2}$	0	96	66	99	97
	0.01	93	13	99	98
	0.10	92	13	99	98
	1.00	93	x	90	79
	5.00	93	x	72	92

(continued)

Table 1 continued

c_{HCl} mole/l	c_{NH_4SCN} mole/l	sorption %			
		Mo	V	W	Re
$1x10^{-1}$	0	62	25	97	97
	0.001	76	8	98	97
	0.10	75	10	89	96
	1.00	94	x	99	78
	5.00	93	x	93^{xx}	95^{xx}
$5x10^{-1}$	0	12	15	79	97
	0.01	24	4	83	97
	0.10	54	x	84	96
	1.00	80	x	97	78
	5.00	84	x	91	95
1.0	0	5	12	66	97
	0.01	25	2	76	96
	0.10	59	6	85	96
	1.00	82	x	98	70
	5.00	84	x	93	92
2.0	0	18	10	55	97
	0.01	39	20	56	96
	0.10	88	26	93	96
	1.00	82	x	97	87
	5.00	xxx	xxx	xxx	xxx

Table 1 continued

c_{HCl}	c_{NH_4SCN}	sorption %			
mole/l	mole/l	Mo	V	W	Re
4.0	0	57	54	38	89
	0.01	74	37	52	97
	0.10	93	42	93	97
	1.00	81	x	96	96
6.0	0	61	66	36	50
	0.01	75	71	65	76
	0.10	92	78	95	76
	1.00	94	x	96	98
8.0	0	66	77	52	42
	0.01	74	87	60	75
	0.10	79	73	75	68
	1.00	96	x	90	98
10.0	0	85	84	59	25
	0.01	68	79	71	78
	0.10	76	77	73	85

x - determination of V in the form of phosphovanadtungstic acid is hindered

xx - independently on these data the dynamic measurements have shown a quantitative sorption of W and complete elution of Re

xxx - SCN^- ions undergo to hydrolysis

In the diluted solutions of hydrochloric acid 1×10^{-5} mole/l sorption values of these ions can reach about 80%. This can be explained by high sorption affinity of AW-17 anion-exchanger for the elements mentioned above. In the experimental conditions in the acidity range used, low concentration of thiocyanate ions does not influence sorption values of the ions investigated, except vanadium. For the concentration of thiocyanate ions equal to 5% ion sorption decreases significantly owing to the competitive action of thiocyanate ions. In the absence of thiocyanate ions in the solutions in which hydrogen ion concentration does not exceed of 0.1 mole/l, vanadium sorption decreases with the increase of acidity during transition of its anionic form to the cationic form according to the following scheme:

$$VO_3^- + 2\ H^+ \rightleftharpoons VO_2^+ + H_2O \qquad (1)$$

In the case of Mo and W decrease of sorption starts at HCl concentration equal to 0.5 mole/l. Minimum sorption of Mo, V and W takes place at acid concentration equal to 1.0 and 1.5 mole/l respectively. At the acidity exceeding 4-6 mole/l, sorption increase of these elements on anion-exchanger starts. At moderate and high acid concentration, the increase in acid concentration promotes the increase of sorption of these elements which can be explained by the formation of anionic thiocyanate complexes of Mo, V and W. This phenomenon is also promoted probably by the liberation of hydrogen sulfide which can reduce the above elements. Thiocyanate ions present at high concentration in the solutions of acidity exceeding 20 mole/l, may undergo hydrolysis according to the schemes:

$$SCN^{+} + 2H^{+} + H_2O \rightleftarrows COS + NH_4^{+} \qquad (2)$$

$$COS + H_2O \rightleftarrows CO_2 + H_2S \qquad (3)$$

From the data listed in Table 1 , it also results that anionic thiocyanate complexes formed sorbs significantly stronger than corresponding chloride complexes of the same metals. Mo, V and W are characterized by a high coordination number and therefore in relation to the concentration of thiocyanate ions in HCl formation of different coordinately saturated and unsaturated thiocyanate complexes both cationic and anionic can be expected. The data relating to the sorption of Re, Mo, V and W on KU-2 cation exchanger the hydrogen form in the presence or absence of thiocyanate ions, are listed in Table 2. The presence of thiocyanate ions reduces the sorption of Mo, V and W. It has been stated that positively charged thiocyanate ion complexes are not formed in the solutions investigated.

Table 2.

Sorption of Mo, V, W and Re on the hydrogen form of KU-2 cation exchanger from acidic solution: HCl in the presence of KSCN

c_{HCl}	c_{KSCN}	Sorption %			
mole/l	mole/l	Mo	V	W	Re
1×10^{-5}	0	38	95	56	7
	0,1	44	45	67	12
	1.0	6	x	49	20
1×10^{-3}	0	55	95	71	7
	0.1	42	55	62	12
	1.0	30	x	46	20
0.01	0	58	95	70	7
	0.1	40	49	61	10
	1.0	31	x	49	12
0.10	0	40	62	65	7
	0.1	34	18	35	12
	1.0	20	x	14	12
0.50	0	23	53	55	7
	0.1	15	6	31	10
	1.0	14	x	0	12
2.0	0	10	31	40	10
	0.1	8	7	11	20
	1.0	13	x	16	12
6.0	0	11	12	11	18
	0.1	10	x	8	20
	1.0	17	x	17	10

x - determination of V in the form of phosphovanad-tungstic acid is hindered

From the data listed in Table 3, it results that in the solutions of hydrochloric acid of the concentrations $\leq 1x10^{-2}$ mole/l Re, Mo and W sorb effectively both on chloride or thiocyanate form of the anion-exchanger. In the case of V, some differences in sorption values take place on a thiocyanate form of the anion exchanger, V is sorbed slightly better.

For the acidities higher than 0.1 mole/l , Mo, V and W are better sorbed by a thiocyanate form of the anion exchanger. It is very interesting that in the case of the sorption on a thiocyanate form of the anion exchanger, the particles of the anion exchanger assume, depending on HCl concentration different colours, typical for corresponding thiocyanate complexes.
If the anion exchanger is used in a chloride form, the change of colour does not occur which indicates that thiocyanate complexes are formed mainly on the anion exchanger and the functional groups of AW-17 anion exchanger are probably included in the molecules of such complexes. Formation of ionic associates of $[(CH_3)_3NR]_2[MoO_2(SCN)_2]$ type is very probable in these cases. At higher concentrations of HCl, (2.0 m/l), significant reduction of Mo (VI) and Mo (V) probably takes place and the substances of the formula : $[(CH_3)_3NR]_2 [MoO(SCN)_5$ are formed which is in good agreement with literature data (16-17) . Analogously,

Table 3 .

Sorption of Mo, V, W and Re on the chloride and thiocyanate forms of AW-17 anion exchanger

c_{HCl} mole/l	sorption %							
	Mo	V	W	Re	Mo	V	W	Re
	Cl^- form				SCN^- form			
1×10^{-5}	97	98	99	98	99	53	98	99
1×10^{-3}	97	97	99	98	99	59	87	98
5×10^{-3}	97	97	99	98	97	59	89	98
1×10^{-2}	96	66	99	97	95	69	88	94
1×10^{-1}	62	25	97	97	93	88	84	98
0.5	12	15	79	97	93	89	95	87
1.0	5	12	66	97	98	92	85	81
2.0	18	10	55	97	98	91	73	76
4.0	57	54	38	89	99	81	75	65
6.0	61	66	37	50	98	89	91	100
8.0	66	77	52	42	97	-	86	94
10.0	85	84	59	25	88	-	59	98

sorption of Re can be explained $[(CH_3)_3NR]_2[ReO(SCN)_5]$ complex is probably formed in the first place and then depending on HCl concentration complexes of different compositions are formed.

In order to examination the possibility of quantitative separation of the ions investigated conditions of the sorption and desorption of these ions were studied in dynamic conditions. Then standard curves were plotted ion exchange method of separation was worked out, 25 ml of the solution containing the mixture of Mo, V and W , Re in 0.5 M HCl was passed through the column containing chloride form of AW-17 anion exchanger, washed previously with 0.1 M HCl, flow rate was 1-2 ml/min. Elution curves presented in Fig.1 suggest that in the dynamic conditions Mo and V are eluted quantitatively filtrate 1 , whereas Re and W are absorbed completely by the anion exchanger. In order to separate Re and W, the column was washed with $1x10^{-4}$ M HCl containing 5% of thiocyanate ions, Re was then eluted and W could be eluted from the column with hot 8 M HCl.

In order to separate Mo and V, the filtrate 1 was acidified,so that the final concentration of HCl was equal to 6.0 M and the solution prepared in this way was passed at the same flow rate through the column, containing thiocyanate form of the anion exchanger. In such conditions, V is eluted quantitively. Desorption of Mo is carried out using 5% solution of NaOH, containing 3% of hydrogen peroxide.

Fig.2 presents another way of ion separation using hydrogen form of KU-2 cation exchanger and chloride and thiocyanate form of AW-17 anion exchanger. The solution containing the equal amount (1 mg) of Re, Mo, W and V in 10^{-3} M solution of HCl was passed at the flow rate of 1-2 ml/min through the column containing hydrogen form of the cation exchanger and then the column

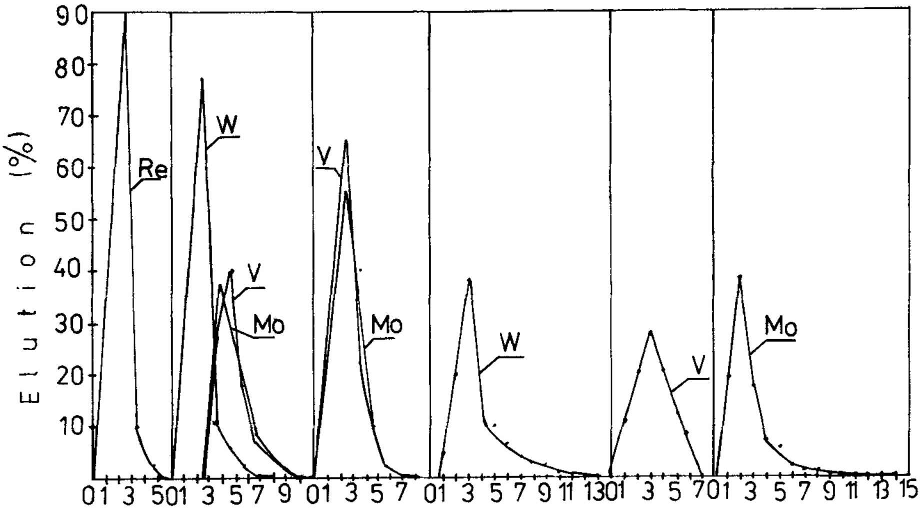

Fig.1 Number of fractins (10 ml each)

Separation of Mo,V,Wa,Re mixture on anionite.

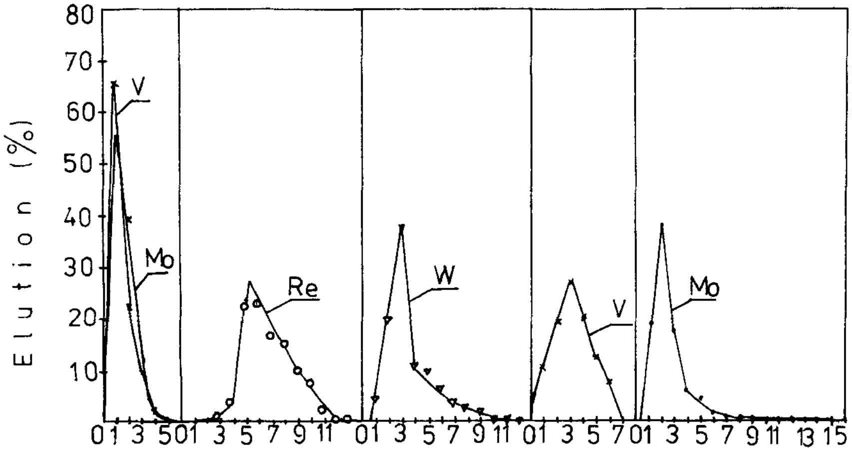

Fig.2 Number of fractions (10 ml each)

Separation of Mo,V, Wa, Re mixture on kationite.

was washed again with the same solution, not containing the ions investigated. The eluate contained only Re and three other metal ions remained on the cation exchanger. Desorption of the mixture of these three elements is carried out using 0.5 M solution of HCl. This mixture is then passed through the column containing chloride form of AW-17 anion exchanger.

Anion exchanger is then washed with 0.5 M solution which leads to elution of Mo and V whereas W is relained quantitatively on the column. In the further stage W is desorbed with hot 8M HCl. In order to separate Mo and V, the solution is acidified so that the final concentration of HCl ia equal to 6 M and then is passed through the column containing thiocyanate form of the anion exchanger. During further washing with 6 M solution of HCl, elution of V occurs due to differences in thiocyanate complex stability. Desorption of Mo is carried out using 5% solution of NaOH.

The results of the investigations permit to conclude that ion-exchange chromatography method can be succesfully used for effective separation of metal ions. However, there are some difficulties consisting in labour-consuming separation process as well as some drastic conditions of this process.

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