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NOTE

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Abstract

Separation of rhenium(VII) from molybdenum, vanadium, chromium, tungsten, iron, cobalt, nickel, copper, manganese, iridium, ruthenium, and uranium is achieved by solvent extraction with 4-methyl-2-pentanol either from sulfuric or hydrochloric acid media. Rhenium is determined directly in the organic phase as its thiocyanate complex at 430 nm. The method is shown to be applicable to synthetic mixtures and alloy steel.

4-Methyl-2-pentanol (methyl isobutyl carbinol) has been used for solvent extraction studies of vanadium (*1*), molybdenum (*2*), tungsten (*3*), and gold (*4*). Extension of these studies has revealed that rhenium(VII) can also be quantitatively extracted with undiluted carbinol from 3 *M* hydrochloric acid solution. The metal ion in the organic phase can be determined photometrically as the thiocyanate complex at 430 nm.

Several solvent extraction methods for rhenium have been reported in the literature and many of them have limitations which have been discussed in earlier communications (*5*, *6*). The proposed method is rapid, simple, and affords clean-cut separation of micrograms of rhenium from metal ions such as molybdenum, vanadium, tungsten, chromium, and other elements in minimum time.

EXPERIMENTAL

Apparatus and Reagents

Absorbances were measured with a Zeiss Spectrophotometer (Jena) employing 1 cm quartz cells.

A standard solution of rhenium was prepared and standardized as described earlier (*5*). A test solution containing 20 μg Re/ml was prepared by suitable dilution.

Potassium thiocyanate solution, 20% w/v in aqueous solution.

Tin(II) chloride solution, 35% w/v in 1:1 HCl.

Methyl isobutyl carbinol (E. Merck, Germany, bp 131 to 134°C) was used as extractant.

General Procedure

An aliquot portion of solution containing 20 μg Re was mixed with an appropriate volume of hydrochloric acid and diluted to 10 ml so that the final concentration of acid in the solution was 3 *M*. The solution was then shaken for 15 sec with 10 ml of 100% carbinol and the layers were allowed to settle and separate. The aqueous layer was carefully withdrawn. To the organic phase, 20 ml of water containing 6 ml of conc HCl, 2 ml of thiocyanate solution, and 1 ml of tin(II) chloride solution were added. After 5 min, the solutions were equilibrated for 1 min, the two phases were allowed to separate, and the absorbance of the yellow thiocyanate complex of rhenium in the organic phase was measured at 430 nm against a reagent blank.

RESULTS AND DISCUSSION

The concentration of carbinol was varied from 15 to 100% with benzene as the diluent, and the hydrochloric acid concentration was varied from 0.25 to 5 *M*. The results (Table 1) show that it is quite possible to extract rhenium(VII) quantitatively even with 50% carbinol from 5 *M* HCl solution, but since at this condition coextractions and interferences are large, extractions for futher studies were performed from 3 *M* HCl solutions using undiluted carbinol. The extraction of rhenium(VII) was also quantitative from 5 to 6 *N* sulfuric acid solution (Table 2).

The chlorides of lithium, potassium, and magnesium were tried as salting-out agents for their effects on extraction. The results (Table 3) showed that for quantitative extraction of rhenium(VII) at low acidity,

TABLE 1

Distribution Ratio as a Function of Acidity and Extractant Concentration. Re(VII) = 20 μg

Carbinol concentration (%)	HCl concentration (*M*)	Extraction (%)	Distribution ratio (*D*)
15	1	—	—
	2	9.52	0.10
	3	14.29	0.16
	4	19.0	0.23
	5	23.81	0.31
25	1	9.52	0.10
	2	19.0	0.23
	3	33.33	0.49
	4	47.62	0.90
	5	57.14	1.33
50	1	28.57	0.39
	2	52.38	1.10
	3	66.66	2.0
	4	90.48	9.50
	5	100.0	∞
75	1	61.90	1.62
	2	85.71	5.9
	3	95.24	20.0
	4, 5	100.0	∞
100	0.25	57.14	1.33
	0.5	66.66	2.0
	1	76.19	3.20
	2	90.48	9.50
	3–5	100.0	∞

TABLE 2

Percentage Extraction of Rhenium(VII) as a Function of Sulfuric Acid Concentration. Re(VII) = 20 μg, 100% Carbinol

H_2SO_4(*N*)	% Extraction	Distribution ratio (*D*)
1	71.43	2.5
2	76.19	3.2
3	85.71	5.9
4	90.48	9.5
5, 6	100.0	∞

TABLE 3

Effect of Lithium Chloride and Magnesium Chloride as Salting-Out Agent. Re(VII) = 20 μg

Salting-out agent		HCl (*M*)	% Extraction	Distribution ratio (*D*)
LiCl	2 *M*	0.25	76.19	3.2
		0.5	85.71	5.9
		1	90.48	9.5
		2	95.24	20.0
	4 *M*	0.25	85.71	5.9
		0.5	90.48	9.5
		1	95.24	20.0
		2	100.0	∞
	6 *M*	0.25	90.48	9.5
		0.5	95.24	20.0
		1–2	100.0	∞
	8 *M*	0.25	95.24	20.0
		0.5–2	100.0	∞
$MgCl_2$	1 *M*	0.25	66.66	2.0
		0.5	80.95	4.24
		1	90.48	9.50
		2	95.24	20.0
	2 *M*	0.25	80.95	4.24
		0.5	85.71	5.9
		1	95.24	20.0
		2	100.0	∞

it is necessary to use either 8 *M* LiCl or 2 *M* $MgCl_2$ as the salting-out agent. Potassium chloride does not show a salting-out effect.

Variation of the shaking time from 15 to 120 sec showed that a minimum of 15 sec shaking is needed for complete extraction of rhenium(VII).

Diverse Ion Effect

The results in Table 4 show the effect of the presence of various ions on the extraction and determination of rhenium in the organic phase. The tolerance limit was set at the amount required to cause a ±1% error in the rhenium recovery. Of the ions tested, molybdenum(VI), osmium(VIII), tellurium(IV), and thiosulfate showed interference. Tungsten was masked with oxalic acid. Interference due to molybdenum could be eliminated by its reduction with hydrazine sulfate and extracting rhenium from sulfuric acid solution.

TABLE 4

Effect of Diverse Ions. Re(VII) = 20 μg, 3 *M* HCl, 100% Carbinol

Foreign ion	Tolerence limit (μg)
V(V)	2,000
Cr(III)	2,000
Mo(VI)	None
W(VI)[a]	700
Mn(II)	2,000
Fe(III)	2,000
Co(II)	2,000
Ni(II)	2,000
Ru(III)	2,000
Os(VIII)	None
Ir(III)	2,000
Cu(II)	2,000
Hg(II)	2,000
Sb(III)	2,000
Se(IV)	2,000
Te(IV)	None
U(VI)	1,000
Oxalate	10,000
Tartrate	10,000
Ascorbate	10,000
Thiocyanate	20,000
EDTA	10,000
Phosphate	5,000
Fluoride	10,000
Thiosulfate	None

[a] W(VI) is masked with oxalic acid.

SEPARATION OF RHENIUM FROM Mo, V, W, Cr, Mn, AND U FROM SULFURIC ACID SOLUTION

A sample solution (5 *N* in H_2SO_4) containing 20 μg of rhenium(VII) and milligram amounts of other elements was boiled with hydrazine sulfate (10 ml of 1% aqueous solution) in order to reduce Mo(VI) and V(V). From this solution rhenium was then quantitatively extracted into carbinol and subsequently determined in the organic phase itself as described in the general procedure. All other metal ions remain in the aqueous phase. Tungsten in the solution was masked with oxalic acid.

TABLE 5

Analyses of Synthetic Mixtures

Composition of the mixture						Re found (μg)
Mo (1 mg)	Re (20/μg)					20
Mo (2 mg)	Re (20 μg)					20. 5
V (1 mg)	W (1.4 mg)	Cr (1 mg)	Mn (1 mg)	Re (20 μg)		20
V (1 mg)	W (1.4 mg)	Cr (1 mg)	U (1 mg)	Re (20 μg)		19. 8
Fe (1 mg)	Co (1 mg)	Ni (1 mg)	Cu (1 mg)	Mn (1 mg)	Re (20 μg)	20
Ir (2 mg)	Ru (2 mg)	Re (20 μg)				19. 9
Alloy 33b[a]	C (2.24%), Si (2%), P (0.11%), Mn (0.64%), Ni (2.24%), Cr (0.61%), Mo (0.4%) + Re (20 μg)					20
Alloy 21b[a]	C (6.84%), Si (0.12%), S (0.04%), P (0.03%), Mn (0.43%), W (0.46%) + Re (20 μg)					20

[a] Bureau of Analysed Samples Ltd., United Kingdom. Dissolution was done as described earlier (*2*).

The method was used successfully for the analysis of an alloy cast iron (No. 33b) to which a known amount of rhenium was added. The results of various synthetic samples are shown in Table 5.

SEPARATION OF RHENIUM FROM Fe, Co, Ni, Cu, Mn, Ir, AND Ru FROM HYDROCHLORIC ACID SOLUTION

Extraction of a microgram of rhenium with undiluted carbinol from a sample solution (3 *M* in HCl) facilitates its separation from metal ions such as Fe, Co, Ni, Cu, Mn, Ir, and Ru. These metal ions are retained in the aqueous phase whereas rhenium in the organic phase was determined as usual. The recovery of a known amount of a rhenium added to an alloy cast iron (No. 21b) was quantitative by the recommended method (Table 5).

CONCLUSION

The proposed method is simple, rapid, and free from interferences. The method affords the separation and determination of rhenium from

Mo, V, Cr, W, Fe, Co, Ni, Cu, Mn, Ir, Ru, and U in a single extraction. The results are reasonably accurate to within ±0.5%. The total operation requires only 20 min. The wide applicability of the method is shown by the satisfactory analysis of a variety of samples.

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