Microdetermination of Rhenium with Sodium Pentacyanonitrosylferrate(III) and Thiocyanate

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A highly simple and sensitive method for the microdetermination of perrhenate ion was developed which is based on the formation of a mixed ligand complex with thiocyanate and pentacyanonitrosylferrate(III) (nitroprusside) in the presence of tin(II) chloride as reductant. The dark yellowish-brown species thus obtained was quantitatively extractable into 3-methyl-1-butanol whose absorption was measured at 410 nm. A large number of transition elements including Pt-metals do not cause any interference in the method and the results obtained are quite reproducible with a standard deviation of 0.002. The method obeys Beer's law in the range of 0.91—2.57 ppm of Re with molar absorptivity and Sandell's sensitivity of 3.86×10^4 $dm^3\,mol^{-1}\,cm^{-1}$ and 0.0048 μg-Re cm^{-2}, respectively. The method handles satisfactorily the analysis of a wide variety of samples. Rhenium, thiocyanate and nitroprusside in the extracted species were found to be in a respective ratio of 2 : 3 : 1.

There has been a growing interest for the trace determination of rhenium using various ligands.[1-5] However, in most of these procedures, the degree and kind of interferences were of great concern and the attention paid to eliminate them is not adequate so far. Another equally important factor while carrying out micro-level determinations, is the sensitivity of these methods. Literature survey reveals that thiocyanate forms colored complexes with rhenium in varying compositions in presence of tin as reductant in acid media.[6-9] Several papers have also appeared to this effect in the past, but the interferences from the associated elements occurring in its minerals and alloys are too many,[10-12] requiring separations before determination of the metal ion. On further investigating the system, we observed that the intensity of the complex formed between lowervalent rhenium and thiocyanate increases considerably in presence of nitroprusside, thereby enhancing sensitivity of the reaction with relatively higher tolerance limits of other ions on extraction into 3-methyl-1-butanol. Therefore, the present paper makes a detailed study of the Re-SCN-nitroprusside system for working out a highly sensitive method for its microdetermination.

Experimental

Reagents. Standard Rhenium Solution, 1 mg ml^{-1}: Dissolve 0.1554 g of potassium perrhenate, $KReO_4$ ('Specpure' Johnson Matthey & Co.) in distilled water containing a few drops of diluted HCl and dilute it to 100 ml. Lower concentrations of rhenium at μg ml^{-1} level were obtained by suitable dilutions therefrom.

Solutions of other elements containing mg ml^{-1} of the metal ion were prepared by dissolving their commonly available salts of chemically pure grade, generally in water or diluted acid solutions and their lower concentrations can be obtained similarly by proportionate dilutions.

Potassium Thiocyanate, 20%: It was prepared by dissolving 20 g of potassium thiocyanate (Qualigens) in distilled water which was made upto 100 ml in a volumetric flask.

Tin(II) Chloride, 30%: To 30 g of tin(II) chloride dihydrate, $SnCl_2\cdot2H_2O$ (Qualigens) in a 100 ml beaker, 40 ml of 1 : 1 HCl were added. It was heated till the solution became clear and then finally diluted to 100 ml after cooling.

Sodium Nitroprusside, 2%: 2 g of sodium nitroprusside was dissolved in water and made upto 100 ml.

3-Methyl-1-butanol (Qualigens) was distilled and the fraction distilling between 128—132 °C was collected for use.

For absorbance measurements, UV-vis 140-02 spectrophotometer (Shimadzu, Japan) was used.

Synthetic and Flue Dust Samples: Synthetic samples were prepared by mixing μg-amounts of rhenium with other metal ions in varying proportions as shown in Table 2.

Reverberatory flue dust samples from copper manufacture, containing no rhenium, were mixed with a solution of known content of rhenium and dried in an oven. After complete fusion of the flue dust sample with sodium peroxide, the leach was neutralized with concentrated H_2SO_4 and was made slightly alkaline with sodium hydroxide solution. It was boiled and the hydroxide precipitate was filtered and washed well with distilled water. The filtrate thus obtained was adjusted to the experimental conditions as described below in the procedure for the determination of rhenium.

Procedure. To an aliquot containing 100 μg Re and/or other ions in a 100-ml separatory funnel were added 2 ml of 30% tin(II) chloride solution, 5 ml 20% potassium thiocyanate solution, and 2 ml of 2% sodium nitroprusside solution. It was diluted to 20 ml with distilled water, gently mixed and allowed to stand undisturbed for 10 min. The colored metal complex thus formed was extracted by equilibrating once with an equal volume of 3-methyl-1-butanol for 2 min. To remove any suspended droplets of water, the organic layer was filtered through a Whatman filter paper No. 41 into a 25 ml volumetric flask which is made upto the mark with the pure solvent. The absorbance of the solution is measured at 410 nm against a reagent blank.

Results and Discussion

Perrhenate ion, on reduction with stannous chloride forms a dark yellowish-brown complex with thiocyanate in presence of sodium nitroprusside. The metal complex is quantitatively extractable into 3-methyl-1-butanol. Absorption spectrum of the complex (Fig. 1)

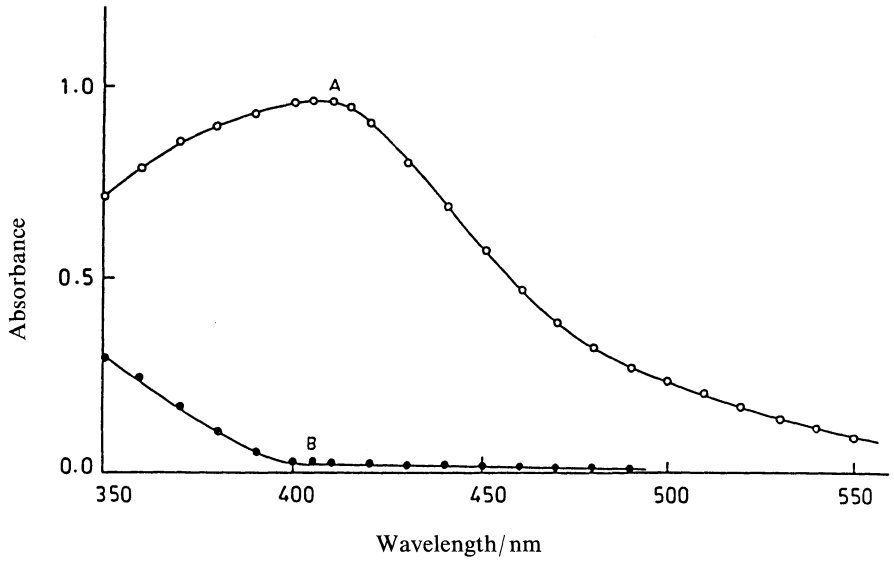

Fig. 1. Absorption spectrum of Re-SCN-Nitroprusside complex in 3-methyl-1-butanol.
Curve A: 4 μg Re ml^{-1} measured against reagent blank,
Curve B: reagent blank measured against 3-methyl-1-butanol.

Table 1. Effect of Various Parameters on the Absorbance of Re-Complex

$SnCl_2 \cdot 2H_2O$[a] (ml)	0.0	0.5—1.0	1.5	1.8	2.0	2.2	2.5	3.0		
Absorbance	0.004	Turbidity appears	1.05	1.10	1.10	1.10	1.06	0.975		
KSCN[b] (ml)	0.0	1.0	2.0	3.0	4.0	4.5	5.0	5.5	6.0	7.0
Absorbance	0.027	0.940	1.040	1.10	1.14	1.16	1.16	1.16	1.12	1.10
Sodium nitroprusside[c] (ml)	0.0	0.5	1.0	1.5	1.9	2.0	2.1	2.5	3.0	
Absorbance	0.479	0.852	0.980	1.080	1.16	1.16	1.16	1.10	0.979	
Color development time[d] (min)	0.0	5.0	8.0	9.0	10.0	11.0				
Absorbance	0.679	0.878	1.155	1.16	1.16	1.16				
Equilibration time[e] (min)	0.5	1.0	2.0	3.0	4.0					
Absorbance	0.990	1.14	1.16	1.16	1.16					

a) Re, 100 μg; KSCN, 3 ml; Sodium nitroprusside, 2 ml; color development time, 10 min; equilibration time, 2 min; $SnCl_2 \cdot 2H_2O$, variable. b) $SnCl_2 \cdot 2H_2O$, 2 ml; other conditions are the same as in (a) except variation in KSCN content. c) KSCN, 5 ml; other conditions are the same as in (b) except variation in sodium nitroprusside content. d) Sodium nitroprusside, 2 ml; other conditions are the same as in (c) except variation in color development time. e) Color development time, 10 min; other conditions are the same as in (d) except variation in equilibration time.

indicates that maximum lies at 410 nm, where the absorbance of the reagent blank is minimal.

The absorbance of the Re-complex decreases in the following order: CH_3COOH (0.93) > HCl (0.76) > H_3PO_4 (0.57) > H_2SO_4 (0.51) at IN acidity; while keeping all other aqueous conditions the same in each case.

Various other operative parameters affecting the formation of the metal complex, namely, conditions of stannous chloride, thiocyanate, sodium nitroprusside, color development time, and equilibration time, are shown in Table 1. It was concluded from these studies that for 100 μg Re: 1.8—2.2 ml of 30% $SnCl_2 \cdot 2H_2O$ solution, 4.5—5.5 ml of 20% KSCN solution, 1.9—2.1 ml of 2% sodium nitroprusside solution, in 20 ml aqueous volume, 9—11 min of color development time, and equilibrating once with an equal volume of 3-methyl-1-butanol for 2 min, are the optimum conditions for the quantitative extraction of the metal complex. The absorption was measured at 410 nm after making up the volume to 25 ml as already described in the procedure.

The extraction of the metal complex has also been attempted with different solvents. The absorbance is found to decrease in the following order: 3-methyl-1-butanol > ethyl ethanoate > 1-butanol > 2-butanone > 4-methyl-2-pentanone. It is almost negligible in cases of chloroform and benzene. Hence, 3-methyl-1-butanol is preferred as the extracting solvent for the metal complex.

Effect of Diverse Ions. Under the optimum conditions of the procedure, chloride (150 mg), sulphate (150 mg), nitrate (100 mg), acetate (50 mg), citrate (50 mg) do not influence the absorbance of the complex; whereas, tartrate (50 mg), oxalate (50 mg) increase it slightly. The presence of fluoride (50 mg), EDTA (50 mg), thiourea (50 mg), results in increasing the absorption of the complex, but H_2O_2, 1 ml of 30% w/v, lowers it. The figure in brackets indicates the amount of sodium salt of the anion present in 20 ml of aqueous solution in each case.

Ca(II), Ba(II), Mg(II), Cd(II), Pb(II), Zn(II), Ni(II), Al(III), Bi(III), Cr(III), Ce(IV), Zr(IV), Sb(V), Cr(VI), 10 mg/20 ml; Ag(I), Cu(II), Fe(II), Hg(II), Fe(III), As(V), 5 mg/20 ml; W(VI), 1.5 mg/20 ml; Rh(III), U(VI), Os(VIII), 0.5 mg/20 ml; Se(IV), 0.25 mg/20 ml; Pd(II), Pt(IV), 0.2 mg/20 ml; Ru(III), V(V), 0.15 mg/20 ml; are without effect. Mo(VI) interferes.

Stability, Reproducibility, Beer's Law Obedience, and Sandell's Sensitivity of the Complex. The metal complex is quite stable and the absorbance remains unchanged even after over one hour. The results obtained are highly reproducible with a standard deviation of 0.002. Beer's law is obeyed in the range of 0—2.6 μg-Re ml^{-1}. The optimum concentration range that can be measured accurately, as evaluated from Ringbom plot, is 0.91—2.57 ppm of Re (Fig. 2). Molar absorptivity, specific absorptivity, and Sandell's sensitivity of the complex are 3.86×10^4 $dm^3\,mol^{-1}\,cm^{-1}$, 2.08×10^{-1} $ml\,g^{-1}\,cm^{-1}$, and 0.0048 μg-Re cm^{-2}, respectively.

Stoichiometry of the Complex. The ratio of rhenium, thiocyanate, and nitroprusside in the extracted species is determined by Job's method of continuous variations as modified by Vosburgh and Cooper[13] for the two phase system.

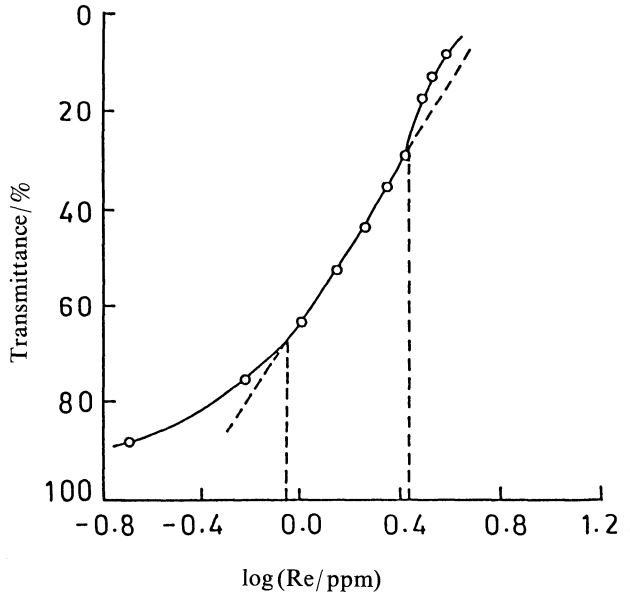

Fig. 2. Ringbom plot of Re-complex at 410 nm.

Rhenium: Thiocyanate. x ml of 5.38×10^{-4} M (1 M=1 mol dm^{-3}) solution of $KReO_4$ and $(0.5-x)$ ml of equimolar KSCN solution are mixed in a separatory

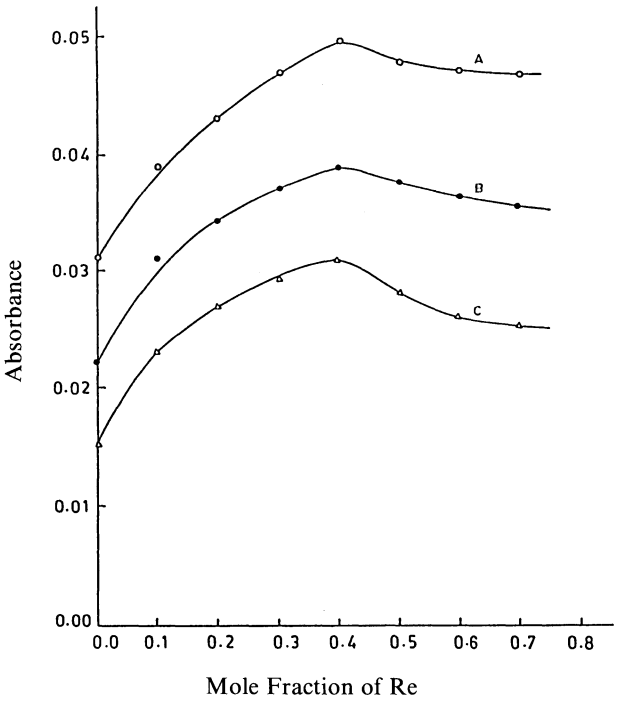

Fig. 3. Continuous variation of rhenium and thiocyanate.
$KReO_4$, 5.38×10^{-4} M; KSCN, 5.38×10^{-4} M.
Solvent: 3-methyl-1-butanol, Curve A: 380 nm, Curve B: 400 nm, Curve C: 410 nm.

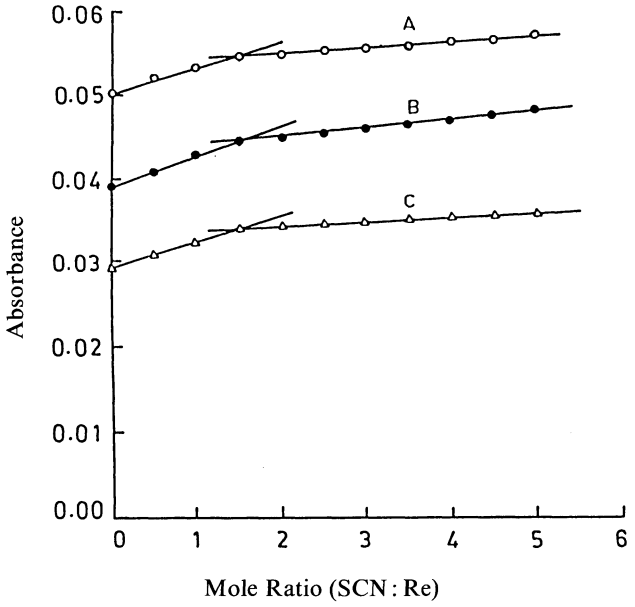

Fig. 4. Mole ratio method.
$KReO_4$, 5.38×10^{-4} M; KSCN, 5.38×10^{-4} M; Re for each operation, 0.2 ml of 5.38×10^{-4} M.
Solvent: 3-methyl-1-butanol, Curve A: 380 nm, Curve B: 410 nm, Curve C: 440 nm.

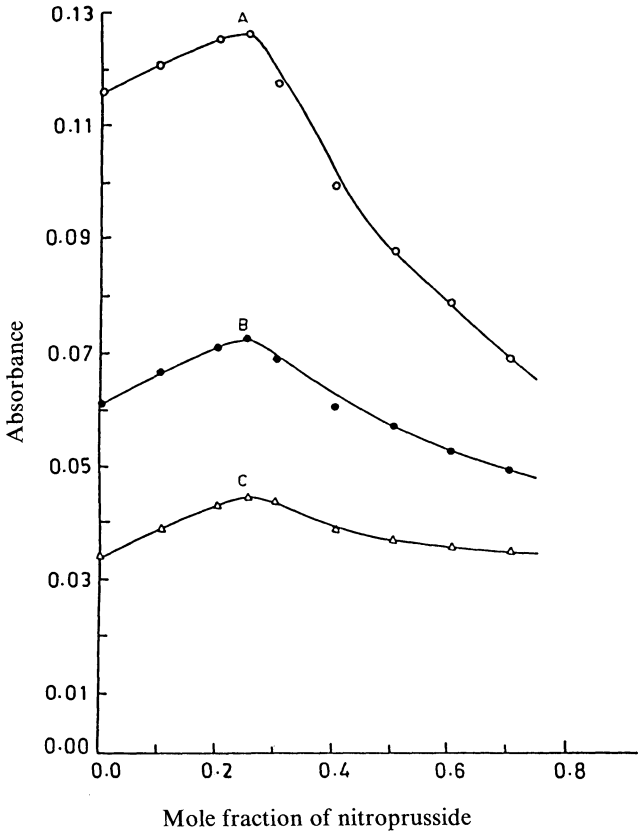

Fig. 5. Continuous variation of sodium nitroprusside and thiocyanate.
Na_2 [$Fe(CN)_5NO$], 5×10^{-2} M; KSCN, 5×10^{-2} M; Re for each operation, 50 μg.
Solvent: 3-methyl-1-butanol, Curve A: 380 nm, Curve B: 410 nm, Curve C: 440 nm.

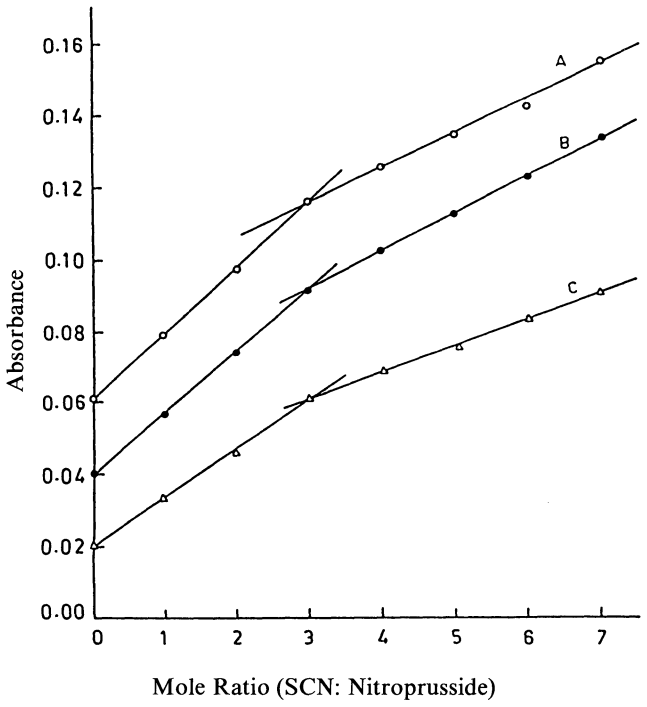

Fig. 6. Mole ratio method.
KSCN, 5×10^{-2} M; $Na_2[Fe(CN)_5NO]$, 5×10^{-2} M; Re for each operation, 50 μg; nitroprusside for each operation, 0.5 ml of 5×10^{-2} M.
Solvent: 3-methyl-1-butanol, Curve A: 380 nm, Curve B: 410 nm, Curve C: 440 nm.

funnel and the extraction with 3-methyl-1-butanol is performed under conditions of the recommended procedure and the absorbance of the complex, after making up the volume, was measured at three different wavelengths, namely, 380, 410, and 440 nm. The plots of mole fractions of Re against their corresponding absorbance values indicated that rhenium and thiocyanate are present in the ratio of 2 : 3 in the complex (Fig. 3). The same result was furthermore obtained by the mole ratio method, wherein, the volume of Re(VII) was kept constant (0.2 ml of 5.38×10^{-4} M) and the content of equimolar solution of thiocyanate was varied from 0 to 1.0 ml and the absorbances were measured following the procedure (Fig. 4).

Thiocyanate : Nitroprusside. In the same way, the ratio of thiocyanate to nitroprusside in the complex was found to be 3 : 1 by Job's Method using equimolar solutions (5.00×10^{-2} M) of both the variables (Fig. 5). This ratio was verified by mole ratio method as well (Fig. 6).

From the above studies it is evident that rhenium, thiocyanate, and nitroprusside in the extracted species are in the ratio of 2 : 3 : 1, respectively.

Applications. Sodium nitroprusside was used for the first time for the determination of trace amounts of rhenium. The method worked out is highly sensitive, selective and separates rhenium quantitatively from a large number of transition elements of interest including Pt-metals. The wide applicability of the procedure was further tested by the analysis of a variety of synthetic

Table 2. Analysis of Different Samples by the Proposed Method

Sr. No.	Composition of sample: Matrix[a)]	Re added (μg)	Re found (μg)
1.	W(1)	15	15.0
2.	V(0.1), W(0.5)	20	20.0
3.	V(0.05), W(1.0)	25	25.0
4.	Cr^{III}(2), Ni(3), Zr(5)	10	10.5
5.	Cr^{VI}(3), Cd(5), Zn(5)	30	30.0
6.	Cu(2), Fe^{II}(2), As(3)	25	25.0
7.	Fe^{III}(2), Cu(2.5), Al(5)	20	20.0
8.	Pt(0.1), Rh(0.2)	35	35.0
9.	Pd(0.1), Rh(0.25), Os(0.25)	40	39.5
10.	Pt(0.075), Ru(0.05), Rh(0.25)	40	40.0
11.	Rh(0.2), Os(0.2)	45	45.0
12.	Synthetic flue dust	15, 35	15.0, 34.0
13.	Reverberatory flue dust, 100 mg	20	20.0
14.	Reverberatory flue dust, 150 mg	50	50.0

a) Figure in brackets indicates the amount of the metal ion in mg.

Table 3. Comparison of the Proposed Method with the Existing Methods for Rhenium Determination

Sr. No.	Aqueous conditions	Extractant λ_{Max}	i) Beer's law range ii) Molar absorptivity iii) Sandell's sensitivity	Interfering ions	Reference
1.	Re(VII), HCl, $SnCl_2 \cdot 2H_2O$, KSCN	Imipramine, 435 nm	i) 0.2—7.4 ppm of Re ii) 2.61×10^4 $dm^3 mol^{-1} cm^{-1}$ iii) 0.007 μg-Re cm^{-2}	Mo(VI), W(VI), Zr(IV), Ru(III), Cr(III,VI)	11
2.	Re(VII), 1.08—1.32 M HCl, $SnCl_2 \cdot 2H_2O$, *N*-(4-methoxyphenyl)-α-thiopicolinamide	$CHCl_3$, 430 nm	i) 1—12 ppm of Re ii) 7.43×10^3 $dm^3 mol^{-1} cm^{-1}$ iii) 0.025 μg-Re cm^{-2}	V(V), Pt(IV), Pd(II), Ir(III)	14
3.	Re(VII), 0.5 M HCl, $SnCl_2 \cdot 2H_2O$, thiobenzhydrazide	CCl_4, 590 nm	i) 1.05—20.90 ppm of Re ii) 8.03×10^3 $dm^3 mol^{-1} cm^{-1}$ iii) 0.023 μg-Re cm^{-2}	Mo(VI), Os(VIII), Ru(III), Cu(II)	15
4.	Re(VII), 1—5 M HCl, $SnCl_2 \cdot 2H_2O$, 4-amino-5-mercapto-3-phenyl-4,1,2-triazole	$CHCl_3$, 380 nm	i) 2—38 ppm of Re ii) 5.21×10^3 $dm^3 mol^{-1} cm^{-1}$ iii) 0.0351 μg-Re cm^{-2}	Cu(II), Pt(IV), Pd(II) Bi(III)	16
5.	100 μg Re(VII), 2 ml of 30% $SnCl_2 \cdot 2H_2O$, 5 ml of 20% KSCN, 2 ml of 2% sodium nitroprusside, in 20 ml volume, 10 min color development time	3-methyl-1-butanol, 410 nm	i) 0.91—2.57 ppm of Re ii) 3.86×10^4 $dm^3 mol^{-1} cm^{-1}$ iii) 0.0048 μg-Re cm^{-2}	29 element of analytical interest including Pt-metals do not interfere	Proposed method

and technical samples and the results obtained were quite in agreement with the amount of rhenium (Table 2). Also, the method compares favorably with the existing methods for the microdetermination of rhenium (Table 3). Besides, it is very simple, less time consuming and makes use of commonly available and cheap reagents.

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