



# Stabilization of rhenium (VI) compounds in solutions and using them in analysis

<sup>1</sup>Borisova L.V., <sup>2</sup> Minin V.V.,

<sup>1</sup> Vernadsky Institute of Geochemistry and Analytical Chemistry  
RAS, Moscow, 119991, Russia

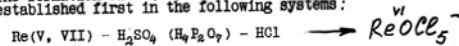
<sup>2</sup> Institute of General and Inorganic Chemistry RAS, Moscow,  
119991, Russia

Borisova19@yandex.ru

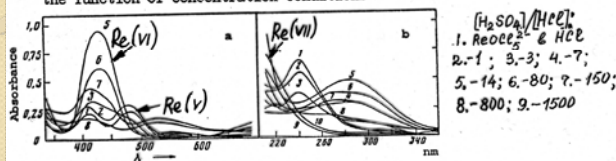
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The forms of Rhenium occurrence and the methods of Re determination in concentrated  $H_2SO_4$

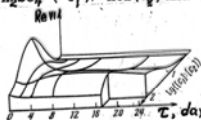
The formation of Re(VI) oxochloride complexes has been established first in the following systems:



The change of UV-VIS spectra of systems were studied as the function of concentration conditions:



The diagram -dependence of content Re(VI) on relative concentrations of  $H_2SO_4$  ( $C_1$ ),  $HCl$  ( $C_2$ ) and time:



The compound of Re(VI), which have one unpaired electron ( $5d^1$ ) possess paramagnetism and characteristic spectra ESR

Parameters of electronic and ESP spectra of Re(VI) oxochloride complexes.

Compound	$\lambda_{max}/nm$ ( $\epsilon_{max}$ )	$g_{II}$	$g_I$	$A_{II}/cm^{-1}$	$A_I/cm^{-1}$
$ReOCl_5^-$ in $H_2SO_4$	275(6000), 420(6000) 520(400)	2.011	1.96	0.939	0.915

It has been established the presence of Re (VII), (VI), (V) oxochloride complexes ( $ReO_2Cl_2^{2-}$ ,  $ReOCl_5^-$  and  $ReOCl_4^-$ ) in equilibrium in a wide range of acids concentration and time.

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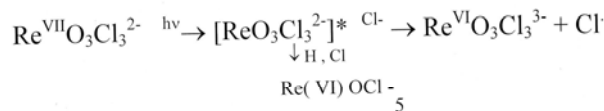


The quantitative and rapid formation of  $\text{ReOCl}_5^-$  complex have been established in systems :

- Re (VII) -  $\text{H}_2\text{SO}_4$  - HCl - Fe (II) ( where Fe(II)-reducer)  $\text{Re} : \text{Fe} = 1 : 1 \frac{M}{M}$
- Re (VII) -  $\text{H}_2\text{SO}_4$  - HCl - photochemical reduction

The photochemical reduction of Re(VII) and reaction between Re(VI) oxochloride complex and aromatical amide were studied by means of flash photolysis.

The scheme for the REDOX reaction of Re(VII) complex may be presented as follows :

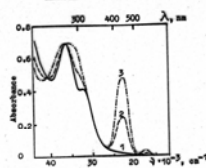


As a result have been established:

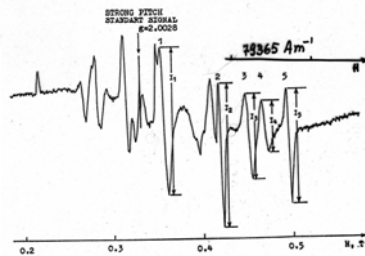
1.  $\text{ReOCl}_5^-$  is stable in  $\text{H}_2\text{SO}_4$  ( 1 - 20 % HCl)
2. Equilibrium Re(VII), (VI) and (V) in  $\text{H}_2\text{SO}_4$  (20-50% HCl)
3.  $\text{ReOCl}_5^-$  is unstable in  $\text{H}_2\text{SO}_4$  (50-100 % HCl)
4.  $\text{ReOCl}_5^-$  is oxidizer of organic substances
5. catalytic activity of Re (VI) in reaction of organic substances oxidation



SPECTROPHOTOMETRIC and ESR methods of Re determination, based on photochemical production  $\text{ReOCl}_5^-$  complex have been proposed



Absorption spectra of rhenium(VII) solution (24.2 µg/ml) in concentrated  $\text{H}_2\text{SO}_4$  in the presence of concentrated HCl (2 vol.%) ( $l = 1 \text{ cm}$ ):  
 1 — before irradiation, 2 and 3 — after irradiation with  $\lambda = 254 \text{ nm}$  during 10 and 30 min respectively



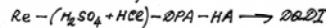
ESR spectrum of rhenium(VII) solution (186 µg/ml) in concentrated  $\text{H}_2\text{SO}_4$  in the presence of concentrated HCl (2 vol.%) after irradiation

It has been shown that a linear dependence of the sum total of the amplitudes of lines 1-5 (Fig. 2):

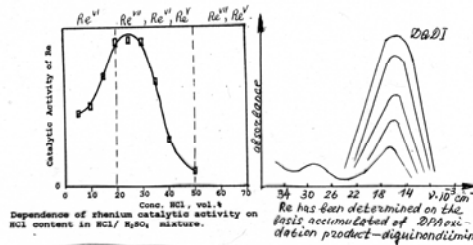
$$I = I_1 + I_2 + I_3 + I_4 + I_5$$

on rhenium content holds over the concentration range of rhenium 0-37 µg/ml.

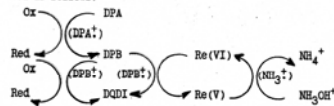
### Kinetic method of Re determination System



The reaction of diphenylamine oxidation by hydroxylamine catalyzed by Re(VI) was found to proceed in mixture of concentrated  $\text{H}_2\text{SO}_4$  and HCl. The maximum of rhenium catalytic activity was found to be in the range from 20 to 30 vol.% of concentrated HCl in  $\text{H}_2\text{SO}_4$ .



The catalytic reaction was found to proceed only in the presence of oxidizing component (Ox) such as  $\text{NO}_3^-$ , inducing the reaction of diphenylamine (DPA) oxidation to diphenylbenzidine (DPB) and diquinondimine (DQDI). A scheme for the catalytic oxidation of diphenylamine can be presented as follows:

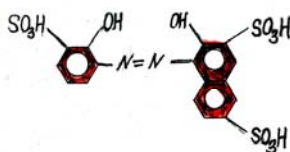
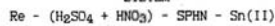


The catalytic reaction of diphenylamine oxidation has been used to develop the kinetic method with spectrophotometric indication of rhenium determination in concentrated  $\text{H}_2\text{SO}_4$ . Optimal reaction conditions: 10 M  $\text{H}_2\text{SO}_4$ , 15 M HCl = 3:1 vol./vol.  $[\text{DPA}] = 10^{-4}$  M,  $[\text{NH}_4\text{OH}] = 2 \cdot 10^{-3}$  M,  $[\text{NO}_3^-] = 2 \cdot 10^{-3}$  M,  $\lambda_{\text{max}} = 615$  nm, 100 min. The limit of detection for Re is  $2 \cdot 10^{-9}$  g/ml. It was established that a larger excess of  $\text{H}_2\text{O}_2$ ,  $\text{U(VI)}$ ,  $\text{Cr(IV)}$ ,  $\text{Os(IV)}$ ,  $\text{Fe(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$  did not interfere. Analysis of rhenium contained in technological solution of sulphuric acid are carried out.

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### RAPID DETERMINATION OF MICROGRAM AMOUNTS OF Re IN SOLUTIONS

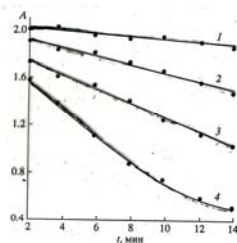
#### SYSTEM



OPTIMUM CONDITIONS  
 80% 5M  $\text{H}_2\text{SO}_4 + 20\%$  10M  $\text{HNO}_3$   
 $C_{\text{spHN}} = 6,25 \cdot 10^{-4}$  M  $\lambda_{\text{max}} = 520$  nm  
 $C_{\text{Sn(II)}} = 8,4 \cdot 10^{-3}$  M  $\tau = 10$  min

ANALYTICAL CHARACTERISTIC  
 SPECTROPHOTOMETRIC METHOD  
 Limited of Detection - 0,2 ng/ml Re  
 Linearity - 0,4-4 ng/ml Re  
 10 min for color development  
 $S_r = 0,2$  for 0,4 ng/ml Re

REACTION SELECTIVITY  
 A 1000-fold excess of each Pt(IV), Os(VIII), Ru(VIII), Rh(III), Pd(II), Ir(III), V(V), Al, W, U(VI), Fe(III).  
 A 100-fold excess of each Mo(VI), Cu(II).  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  do not interfere with the reaction



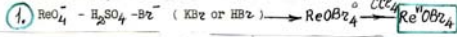
Variations in the absorbance of the Re (80% of 5M  $\text{H}_2\text{SO}_4 + 20\%$  of 10M  $\text{HNO}_3$ ) -  $\text{SnCl}_2$  with time for various concentrations of Re.  $C_{\text{Re}}$  M: (1), (2)  $4,4 \cdot 10^{-9}$ , (3)  $1,1 \cdot 10^{-8}$ , (4)  $1,76 \cdot 10^{-8}$ ;  $C_{\text{Re}} = 6,25 \cdot 10^{-9}$  M;  $C_{\text{SnCl}_2} = 8,4 \cdot 10^{-3}$  M

ANALYTICAL APPLICATIONS  
 Direct determination of Re in the fumarole rock samples, ground water, plants on slopes of Kudravy of volcano, technological solutions, industrial waters, oils

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THE METHODS BASED ON THE PROPERTIES OF Re(VI)  
OXOBROMIDE COMPLEX

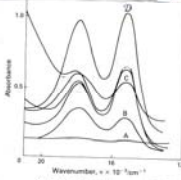
The quantitative and rapid formation of the stable  $\text{ReOBr}_4$  complex (and quantitative extraction) have been established in system ;



OPTIMAL CONDITIONS:

16 M  $\text{H}_2\text{SO}_4$ , Re : Br<sup>-</sup> = 1 : 20 ± 50  
T = 20 min

The range of determination  
(0,2 - 7,0) × 10<sup>-9</sup> M (UV-VIS)  
(1,0 - 6,0) × 10<sup>-3</sup> M (ESR)



Variation of absorption spectra of ReOBr<sub>4</sub> solution with the concentration. [Re] = 2 × 10<sup>-4</sup> M. [Br<sup>-</sup>] = A, 4 × 10<sup>-4</sup> M; B, 1 × 10<sup>-3</sup> M; C, 2 × 10<sup>-3</sup> M; D, 4 × 10<sup>-3</sup> M.

Parameters of electronic and ESR spectra of Re(VI)

Compound	$\lambda_{\text{max}}$ /nm ( $\epsilon_{\text{max}}$ )	$g_{11}$	$g_{12}$	$A_{11}/\text{cm}^{-1}$	$A_{12}/\text{cm}^{-1}$
ReO Br <sub>4</sub> in H <sub>2</sub> SO <sub>4</sub>	560(2290), 650(2050)	2.173	1.770	1.019	0.826
ReO Br <sub>4</sub> in toluene	560(2560), 650(4270)	—	—	—	—
Re (TDP) <sub>3</sub>	695(16000)	—	—	—	—



The formation of ReOBr<sub>4</sub> in sulphuric acid from the ReO<sub>4</sub><sup>-</sup> ion and KBr was used for the development of a selective spectrophotometric method for the determination of rhenium and the ability of ReOBr<sub>4</sub> to be extracted into organic solvents was used for rhenium determination by ESR.

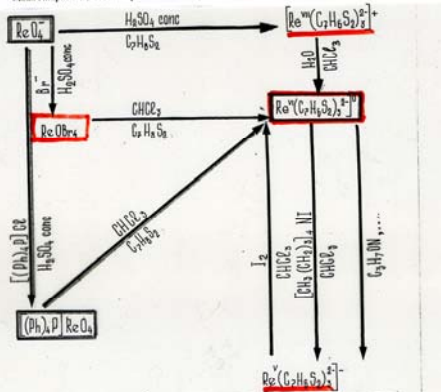
ESR spectrum of ReOBr<sub>4</sub> solution in toluene. [Re] = 2 × 10<sup>-4</sup> M; [Br<sup>-</sup>] = 1 × 10<sup>-3</sup> M; range 300-600 Å m<sup>-1</sup>,  $\epsilon_{\text{max}}$  242750 Å m<sup>-1</sup>, and temperature -120°C. A. Perpendicular orientation and B. parallel orientation. Strong Pith.  $g = 2.0023$ .

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SCHEME OF INTERACTION BETWEEN Re AND L

System  $\text{ReOBr}_4 / (\text{Ph}_3\text{P}(\text{ReO}_4)) - \text{H}_2\text{R} - \text{CHCl}_3$

(H<sub>2</sub>R - Toluene-3,4-dithiol, Quinoxaline-2,3-dithiol, MonoThiophenols, dithionaphthol and others.)



Organic ligands:  $\text{OH}$ ,  $\text{SH}$ ,  $\text{S}_2\text{H}$ ,  $\text{CH}_3\text{SH}$ , etc.

On the basis  $\text{ReOBr}_4 - \text{C}_7\text{H}_6\text{S}_2 - \text{CHCl}_3$  system the high selectivity and sensitivity spectrophotometric ( $\lambda = 695 \text{ nm}$ ,  $\epsilon = 2 \cdot 10^4 \text{ cm}^2 \text{ mol}^{-1}$ ) and ESR ( $g_1 = 2,044$ ,  $g_2 = 2,016$ ,  $g_3 = 1,999$ ) methods for Re determination have been worked out.

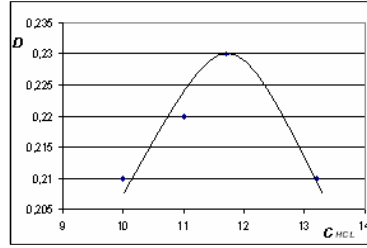
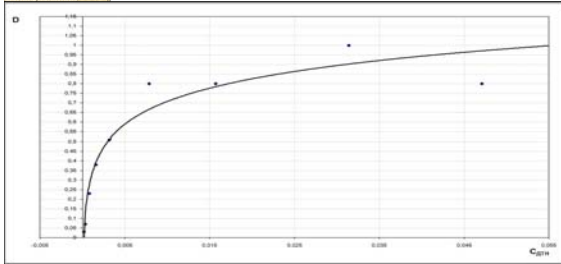
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OPTIMAL CONDITIONS

REAGENT	ACID, N	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}} \cdot 10^4$	Parameters of ESR
$\text{H}_2\text{R}$				
OMTPH	8-9 HCl, 13-14 H <sub>2</sub> SO <sub>4</sub>	500	3.45	Spectra ESR +
OBTPH	10-11 HCl, 12-13 H <sub>2</sub> SO <sub>4</sub>	503	3.08	— — — — +
OATPH	8.5-9 HCl, 14.5 H <sub>2</sub> SO <sub>4</sub>	509	2.0	— — — — +
OOTPH	11.0 HCl, 15.5 H <sub>2</sub> SO <sub>4</sub>	505	1.9	— — — — +
ODTHN, dithionaphthol	11.5 HCl, 16.5 H <sub>2</sub> SO <sub>4</sub>	505	1.5	$g_{11} = 2.059$ , $g_1 = 1.979$ , $A_{11} = 446 \text{ G}$ , $A_1 = 34.9 \text{ G}$

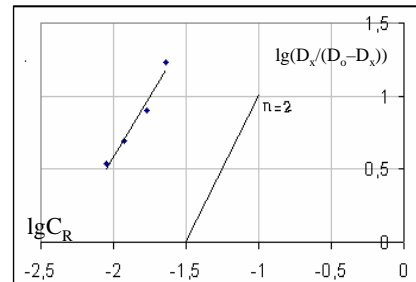
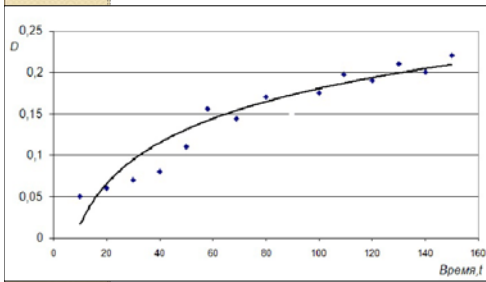
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Optimal conditions of formation of complex rhenium- oxidithionaphtol (DTN)



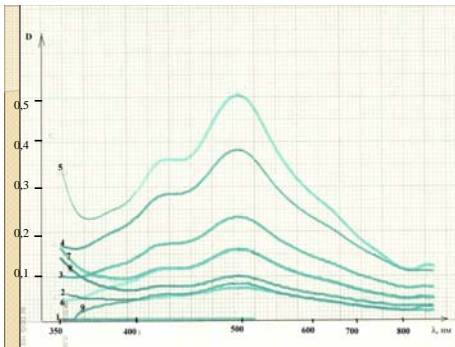
$D = f(DTN)$  ;  $C_{Re} = 29.8 \mu\text{g/ml}$ ,  $C_{HCl} = 11.4 \text{ M}$ ,  $\tau = 100 \text{ min}$

$D = f[HCl]$ ,  $\lambda_{\text{max}} = 503 \text{ nm}$ ,  $C_{Re} = 29.8 \mu\text{g/ml}$ ,  $C_R = 0.03 \text{ M}$

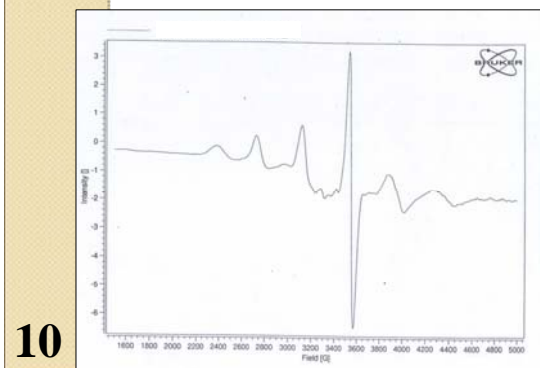


**9**  $D = f(\tau)$ ,  $\lambda_{\text{max}} = 503 \text{ nm}$ ,  $C_{Re} = 29.8 \mu\text{g/ml}$ ,  $C_R = 0.03 \text{ M}$ ,  $l = 0.2 \text{ cm}$

Re : DTN = 1 : 2



**Absorbance spectra of complex Rhenium with oxidithionaphtol**  
 $\lambda = 503 \text{ nm}$ ,  $\epsilon = 1.5 \cdot 10^4$

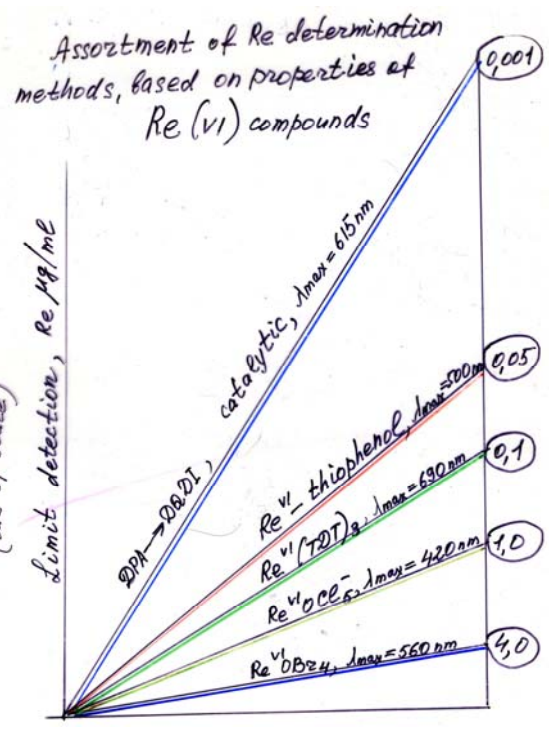


**ESR spectrum of rhenium (VI) complex with oxidithionaphtol –  $[\text{ReO}(\text{C}_{10}\text{H}_5\text{OHS}_2)_2]$**

**Parameters of ESR spectrum :**

$g_{\parallel} = 2.059$ ,  $g_{\perp} = 1.979$ ,  $A_{\parallel} = 446 \text{ G}$ ,  $A_{\perp} = 34.9 \text{ G}$

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Спасибо за внимание!