

DETERMINATION OF MICROQUANTITIES OF RHENIUM BY AN OSCILLOPOLAROGRAPHIC METHOD WITH ACCUMULATION ON A STANDARD MERCURY MICROELECTRODE

A. M. Demkin and S. I. Sinyakova

UDC 546.719:543.253.063

We showed in a previous article [1] that rhenium can be concentrated on a standard mercury microelectrode at constant potential. This provides a means of increasing the sensitivity of determining Re by one to two orders of magnitude compared with its determination using a dropping mercury electrode [2-5].

This article deals with a method of determining up to $10^{-6}\%$ Re in natural and production samples.

The polarographic curves were registered on a type OP-1-61 oscillographic polarograph. Cells with stationary electrodes in the form of a pendant [6] and a stationary [7] drop of mercury were used as the "pickup." All the potentials were measured relative to a saturated calomel electrode. The standard solutions of rhenium were prepared from the salt NH_4ReO_4 which was purified by recrystallization from water. Chemically pure orthophosphoric acid was used as the electrolyte. Surface-active substances have a considerable effect on the value of the current required for dissolving rhenium. Accordingly, the water used was demineralized with ion exchange resins, and further distilled once with KMnO_4 , in order to remove trace of organic substances, and again without KMnO_4 . The dish was cleaned by heating with sulfuric acid (sp. gr. 1.84). The oxygen was removed by sweeping the solution with a stream of pure nitrogen [8].

The rhenium was concentrated on the electrode at an accumulation potential of -0.90 to -1.0 V, using a 4-5 M solution of H_3PO_4 . Under these conditions Re (VII) is reduced to the quadrivalent state. The film of ReO_2 formed on the surface of the electrode [9] was dissolved by the application of a linear sweep voltage varying from -0.90 to -1.0 V to less negative values.

The curve for the peak current (i_p) as a function of the accumulation time (t_{acc}) exhibits a maximum, which indicates the retarding effect of a film. For $t_{\text{acc}} = 5$ min the value of i_p at $\phi_p = -0.70$ V and the concentration of rhenium (C_{Re}) are directly proportional over the range $1 \cdot 10^{-8}$ - $2 \cdot 10^{-7}$ M (Fig. 1). On reducing t_{acc} to 1-2 min the linear part of the curve for i_p against C_{Re} is somewhat displaced in the direction of larger values of C_{Re} .

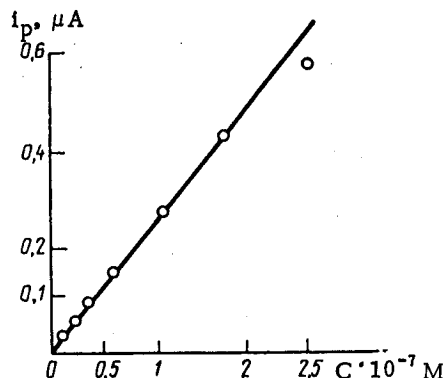


Fig. 1. The current i_p for electrolytic solution as a function of the concentration of the solution.

The sensitivity of the method is $5 \cdot 10^{-7}\%$ Re for 1 g of sample and a final volume for the solution being polarographed of 5 ml. Lead and copper do not affect the peak for rhenium for the weight ratios Cu, Pb: Re $\leq 25,000:1$. Also, the alkali and alkaline earth metals do not affect the determination, nor Al, Fe, Ni, Co, or Mo, Cr (VI), Se (VI), W (VI) at the ratios: Mo:Re $\leq 20,000:1$, Cr:Re $\leq 500:1$, Se:Re $\leq 400:1$, and W:Re $\leq 100:1$.

Te in three-fold excess, Mn(VII) in twenty-fold excess, and also NO_3^- and ClO_4^- ions do interfere.

The following method of determining rhenium is recommended. Place 5-10 ml of the solution to be analyzed in the electrolytic cell. Sweep the solution with nitrogen for 10 min, establish conditions of anodic polarization on the polarograph and the potential of the standard mercury microelectrode, namely -0.95 V. Accumulation is car-

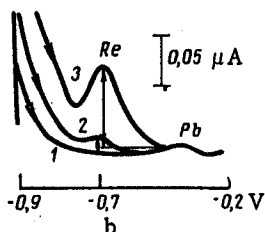
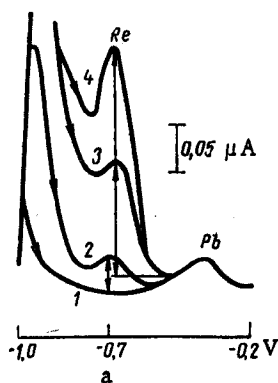


Fig. 2. Differential anodic oscillograms for the solutions: a) Mo sample containing $4 \cdot 10^{-4}\%$ Re: 1) blank run; 2) test solution; 3) test solution with the addition of $0.17 \mu\text{g}$ Re; 4) test solution with the addition of $0.34 \mu\text{g}$ Re; b) sample of meteorite: 1) blank run; 2) test solution; 3) test solution with the addition of $0.05 \mu\text{g}$ Re.

sintering with CaO [4]. A small quantity ($0.1\text{--}0.2\text{ g}$) is placed in a nickel crucible and is carefully mixed with $0.3\text{--}0.6\text{ g}$ CaO and about 0.1 g Na_2O_2 , and the mixture is covered with a layer of calcium oxide and moistened with a few drops of water. The crucible is then placed in a cold muffle furnace, and the temperature of the furnace is gradually raised to about 600°C , and the sample is sintered for $1.5\text{--}2\text{ h}$. After cooling the sintered mass is finely ground and transferred to a 100 ml vessel, 50 ml of water is added, and the mixture is boiled for 30 min . This leaches out the rhenium and decomposes the peroxides.

The solution is then filtered, the residue is washed with hot water, once by decanting and once on the filter. The filtrate is transferred to a 50 ml volumetric flask, and H_3PO_4 is added in such concentration as to ensure that the final solution is 4 M on being made up to the graduation mark. A 10 ml aliquot of this solution is placed in the cell and accumulation is carried out for 2 min , after which the electrolytic solution curve is plotted at a potential change of 0.25 V/sec .

The curves obtained (Fig. 2a) show that in the solution studied the height of the rhenium peak is directly proportional to the quantity of standard rhenium solution added.

The method used for analyzing the MoO_3 was similar to the first method, but to improve the accuracy of the measurements the final volume of the solution should be reduced to 15 ml by first evaporating the filtrate to about 10 ml .

In analyzing the stony meteorite and H_2WO_4 the rhenium was isolated after fusion or sintering by extraction from 5 M NaOH solution [10] using methyl ethyl ketone. In analyzing the stony meteorites a weighed quantity of $0.3\text{--}0.6\text{ g}$ was fused in a nickel crucible with 4 g Na_2O_2 at 600°C . The cooled melt was flushed with water and transferred to a vessel. The solution was boiled for 5 min to remove peroxides and then filtered through a dense filter. The filtrate was then evaporated down to 15 ml , poured into a separating funnel, to the funnel was then added 3 g NaOH, followed by 15 ml of methyl ethyl ketone, and the rhenium was extracted into the organic phase over a period of 1 min . The organic phase was then separated off and was washed twice with 15 ml portions of 5 M NaOH. A further extraction was then carried out by adding 7 ml water and 15 ml chloroform.

TABLE 1. Determination of Rhenium in Samples Containing Added Rhenium

Compound analyzed	Content in sample	Amount added	Total content	Found	% Rel. error
Molybdenite	0.40	0.50	0.90	0.92	+3
	0.42	0.50	0.92	0.83	-10
MoO_3	0.08	0.32	0.40	0.37	-10
	0.06	0.32	0.38	0.37	-4
H_2WO_4	0.02	0.05	0.07	0.06	-15
	0.02	0.05	0.07	0.06	-15

ried out over 2 or 5 min , depending on the concentration of rhenium, the solution being stirred with a stream of nitrogen. Every 5 sec a single sweep is made of sawtooth voltage amplitude $0.5\text{--}1.0\text{ V}$, and the differential curve for the electrolytic solution of rhenium is recorded.

In differentiating the i, φ curves, peaks are obtained which enable the current to be measured accurately and the resolving power of the method to be increased. The concentration of rhenium is measured by the addition method, and should not exceed about $0.1\text{ }\mu\text{g/ml}$ in the solution being polarographed. More concentrated solutions are diluted with the base electrolyte. The method is used for determining rhenium in natural substances, such as molybdenites and stony meteorites, and in production samples, such as pure MoO_3 and oscillographically pure H_2WO_4 .

In analyzing molybdenites containing $10^{-4}\text{--}10^{-5}\%$ Re molybdenum must be removed. This is done by precipitating it in the form of the insoluble compound CaMoO_4 by

TABLE 2. Results Obtained in the Analysis of Samples and Comparison with Those Obtained by Other Methods

Sample	No. of determination, n	$\bar{X}$, %	S, %	$\pm \Delta X$, % at $\alpha = 0.95$	Re content, %	Re found, %, by other methods
Molybdenites	6	$4.3 \cdot 10^{-4}$	$0.62 \cdot 10^{-4}$	$0.65 \cdot 10^{-4}$	$(4.3 \pm 0.65) \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$ (colorimetrically)
Leucocratic granite with ingrain molybdenite	2	—	—	—	$7.0 \cdot 10^{-5}$	About $1 \cdot 10^{-5}$ (colorimetrically)
MoO ₃ , pure	6	$5.1 \cdot 10^{-5}$	$0.73 \cdot 10^{-5}$	$0.77 \cdot 10^{-5}$	$(5.1 \pm 0.77) \cdot 10^{-5}$	—
Stony meteorite	4	$4.0 \cdot 10^{-6}$	$0.7 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$(4.0 \pm 1.1) \cdot 10^{-6}$	$4 \cdot 10^{-6}$ (neutron activation method)
H ₂ WO ₄ , oscillographically pure	6	$6.4 \cdot 10^{-6}$	$0.8 \cdot 10^{-6}$	$0.7 \cdot 10^{-6}$	$(6.4 \pm 0.7) \cdot 10^{-6}$	—

After one hour the aqueous phase was removed and evaporated to dryness in a quartz cup, using a hot plate. The cup was then covered, and the residue was calcined on the hot plate at about 300-400°C for 5 min, to remove organic matter. To the residue was added 3.7 ml water and 1.3 ml H₃PO₄, to dissolve the residue. The solution obtained was placed in an electrolytic cell and polarographed at a t_{acc} of 4 min (Fig. 2b).

In analyzing the H₂WO₄, a weighed quantity of 0.5-0.6 g was sintered with three times its weight of CaO and 0.3-0.4 g Na₂O₂ for 1.5 h at 600°C. Raising the temperature to 700°C resulted in a significant loss of rhenium. The sintered mass was transferred to a vessel, boiled for 20 min, and the solution was filtered. Extraction was then carried out as in the analysis of the meteorite. Two washings of the ketone layer with 5 M NaOH was sufficient to remove all traces of tungsten, which passes partially into solution on leaching out the sintered mass, and interferes in the determination of Re.

The possibility of Re loss during extraction and calcining was assessed by means of artificially prepared solutions. It was established that the losses never exceeded 10%.

The Re losses during sintering in the muffle furnace and subsequent leaching were assessed on samples of molybenite, MoO₃, and H₂WO₄. This was done by adding known quantities of rhenium to the test samples before calcining them with CaO. The results are presented in Table 1. The deviations of the individual determinations from the true overall Re content did not exceed 15%.

In Table 2 the rhenium assay results obtained with different samples are compared. These data confirm the removal of interfering elements during the process of preparing the samples for analysis.

LITERATURE CITED

1. A. M. Demkin and S. I. Sinyakova, Izvestiya AN SSSR, Ser. Khimich., 1620 (1968); Determination of Microimpurities [in Russian], MDNTP, 2 (1968), p. 31.
2. K. S. Pakhomova and L. P. Volkova, Zavod. Lab., 25, 1291 (1959).
3. K. Byorbiro, Acta Chim. Acad. Scient. Hung., 27, 120 (1961).
4. T. A. Kryukova, S. I. Sinyakova, and T. V. Aref'eva, Polarographic Analysis [in Russian], Goskhimizdat (1959), p. 351.
5. V. V. Zhirona and E. V. Kravchenko, ZhAKh, 23, 1179 (1968).
6. A. Ya. Gokhshtein and Ya. P. Gokhshtein, Zh. Fiz. Khim., 36, 651 (1962).
7. S. I. Sinyakova and I. V. Markova, Zavod. Lab., 27, 521 (1961).
8. G. V. Prokhorova, E. N. Vinogradova, and N. V. Lukashenkova, Methods of Analysis of Chemical Preparations and Reagents [in Russian], IREA, 5-6, 127 (1963).
9. K. B. Lebedev, Rhenium [in Russian], Metallurgizdat (1963), p. 34.
10. Yu. B. Gerlit, Proceedings of the First International Conference on the World Utilization of Atomic Energy [in Russian] (1958), p. 183.