

COULOMETRIC TITRATION OF MOLYBDENUM (VI) BY ELECTROGENERATED TIN (II)

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The electrogeneration of Sn II ions with a current efficiency approaching 100% in a strongly acidic medium is only possible in the presence of an electrode with a high hydrogen overvoltage.

The possibility of attaining a sufficiently high current efficiency in producing tin II at a tungsten electrode has been shown in [1]. However, the results were negative in attempts to use this method to determine molybdenum. Descriptions have also been given [2, 3] of using platinum generating electrodes, the hydrogen overvoltage of which appreciably increases due to precipitation of metallic selenium and tellurium on the surface during electrolysis. Hydrogen discharge also takes place in a more negative potential region on a graphite electrode impregnated with an inert filler [4, 5].

This article deals with the possible electrogeneration of Sn (II) ions on graphite impregnated during in vacuo heating with paraffin and epoxy resin, and brings out the conditions for the potentiometric and biamperometric indication of the end point in the coulometric titration of molybdenum (VI) by these ions. Methods have been suggested [1, 6, 7] for preparing the solutions, impregnating the electrodes, and making the electrometric measurements, and descriptions have been given of the apparatus used.

Tests were carried out at room temperature in a nitrogen atmosphere. The conditions for maximum current efficiency in generating Sn (II) ions were established from the $i = f(E)$ curves of a 6M solution of HCl, both in the absence and in the presence of different amounts of SnCl_4 (1×10^{-1} and 4×10^{-1}), for the electrodes being studied.

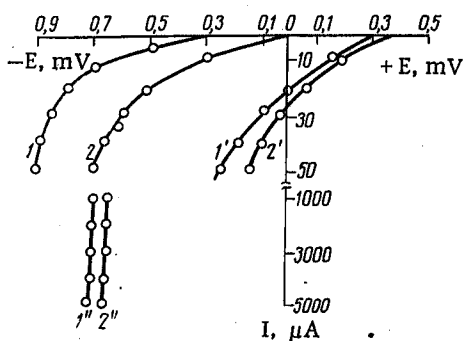


Fig. 1. I, E curves for a graphite electrode impregnated during heating by 1) paraffin or 2) epoxy resin under vacuum: 1, 2) base electrolyte 6M HCl; 1', 2') in the presence of 0.2 mequ/30 ml of Mo (VI); 1'', 2'') in the presence of 3.0 mequ/30 ml Sn (IV).

TABLE 1. Titration Results for Mo (VI) ($n = 3$, $\alpha = 0.95$, $V = 30-40$ ml) (PS = pure for spectroscopy)

Substance analyzed	Taken	Found
Solution containing	0,22 mg	$0,22 \pm 0,01$ mg
Mo(VI):Cr(III):	0,45 »	$0,45 \pm 0,02$ »
:Ni(II)=1:10:10	0,91 »	$0,90 \pm 0,01$ »
Mo(VI):W(VI)=	0,45 »	$0,46 \pm 0,03$ »
=1:0,5	0,45 »	$0,46 \pm 0,01$ »
PS31-B (Mn, Cr, Ti, Ni, Cu)	0,27%	$0,26 \pm 0,02$ %
PS197 (Mn, Cr, Ni, 15,72% W)	0,97%	$0,97 \pm 0,01$ %
PS164 (Mn, Cr, Ni, Ti)	3,21%	$3,19 \pm 0,04$ %
PS159 (Mn, Cr, Ni, Cu)	5,28%	$5,29 \pm 0,01$ %

It was found that in a ≥ 0.1 M solution of SnCl_4 with 6M HCl as base electrolyte and $I \geq 3$ mA/cm², the current efficiency in generating tin (II) reaches 99.7, and 99.3% on graphite electrodes impregnated with paraffin and epoxy resin (see Fig. 1). However, both types of graphite electrodes may be used as generators, regardless of the nature of the impregnator. The activity of the Mo (VI) ions under the electrolysis conditions used on these electrodes gives 100% titration efficiency. In order to bring out the conditions required for the biamperometric indication of the coulometric titration endpoint, Mo (VI) was titrated with a standard solution of SnCl_2 using Pt/Pt electrodes and Pt/W electrodes at different polarizations. When the applied voltage was ≥ 200 mV a sharper end point was obtained using the bimetallic pair (-)W/Pt(+), the curve being V-shaped. Table 1 shows that coulometric titration with the stated pair of electrodes gives excellent accuracy, reproducibility, and sensitivity (2×10^{-5} M). Table 1 also shows that the elements accompanying molybdenum at certain weight ratios do not interfere with its determination.

Potentiometric indication of the coulometric titration endpoint is of little use in this case since the potential jumps are too small and are not always clearly defined.

The coulometric method developed for determining Mo (VI) by electrogenerated Sn (II) ions has been approved for the analysis of molybdenum in some standard test pieces of steel.

A weighed sample of steel containing 15-20 mg of Mo was placed in a 200 ml vessel and 5 ml HCl (1.19) and 5-10 drops of 30% H_2O_2 were added. The vessel was covered with a watch glass and heated on a sand bath until the sample was completely decomposed, and then evaporated to dryness. The deposit was wetted with concentrated HCl and again evaporated to a damp state in order to complete the decomposition of the peroxide. Distilled water (20-30 ml) was then added, and the mixture was heated to dissolve the salts. The solution was transferred to a 100 ml measuring flask after cooling. If the solution contained an insoluble compound ($\text{WO}_3 \cdot x\text{H}_2\text{O}$) a certain portion was filtered through a dry filter into a beaker and the first portion of filtrate was rejected. A 5 ml portion of the filtrate was introduced into a beaker containing 5 ml of hot 20% NaOH, then heated on a water bath and filtered through a dry filter, the deposit being washed several times with small amounts of hot distilled water. The filtrate and washing were collected into an electrolytic cell, neutralized with concentrated hydrochloric acid using indicator paper, and 2 ml of 2 M SnCl_4 dissolved in HCl (1:1) was added. The total volume should be 30-40 ml. The Mo (VI) was titrated coulometrically at $I \geq 3$ mA/cm², using as a generator a graphite electrode which has been saturated with paraffin while hot. The coulometric titration endpoint was obtained biamperometrically, using (-)W/Pt(+) indicator electrodes and $\Delta E \geq 200$ mV

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