

COULOMETRIC TITRATION OF MOLYBDENUM (VI) WITH ELECTRICALLY GENERATED IRON (II)

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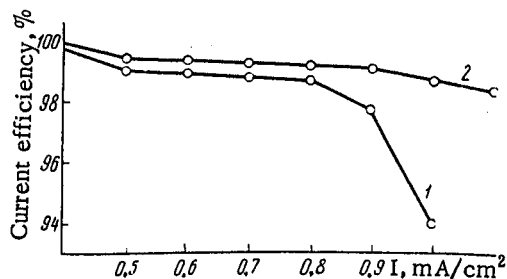
A coulometric method has been developed for the titration of Mo(VI) with electrically generated Fe(II), with amperometric indication of the end point, using one ($E = 0.8$ V) and two polarized ($\Delta E = 50$ -100 mV) electrodes. The sensitivity was $7 \cdot 10^{-5}$ M. The method was suitable for analyzing samples of steels and alloys.

Only one paper has been found in the literature on the coulometric titration of molybdenum with electrically generated titanium (III) [1]. The high reducing power of Fe(II) in ≥ 11 M H_3PO_4 has been used for the titrimetric determination of several elements, including Mo(VI) [2, 3]. It was therefore of interest to try this reducing agent for the coulometric determination of Mo(VI). The auxiliary reagent used consisted of the Fe(II) ions, obtained by dissolution of the molybdenum-containing steels and iron-based alloys to be analyzed.

It has been stated [4] that 100% efficiency for the generation of Fe(II) in a sulfuric/phosphoric acid medium can be achieved under the following conditions: $C_{H_2PO_4} = 4$ M, $C_{H_2SO_4} = 2$ M, $C_{Fe(III)} \geq 0.1$ M, current density up to 7.5 mA/cm². However, under these conditions the reaction between Fe(II) and Mo(VI) did not proceed quantitatively. We therefore had the problem of establishing the optimum concentrations of the above components for the development of a coulometric variant to the determination of Mo(VI), with electrically generated Fe(II) ions, and of finding an appropriate method for establishing the end point.

The following starting solutions were prepared: 0.05 M ammonium paramolybdate (chemically pure) standardized gravimetrically by the $PbMoO_4$ method; 0.2279 N ferrous ammonium sulfate (chemically pure) standardized by potentiometric and amperometric titration with $K_2Cr_2O_7$; N ferric alum solution (chemically pure), made up from $(NH_4)_2Fe_2(SO_4)_4 \cdot 24H_2O$.

The experiments were carried out at room temperature, under an atmosphere of nitrogen which had been freed from traces of oxygen. The working electrode (the cathode) was of platinum or tungsten, and the auxiliary electrode (the anode) was a 1×1 cm platinum plate. Before each experiment the platinum electrodes were treated with hot 1:1 hydrochloric acid, and then with distilled water. The surface of the tungsten electrode was cleaned with emery paper. The coulometric titration was carried out with the apparatus described previously [5].



Curves relating current efficiency for generation of Fe(II) and current density for 1) platinum and 2) tungsten electrodes.

It was found that the efficiency of Fe(II) generation, from a solution of Fe(III) in a sulfuric/phosphoric acid medium (11 M $H_3PO_4 + 2$ M H_2SO_4), was somewhat less than 100%. The efficiency fell with increasing current density, and more so when a platinum working electrode was used (see figure). However, owing to the electrical activity of Mo(VI) [6], 100% titration efficiency was achieved with current densities up to 1 mA/cm².

Potentiometric titration with a standard solution of ferrous ammonium sulfate, with 11 M H_3PO_4 as electrolyte and in an 11 M $H_3PO_4 + 2$ M H_2SO_4 medium showed a marked potential step at the end point. However, if the test solution originally contained more than 0.14 M Fe(III), the step on the titration curve became less distinct, because of a shift to the left in the equilibrium: $Fe(II) + Mo(VI) \rightleftharpoons Fe(III) + Mo(V)$.

TABLE 1. Results for the Determination of Mo(VI) (V = 30 ml; n = 3; $\alpha = 0.95$)

Ratio w/w	Mo taken, mg	Coulometric titration	
		Pt cathode	W cathode
Mo (VI):W (VI)	0.95	0.95 ± 0.08	0.95 ± 0.05
	0.48	0.47 ± 0.14	0.47 ± 0.12
	0.24	0.23 ± 0.04	0.23 ± 0.04
	1:2	0.47	0.47
	1:20	0.47	0.47
	1:30	0.23	0.23
		Amperometric titration	
		Pt microelectrode	Two polarized electrodes
	9.66	9.64 ± 0.11	9.60 ± 0.32 Pt/Pt
	9.50	—	9.70 ± 0.14 W/W
Mo (VI):Fe (III)	9.50	—	9.66 ± 0.31 Pt(+)/W(-)
	9.50	—	9.59 ± 0.14 W(+)/Pt(-)
	4.83	4.80 ± 0.15	—
	2.41	2.42 ± 0.18	—
	4.83	4.90	
	1:35	4.86	
	1:70	2.43	
	1:90	2.26	
	1:120	Not determined	
Mo (VI):Cr (III)	2.41	2.39	
	1:10	1.23	
	1:80	1.23	
	1:130	1.23	
Mo (VI):Ni (II)	2.41	2.40	
	1:10	2.43	
	1:30	1.23	
	1:120		

TABLE 2. Determination of Mo(VI) in Alloys (V = 30 ml; n = 3; $\alpha = 0.95$)

Alloy	Coulometric titration, Pt(+)/W(-)	Amperometric titration	
		Pt microelectrode	Pt(+)/W(-)
237, 0.77% Mo	0.77 ± 0.04	0.75 ± 0.10	0.77 ± 0.08
164-v 3.50% Mo	3.53 ± 0.14	3.48 ± 0.10	3.56 ± 0.02
159-a, 6.33% Mo	6.32 ± 0.29	6.36 ± 0.20	6.32 ± 0.08
NIMO-28, 27.86% Mo	27.85 ± 0.20	27.80 ± 0.17	27.86 ± 0.05

In subsequent work on the coulometric titration we used amperometry with two indicator electrodes to establish the end point.

It was found that it was best to apply a potential difference $\Delta E = 50-100$ mV between the electrodes, in the amperometric titration of Mo(VI) with standard Fe(II) solution, in a sulfuric/phosphoric acid medium, with two polarized electrodes. Regardless of the nature of the pair of electrodes, Pt/Pt, W/W, Pt(+)/W(-), or W(+)/Pt(-), the titration curve was always J-shaped. Thus the limiting electrode process at the equivalence point was oxidation of excess Fe(II).

For coulometric titration in the presence of Fe(III), it was found to be most effective to use Pt(+)/W(-) as the pair of polarized electrodes. The curve was J-shaped, but, above a certain concentration of Fe(III), the indicator current began to increase before the equivalence point, so that the slope of the left hand limb of the curve increased and, when $C_{Fe(III)} = 0.14$ M, the bend in the curve at the equivalence point disappeared. This happened at quite a high concentration of Fe(III) such that, with the applied potential used, it was possible for Fe(III) to be reduced and Mo(V) to be oxidized anodically [7] before the equivalence point. The phenomenon could also be explained by participation in the anodic process of the increasing proportion of Fe(II) which did not read with Mo(VI) owing to the shift in chemical equilibrium so that it was impossible to detect the end point of the titration.

Table 1 shows examples of the determination of Mo(VI) in pure solutions and in artificial mixtures. The results were obtained by amperometric titration with a platinum microelectrode at $E = 0.8$ V [8]. The presence of certain other elements in the steels and alloys, even in considerable excess, did not affect the precision of Mo(VI) determination. Particular interest attaches to the coulometric titration of Mo(VI) with adequate precision, in the presence of 30 times as much W(VI).

The above methods were tested for approval in the analysis of a number of steels and alloys at the experimental plant of the Central Scientific-Research Institute for Ferrous Metallurgy (Table 2). A comparison of the results showed that the coulometric method for titration of Mo(VI) was better than the amperometric method with one polarized electrode, and had a reproducibility and sensitivity of $4 \cdot 10^{-4}$ and $7 \cdot 10^{-5}$ M.

CONCLUSIONS

1. Optimum conditions have been determined for the generation of Fe(II) at Pt or W electrodes, for the coulometric titration of Mo(VI): $C_{\text{Fe(III)}} = 0.1$ M, $I = 1$ mA/cm², electrolyte 11 M H₂PO₄/2 M H₂SO₄.
2. Amperometric titration with two indicator electrodes, used in the coulometric titration as a means of indicating the end point, can be used as an independent method for determining Mo(VI) in a strong phosphoric acid medium, with a standard solution of ferrous ammonium sulfate.

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