

COULOMETRIC TITRATION OF CERIUM, MANGANESE, CHROMIUM, AND TIN BY ELECTROCHEMICALLY GENERATED VANADYL

V. N. Basov, P. K. Agasyan, and A. I. Kostromin

UDC 543.253

The standard potentials of the $V(V)/V(IV)$ and $V(IV)/V(III)$ redox systems are equal to 1.0 and 0.36 V respectively [1]. Consequently vanadium (IV) can exhibit oxidizing and reducing properties depending on the conditions. We have used vanadyl ions, generated externally by anodic dissolution of metallic vanadium, for the quantitative determination of bichromate, permanganate, cerium (IV), and tin (II).

The conditions for the electrochemical generation of vanadium (IV) with 100% current efficiency, obtained by anodic dissolution of a vanadium electrode, have been described before [2]. An electrolyzer with a capacity of ~ 0.3 ml (Fig. 1), of our own design, was used for the external generation of the titrant. The cathode compartment of the cell was filled with 5% potassium sulfate solution. The indifferent electrolyte was 0.1 N sulfuric acid solution and was admitted from a bottle the tube of which was connected to the inlet of the electrolyzer by a rubber hose through a stopper and glass tube. The electrolyte flow rate through the cell was ~ 0.015 ml/sec and was controlled by a Bunsen clip.

To record the readings of the indicator circuit the electrolyte flow was periodically stopped by the Mohr clip, and the generating current and stop watch were stopped at the same time. The titration was performed in a glass cell with a capacity of ~ 50 ml.

The end point of the titration was determined by biamperometric and potentiometric methods. In the biamperometric titration platinum electrodes 1×1 cm in size were used with an M193 microammeter, a source of direct current, and a potential divider for applying the required potential (V) to the indicator electrodes. Two variants of the potentiometric method were used ($i = 0$ and $i \neq 0$) with an R-307 potentiometer, a platinum indicator electrode, and a saturated calomel reference electrode and also two platinum electrodes 1×1 cm in size. The latter were polarized with a current of $\sim 5 \mu A$ by means of a direct-current source (~ 200 V and a radioresistance of $\sim 40 M\Omega$).

The need to generate the titrant externally was conditioned by the incompatibility of the chemical and electrochemical processes and also by the direct chemical reduction of strong oxidizing agents by metallic vanadium (anode). An advantage of external electrochemical generation of vanadium (IV) over interval generation from vanadate is the possibility of determining, in different aliquot portions of the investigated solution, manganese (VIII), chromium (VI), and cerium (IV), which are frequently present together in various materials.

The Coulometric titration of manganese VII by vanadyl ions generated internally from dilute acidic vanadate solutions, realized by Davis [3], is unsuitable for the determination of chromium (VI) since its reduction only takes place in ≥ 12 -mole/liter phosphoric acid solution, and under these conditions the current efficiency for the generation of vanadyl is extremely small. The results from the determination of these ions are given in Table 1.

Determination of Cerium (IV). Willary and Young [4] titrated cerium (IV) potentiometrically with a solution of $VOSO_4$ in hot, dilute, sulfuric acid medium. Cerium (IV) in loparite has been titrated amperometrically by Zolotavin and Ponomareva [5]. Dikshitulu and Rao [6] have perfected the method, by showing that in the presence of a certain amount of phosphoric acid cerium (IV) can be titrated with vanadyl even at room temperature.

In order to find the optimum conditions for the end point determination the $E = f(i)$ polarization curves were investigated for platinum electrodes in solutions containing the vanadium (V)/vanadium (IV) and cerium (IV)/cerium (III) redox systems and an indifferent electrolyte (1 N sulfuric acid + 1 M phosphoric acid). It was found that

TABLE 1. Results from Coulometric Titration with Externally Generated Vanadyl ($n = 5$; $\alpha = 0.95$; $v = 30$ ml; $\bar{x} \pm S\bar{x}\alpha$, mg)

End point determination	Mn (VII) taken	Mn (VII) found	Cr (VI) taken	Cr (VI) found	Ce (IV) taken	Ce (IV) found	Sn (II) taken	Sn (II) found
Biamperometric	0,110	$0,111 \pm 0,002$	—	—	0,895	$0,9 \pm 0,1$	—	—
	0,0110	$0,0109 \pm 0,0002$	—	—	0,0895	$0,09 \pm 0,01$	—	—
		$i = 0$		$i = 0$		$i = 5 \mu A$		$i = 0$
Potentiometric	0,110	$0,110 \pm 0,001$	0,442	$0,441 \pm 0,006$	0,895	$0,893 \pm 0,004$	0,125	$0,124 \pm 0,001$
	0,0110	$0,0110 \pm 0,0002$	0,094	$0,0943 \pm 0,0009$	0,0895	$0,0891 \pm 0,0003$	0,0125	$0,0123 \pm 0,0002$

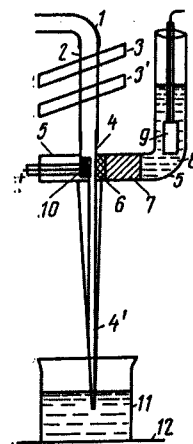


Fig. 1. Electrolyzer for external generation of vanadyl ions: 1) glass tube; 2) rubber tube; 3 and 3') Mohr and Bunsen clips; 4) glass tube with two side outlets; 5 and 5') terminating in a capillary (4'); 6) porous plates; 7) agar-agar gel with 5% potassium sulfate solution; 8) 5% potassium sulfate solution; 9) auxiliary platinum cathode; 10) vanadium generator anode; 11) glass cell for titration; 12) magnetic stirrer.

these systems are irreversible under these conditions. The Γ -shaped form of the curves for the coulometric titration of cerium (IV) with vanadyl (biamperometric end point determination) at $V = 1100$ mV leads to the supposition that up to the equivalence point the current is limited by the cathodic cerium (IV) reduction process. (The anodic process is oxidation of the indifferent electrolyte.) The coulometric titration of cerium (IV) with externally generated vanadyl was also carried out with potentiometric end point determination ($i = 5 \mu A$). In the latter case the curve for the variation of the potential difference (ΔE) between the two polarized electrodes with the amount of electricity (mC) passing through the cell near the end point has a Γ -shaped form.

Satisfactory results can only be obtained by the potentiometric method of end point determination ($i = 5 \mu A$). This method was used to determine cerium (IV) in a synthetic mixture simulating the alloy MA-8. This alloy has the following composition: 0.15% cerium, 2% manganese, 97.85% magnesium, 0.1% aluminum, 0.05% copper, 0.05% iron, 0.01% nickel, 0.1% zinc.

Magnesium, aluminum, copper, iron, nickel, and zinc sulfates were dissolved in 1 N sulfuric acid solution, and to this solution were added the appropriate quantities of manganese (VII) and cerium (IV). In order to deoxidize the MnO_4^- the solution was kept on a boiling water bath until the permanganate color disappeared (20-25 min). The solution was then cooled and transferred to a measuring

TABLE 2. Results from Determination of Oxidants in Samples ($n = 3$, $\alpha = 0.95$, $v = 30$ ml, $\bar{x} \pm S\bar{x}t_{\alpha}$, %)

	Mn according to certificate	Mn found	Cr according to certificate	Cr found	Ce introduced	Ce found
Steel 127b	1.15	1.14 $\pm$ 0.02	1.62	1.58 $\pm$ 0.01	—	—
Steel 127 + Ce	1.15	1.15 $\pm$ 0.01	1.62	1.59 $\pm$ 0.01	0.26	0.26 $\pm$ 0.01
Armco iron	0.025	0.025 $\pm$ 0.003				
Iron-manganese brass	0.66 $\pm$ 0.01	0.650 $\pm$ 0.007				

flask. An aliquot portion (10 ml) was titrated under the conditions indicated above. For a cerium concentration of 0.150% the result obtained was 0.150 $\pm$ 0.006% ($n = 3$, $\alpha = 0.95$).

Determination of Manganese (VII). The volumetric visual titration of MnO_4^- by vanadyl is well known from the literature. Müller and Just [7] showed that the potentiometric titration of MnO_4^- by vanadyl in 0.1 N sulfuric acid medium is only possible at 70–80°C. Dikshitulu and Rao [8] improved the method by using phosphoric acid as catalyst, by which means it was possible to perform the titration at room temperature. The coulometric titration by externally generated vanadyl ions has been described before [3]. We titrated MnO_4^- with externally generated vanadyl against 0.1 N sulfuric acid + 1 M phosphoric acid as indifferent electrolyte using the biamperometric and potentiometric ($i = 0$) methods for end point determination. In the first case a potential of $V \approx 400$ mV was applied to the electrodes. The titration curve has a $\searrow$ -shaped form. With potentiometric ($i = 0$) end point determination, potential jumps of 10 and 0.5 mV/mC were observed for $C_{Mn} = 10^{-4}$ and 10^{-5} g/30 ml respectively.

Manganese was determined in iron-manganese brass and in Armco iron. An appropriate sample was dissolved and oxidized as described in [9]. The manganese was titrated in an aliquot portion of the solution without the removal of chromium (VI) and iron (III), since vanadium (IV) reacts selectively with MnO_4^- under the selected conditions. The results are shown in Table 2.

Determination of Chromium (VI). In [10] Rao showed that the difference between the real potentials of the chromium (VI)/chromium (III) and vanadium (V)/vanadium (IV) redox systems in 12 M phosphoric acid is 0.273 V. Taking this fact into account they realized the potentiometric titration of milligram quantities of vanadium (IV) in 12 M phosphoric acid [10]. We have titrated chromium (VI) coulometrically with externally generated vanadyl against concentrated phosphoric acid as indifferent electrolyte using the potentiometric method for end point determination ($i = 0$).

Analysis of Mixtures of Manganese (VII) + Chromium (VI) and of Manganese (VII) + Chromium (VI) + Cerium (IV) in Steels. The steel used for analysis was Steel 127b, which contains 0.11% nickel, 0.10% titanium, 0.37% silicon, 0.020% phosphorus, 0.16% carbon, and 0.010% sulfur. The solution for titration was prepared in a manner similar to that described before. The manganese (VII) was determined in 0.1 N sulfuric acid + 1 M phosphoric acid, while chromium (VI) was determined in concentrated phosphoric acid. In the latter case, when an aliquot portion of the solution was added to the indifferent electrolyte at room temperature rapid spontaneous reduction of MnO_4^- took place, and this obviated the necessity of heating the solution.

The solution was prepared similarly in the analysis of the steel for manganese, chromium, and cerium. Since the steel did not contain cerium, a known amount of cerium was added to the solution, and the solution was transferred to a measuring flask. Firstly, in one portion of the solution, the number of millicoulombs required for the reduction of manganese (VII) + cerium (IV) was determined. In another portion of the solution the manganese (VII) was deoxidized by heating on a boiling water bath, and the number of millicoulombs required for the titration of cerium (IV) was determined. The manganese content was determined from the difference in the number of millicoulombs required for these two operations. The chromium (VI) was titrated in concentrated phosphoric acid. Under these conditions the cerium is combined into a complex with phosphoric acid and does not interfere with the chromium determination, while the manganese is spontaneously reduced.

Determination of Tin (II). Since the difference between the normal potentials of the tin (IV)/tin (II) (0.15 V) and vanadium (IV)/vanadium (III) (0.36 V) is 0.21 V it can be supposed that the reaction between tin (II) and externally generated vanadium (IV) ions should take place almost quantitatively. A 7 N sulfuric acid solution was selected as indifferent electrolyte in order to increase the difference between the real redox potentials of these systems. The end point was determined potentiometrically.

LITERATURE CITED

1. Yu. Yu. Lur'e, Reference Book on Analytical Chemistry [in Russian], Goskhimizdat (1962), p. 199.
2. A. I. Kostromin, P. K. Agasyan, and V. N. Basov, Zh. Analiticheskoi Khim. (1970).
3. D. G. Davis, Anal. Chem., 31, 1460 (1959).
4. H. H. Willard and Ph. Young, Ind. Eng. Chem., 20, 972 (1928).
5. V. L. Zolatavin and L. K. Ponomareva, in: Rare-Earth Elements [in Russian], Izd. Akad. Nauk SSSR (1958), p. 176.
6. L. S. A. Dikshitulu and G. G. Rao, Talanta, 9, 289, 857 (1962).
7. E. Müller and H. Just, Z. Anorg. Chem., 125, 155 (1922).
8. L. S. A. Dikshitulu and G. G. Rao, Z. Anal. Chem., 189, 421 (1962).
9. A. M. Dymov, Technical Analysis of Ores and Metals [in Russian], Metallurgizdat (1949), p. 280.
10. G. G. Rao and P. K. Rao, Talanta, 10, 1251 (1963); 11, 4, 703 (1964).