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Applications Involving Reduction with Hydrazine—Rapid Potentiometric Methods for Chromium(VI)—Analysis of Industrially Synthetic Mixtures

M. ZAKY

Department of Chemistry
Faculty of Science, Zagazig University, Zagazig, Egypt

A new rapid, reliable and accurate procedure is adopted for estimation of small amounts of chromium based on its reduction with known excess of hydrazine sulphate in acid medium whereupon the chromium(VI) solution is reduced to the chromium(III), and the unreacted hydrazine is determined through oxidation with freshly prepared ethanolic iodine to produce iodide which is titrated with Hg(II). The method finds application to the determination of the element in some industrially important products.

INTRODUCTION

Marston[1] made use of iron(III) for potentiometric titration of both Cr(II) and Cr(VI) respectively with $K_2Cr_2O_7$ in slag using Pt electrodes. Rozovskii[2] adopted a procedure for tervalent chromium based on potentiometric titration of Cr(III) with $K_3Fe(CN)_6$ in presence of platinum and silver-silver chloride electrodes. Syamsunder[3] described a potentiometric method for determination of Cr(VI) by the use of hydrazinium sulphate in HCl as titrant. Duczmal[4] adopted a chelatimetric method for Cr(III) based on boiling the Cr(III) solution with EDTA for 5 min., cooling, adding NH_4OH until the solution is blue. Excess of EDTA is back titrated against lead acetate in presence of 4-(2-pyridylazo) as indicator. Piryutko[5] determined small amounts of Ce(IV), Cr(VI) or V(V) in H_3PO_4 solution by titration with Fe(II), using sodium phenyl aminesulphonate as indicator. Hopirtean[6] used Hg(II)-sensitive membrane electrode in the complexometric determination of Cr(III). Malik[7] adopted a spectrophotometric method for the same element using potassium hexacyanoferrate(II) at pH=4.

EXPERIMENTAL

Solutions

All solutions were prepared from high purity chemicals and deionized water and were standardized by the recommended methods. 0.032M hydrazine sulphate solution was prepared by dissolving the calculated amount into requisite volume of water. The resulting solution was standardized by the method involving oxidation[8] with ethanolic iodine and titration of the liberated iodine potentiometrically against Hg(II) using silver amalgam as indicator electrode according to:

$$N_2H_4 + 2I_2 = N_2 + 4HI$$

Apparatus

The titration assembly consisted of a 100 ml beaker fitted with a silver amalgam indicator electrode and a saturated calomel electrode, a 5 ml burette, a magnetic stirrer, and a potentiometer (E512 Metrohm Herisau).

Procedures

A. Determination of Chromium

Transfer to a 100 ml breaker a solution (0.1–1.5 ml 0.027M Cr(VI). Add 5 ml 0.032M hydrazine sulphate, make the solution slightly acidic medium, then add 25 ml water and boil about 10 min. to ensure complete reduction of Cr(VI) to Cr(III). Cool, then add excess ethanolic iodine and titrate liberated iodine with Hg(II) using silver amalgam as indicator electrode. Calculate $N_2H_4 = I^- = Cr$.

TABLE 1

DETERMINATION OF CHROMIUM(VI)

No.	Cr(VI) (mg) Taken	Cr(VI) (mg) Found	Error ±%	Titrant (mV/0.1 ml)
1.	0.140	0.141	0.71	160
2.	0.280	0.281	0.36	147
3.	0.420	0.422	0.48	132
4.	0.562	0.563	0.18	141
5.	0.702	0.704	0.28	152
6.	0.842	0.843	0.12	161
7.	0.983	0.982	0.10	159
8.	1.123	1.125	0.18	138
9.	1.264	1.266	0.16	160
10.	1.404	1.406	0.14	162
11.	1.544	1.547	0.19	159
12.	1.685	1.683	0.12	161
13.	1.825	1.827	0.11	162
14.	1.966	1.963	0.15	165
15.	2.106	2.102	0.19	168

B. Analysis of a Synthetic Mixture Similar in Composition of Chromite (a) or Chrome Magnesite (b)

Dissolve separately the following salts in small amounts of water and then mix together.

(a) 1.4284 g K_2CrO_4 + 1.0174 g $Al(NO_3)_3 \cdot 9H_2O$ + 0.7124 g $Fe(NO_3)_3 \cdot 6H_2O$ + 0.9543g $Mg(NO_3)_2 \cdot 6H_2O$.

(b) 0.628 g K_2CrO_4+1.086 g $Al(NO_3)_3 \cdot 9H_2O$+0.5609 g $Fe(NO_3)_3 \cdot 6H_2O$ + 2.8069 g $Mg(NO_3)_2 \cdot 6H_2O$. Then 25 ml of 70% $HClO_3$ was added and the resulting solution was subjected to the dense white fumes of $HClO_4$. Cooled, and completed to 500 ml water.

TABLE 2

ANALYSIS OF SYNTHETIC MIXTURES IDENTICAL TO CHROMITE(1), CHROME MAGNESITE(2) AND NICKEL-CHROME STEEL(3)

	Cr (mg)		Mn (mg)		Fe (mg)		Al (mg)		Ni (mg)	
	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found
(1)	3.826	3.812	—	—	1.136	1.400	0.736	0.731	—	—
(2)	1.681	1.676	—	—	0.895	0.891	0.782	0.785	—	—
(3)	1.412	1.416	0.024	0.021	6.951	6.942	—	—	1.615	1.612

1. Estimation of Cr(VI) and Fe(III)

Transfer to a 150 ml beaker a 5 ml aliquot, dilute with 30 ml water, add 5 ml N_2H_4 to enhance the reduction process of Cr(VI) and Fe(III), boil for 10 min. to ensure its complete transformation to Cr(III) and Fe(II), cool, then add excess of iodine solution, and titrate liberated iodine against Hg(II). Determine Hg(II) = Iodide = Cr + Fe.

2. Estimation of Fe(III)

Dilute another 5 ml aliquot with 30 ml water, add 1 ml 5% H_2O_2, boiled to decompose excess peroxide during which Cr(VI) is reduced to Cr(III), cool, add 2 ml 10% Na_2SO_3 to bring down the oxidation state of Fe(III) to Fe(II), add a few drops of 10% H_2SO_4, and boil for 10 min. to remove excess SO_2, while passing a moderate stream of N_2. Cool in ice water, carefully add drops of 0.5% bromine water until the appearance of its persistent color, boil for 10 min. to expel excess bromine, cool, and titrate the Br^- produced against Ag(I).

Determine Br^- = Fe. From (1) and (2) determine the concentration of Cr.

3. Estimation of Al(III)

Take another 5 ml aliquot with 30 ml H_2O, add 1 ml 5% H_2O_2, boiled to decompose excess peroxide during which Cr(VI) is reduced to Cr(III), cool, add 5 ml 0.05M EDTA, boil for 15 min. to ensure complete complexation of Cr(III), Al(III) and Fe(III), cool, buffer with 8 ml 10% urotropine, and titrate excess complexone with Hg(II) at pH 6.5 to obtain EDTA = Cr(III) + Al(III) + Fe(III). Calculate EDTA = Al by difference.

C. Analysis of Synthetic Mixture of Similar Composition to Chrome Nickel Steel

Dissolve separately the following salts in a small amount of water and then mix together.

0.5303 g K_2CrO_4 + 0.7922 g $Ni(NO_3)_2 \cdot 6H_2O$ + 0.0104 g $Mn(NO_3)_2 \cdot 6H_2O$ + 4.3609 g $Fe(NO_3)_3 \cdot 6H_2O$. Treat the solution as described in section B; then complete to 500 ml with water.

1. Estimation of Cr(VI) + Fe(III)

Dilute a 5 ml aliquot with 30 ml water. Add 5 ml hydrazine, and continue as described in section A, to obtain $N_2H_4 = I^- = Cr + Fe$.

2. Estimation of Mn(II)

Transfer a 30 ml aliquot to a 150 ml platinum dish. Add 10 ml 70% $HClO_4$, fume on a sand bath, in the dense white fumes of the acid. While fuming, cautiously add drops of HF to volatilize Cr(VI) as CrO_2F_2. Repeat addition of HF several times to ensure complete removal of Cr(VI), fume again for one min. to expel excess HF during which Mn(II) is oxidized to the dark brown precipitate of $MnO(OH)_2$, cool, transfer quantitatively to a 150 ml beaker, and dilute with 50 ml water and 5 ml KBr. Boil for 10 min. to ensure complete reduction of Mn(IV) to Mn(II) and to expel liberated Br_2. Cool and titrate unreacted Br^- with Ag(I). Determine $Br^- = Mn$.

3. Estimation of Fe(III)

Dilute a 5 ml aliquot with 30 ml water and proceed exactly as described in section B2 to obtain $Br^- = Fe(III)$.

4. Estimation of Ni(II)

To a 5 ml aliquot, add 5 ml EDTA and obtain EDTA = Ni + Fe + Mn. Determine EDTA = Ni by difference.

RESULTS AND DISCUSSION

Table 1 lists the results of the estimation of small amounts of chromium (IV) in pure solutions based on reduction with hydrazine. Table 2 lists the results of the analysis of synthetic mixtures identical to chromite, chrome magnesite and nickel-chrome steel.

The results show good agreement with conventional methods. Equivalence points were accurately determined with potential breaks ranging from 168 to 132 mV/0.1 ml Hg(II), which are sharp enough for the accurate determination of the end point.

The quantitatives of the redox reactions involving N_2H_4 as reductant and Cr(VI) as oxidant may be predicted by considering the standard reaction potentials of the half-reactions involved:

$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^- \qquad E^\circ = +0.22V$$

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad E^\circ = +1.20V$$

By the use of relation $E^\circ = (0.0591/n) \log K$, where E° is the standard potential, n is the number of electrons evolved to reduce one mole of Cr(VI) to Cr(III), and K is the equilibrium formation constant of the reaction. The log K value was calculated to be 73.096. Such values indicate that the above reaction should proceed quantitatively toward completion. The degree of completion of the reaction (α) is calculated according to $\alpha = \log K/n_1 + n_2 = 10.44$.

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