Colorimetric Microdetermination of Chromium and Manganese in Aqueous Solutions

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Introduction

Sometimes it becomes necessary to determine a small amount of chromium and manganese in natural waters and industrial solutions. Heavy metal impurities in the electrolyte (concentrated NaCl solution) have a marked influence on the chlorine-caustic electrolysis by the mercury cell process.[1] In the present study, the method of analysis of chromium and manganese in the electrolyte was established; ferric hydroxide was used as collector and reduction of ferric ion followed by aluminum hydroxide precipitation made it possible to separate chromium from manganese and iron.

Separation of Chromium from Manganese

Chromium and manganese being collected by ferric hydroxide, as will be described later, chromium must be separated from manganese and iron, both of which interfere more or less with the colorimetric determination of chromium.

If an acidic solution containing aluminum and ferrous ions is just neutralized with ammonium hydroxide to bromocresol purple, aluminum hydroxide is precipitated, while a bulk of ferrous iron remains in solution. In this procedure, chromium coprecipitates with aluminum hydroxide and thus manganese

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[1] Gösta Angel and Tage Lundén, *J. Electrochem. Soc.*, **99**, 435 (1952).

together with a greater part of iron was separated from chromium.

The following experiment is carried out to check this point.

Various amounts of manganese and chromium are added to 25 ml. dilute sulfuric acid solution (1:50) containing 10 mg. of ferric iron and aluminum respectively and then one ml. of 5% hydroxylamine sulphate solution is added. And after boiling to hasten the reduction of any ferric iron to ferrous, the solution is cooled to room temperature and neutralized with ammonium hydroxide (1:5) using B.C.P. as indicator.

After filtration, aluminum hydroxide is dissolved with 10 ml. of hot sulfuric acid (1:20) and reprecipitated with ammonium hydroxide in the same manner.

Aluminum hydroxide containing chromium on the filter paper is dissolved with 10 ml. of sulfuric acid (1:20) and 1 ml. of 85% phosphoric acid,2) and transferred to a 50 ml. volumetric flask. Chromium coprecipitated with aluminum hydroxide is oxidized to sexivalent state by silver peroxide.2) After the decomposition of excess of the oxidizing agent by dipping the volumetric flask in boiling water for 2 or 3 minutes, the solution is cooled to room temperature by tap water. Distilled water is added to the mark and 2 ml. of 0.2% of diphenylcarbazide solution (acetone 1 : water 1) are added. The optical density of the solution is then measured by the spectrophotometer at the wave length of 540 mμ.

One ml. of 30% hydrogen peroxide solution and the excess of ammonium hydroxide are added to the jointed filtrates containing iron and manganese.3) The solution is warmed to about 80°C.

Ferric hydroxide together with all of the manganese is filtered and dissolved with 10 ml. of hot sulfuric acid (1:40) containing a small amount of hydrogen peroxide. The solution is boiled to destroy hydrogen peroxide. Then it is transferred into a 25 ml. volumetric flask and manganese is oxidized to permanganate by silver peroxide.3,4) After the excess of the oxidizing agent is decomposed by the same procedure as before, the volumetric flask is filled with distilled water to the mark and the optical density is measured at the wave length of 535 mμ.

If any chloride is present, the solution becomes turbid; an addition of mercuric sulfate5) solution, however, is successfully employed to mask the silver chloride formation.

Results are shown in Table I.

TABLE I

SEPARATION OF Cr FROM Mn WHEN PRESENT TOGETHER

No. of experiment	Cr taken μg.	Cr found μg.	Mn taken μg.	Mn found μg.
1	0.0	0.0	44	41
2	4.0	4.0	88	88
3	8.0	8.2	0	0
4	8.0	8.3	22	23
5	8.0	8.2	22	22
6	16.0	16.4	66	68
7	100.	97.0	220	222
8	200.	196.	220	216

As shown in this table, 0—200 μg. of chromium and manganese can be separated and determined.

Coprecipitation of Cr and Mn with Ferric Hydroxide

One litre of water containing 10 mg. of ferric ion and various amounts of chromium and manganese are neutralized with excess of ammonium hydroxide at 30 to 40°C. The precipitate of ferric hydroxide with chromium and manganese is filtered and dissolved with 10 ml. of hot sulfuric acid (1:20) and determination of both elements is carried out by the same procedure as in section II. Table II shows the results.

TABLE II

COPRECIPITATION OF Cr AND Mn WITH FERRIC HYDROXIDE

No. of experiment	Cr taken μg.	Cr found μg.	error μg.	Mn taken μg.	Mn found μg.	error μg.
9	4.0	3.9	0.1	22	23	1
10	16.0	15.8	0.2	44	45	1
11	20.0	19.1	0.9	88	85	3
12	100.	97.0	3.0	110	112	2

We can thus determine manganese and chromium with the mean probable error of 2.5% and 2.4% respectively. Results for chromium appear to be slightly low. The use of an empirical curve is therefore recommended for the estimation of chromium.

When this method is applied to nearly saturated sodium chloride solution (purified electrolyte), particular attention should be taken to remove chloride ion by repeated precipitation of ferric and aluminum hydroxide. As shown in Table III, no trace of

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2) M. Tanaka, This Bulletin, **23**, 165 (1950).
The interference of few mg. of iron can be avoided by phosphoric acid or fluoride.

3) M. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sect.* **72**, 129 (1950).

4) Y. Murakami, This Bulletin, **22**, 159 (1949); K. Kimura and Y. Murakami, *Mikrochemie*, **36**, 727 (1950).

5) M. Tanaka, *J. Chem. Soc. Japan. Pure Chem. Sect.*, **72** 136 (1950).

manganese or chromium was found in this sample, and the added amounts of these elements were almost quantitatively recovered.

TABLE III

ANALYSIS OF 500 ml. SAMPLE SOLUTION

No. of experiment	Cr added μg.	Cr found μg.	Mn added μg.	Mn found μg.
13	0.0	0.0	0	0
14	8.0	7.8	44	46
15	20.0	19.3	88	87
16	100.	96.0	110	102

Behavioar of Sexivalent Chromium

A sample solution after electrolysis by the mercury cell process contains some free chlorine, so chromium may exist as sexivalent. The brine sample after electrolysis is analysed by the above mentioned procedure; after removal of trivalent chromium and manganese ions by ferric hydroxide, the filtrate is acidified with sulfuric acid and warmed after addition of some sodium sulfite (2–3 g.) for the reduction of chromate to chromic state. Ten mg. of aluminum, collector of chromium, are added to the solution which is subsequently neutralized with excess of ammonium hydroxide. After filtration of aluminum hydroxide, chromium in the hydroxide is determined as is in the case of trivalent chromium. Results are shown in Table IV.

TABLE IV

ANALYSIS OF BRINE CONTAINING FREE CHLORINE

No. of experiment.	Cr III added μg.	Cr III found μg.	Cr IV added μg.	Cr VI found μg.	Mn added μg.	Mn found μg.
17	0.0	0.8	0.0	1.3	0	12
18	8.0	9.0	11.6	11.6	44	56

From these results, it will be clear that small amounts of chromate scarcely ever associate with ferric hydroxide precipitate in our procedure.

Summary

Chromium and manganese less than 100μg. in 500–1000 ml. of solution are separated from a bulk of the solution by ferric hydroxide precipitation and the separation of chromium from manganese and iron can be carried out by the reduction of ferric iron to ferrous followed by the precipitation of aluminum hydroxide. And each element was determined colorimetrically using the silver peroxide as oxydant. No coprecipitation of chromate could be observed in this procedure.

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