A Method of Oxidizing Cr^{+3} for the Determination of Trivalent Chromium

Key words: Colorimetric determination—Trivalent chromium—Hexavalent chromium—Diphenylcarbazide—Chelating agent—Oxidizing agent

The chromium of most chromium compounds exists in the form of tri- and hexa-valences. Application of a chemical method of determination of the former is difficult because the former is far more inactive than the latter. For example, neither an extraction method by organic solvents or a colorimetric method with diphenylcarbazide is suitable to determine Cr^{+3} , because Cr^{+3} does not react with diphenylcarbazide and other chelating agents such as APDC and DDTC etc. Therefore, a method of oxidizing Cr^{+3} to Cr^{+6} is necessary for the determination of Cr^{+3} .¹⁾ The author proposed the following method by which Cr^{+3} was oxidized to Cr^{+6} in a water-soluble state without difficulty.

The sample solution containing Cr^{+3} was made acidic by adding H_2SO_4 , and then a small quantity of a strong oxidizing agent was added to it. Powdery MnO_2 or PbO_2 was used for the oxidizing agent in the present experiment. Then the solution was boiled for a while. The oxidizing reaction proceeded easily by the above procedure, and Cr^{+3} changed to Cr^{+6} rapidly as follows:

Fig. 1. The effect of the concentration of H_2SO_4 on the oxidation of Cr^{+3} .

—○—○—: MnO_2 was used

—●—●—: PbO_2 was used

Cr^{+3} : 10 mg

sample solution: 50 ml

MnO_2 or PbO_2 : about 0.1 g

boiling time: 30 min.

The concentration of H_2SO_4 affected this oxidizing process considerably. Fig. 1 shows that 0.2 N H_2SO_4 was the most effective, and that MnO_2 was more effective than PbO_2 . The boiling time to complete this oxidizing reaction sufficiently was only five minutes (Fig. 2). The Cr^{+6} solution thus produced was very stable.

Fig. 2. The effect of the boiling time on the oxidation of Cr^{+3} .

Cr^{+3} : 1 mg

sample solution: 100 ml (0.2 N H_2SO_4)

MnO_2 or PbO_2 : about 0.1 g

Fig. 3. The relation between the concentration of H_2SO_4 and unreduced Cr^{+6} .

—△—△—: 1000 μg of Cr^{+6} contained

—●—●—: 100 μg of Cr^{+6} contained

—○—○—: 10 μg of Cr^{+6} contained

25 ml of Cr^{+6} solution were filtered, respectively, and the following paper was used for every filtration.

"Filter Paper: Toyo Roshi No. 5B, 11 cm ϕ "

(folded into pleats)

After boiling, MnO_2 or PbO_2 left as unreacted in the sample solution could be removed easily by the process of filtration or centrifugal separation. The concentration of H_2SO_4 should be low as possible, because a filter paper reduced Cr^{+6} to Cr^{+3} in the filtrating process when the concentration of H_2SO_4 in the sample solution was too high.²⁾

Fig. 3 shows the percentage of unreacted Cr^{+6} in the filtrate when 25 ml each of various concentrations of H_2SO_4 containing Cr^{+6} were filtered through filter paper. The reduction of Cr^{+6} was considered to be negligible when the concentration of H_2SO_4 was lower than 0.2 N.

An oxidizing agent such as $\text{K}_2\text{S}_2\text{O}_8$ was also very effective for the oxidation of Cr^{+3} to Cr^{+6} . But $\text{K}_2\text{S}_2\text{O}_8$ left in the solution caused the color of the measuring solution for colorimetric determination of Cr^{+3} with diphenylcarbazide to fade and it was difficult to remove the remaining $\text{K}_2\text{S}_2\text{O}_8$ from the solution because $\text{K}_2\text{S}_2\text{O}_8$ dissolved easily in the solution. Therefore, in the present method, $\text{K}_2\text{S}_2\text{O}_8$ was impossible to use as the oxidizing agent.

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(Received July 4, 1983 and in revised form August 22, 1983)