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Spectrophotometric Determination of Chromium in Ores, Steels and Pure Nickel Samples using Phenothiazines

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A new, simple, and sensitive method has been developed for the spectrophotometric determination of Cr^{VI} based on its reaction with chlorpromazine-HCl (CPH) to give a red product. Under the optimum conditions, the linear range of the calibration graph was 0.00–0.33 μg mL^{-1} of Cr^{VI}. The molar absorptivity and the detection limit were 3.28×10^4 dm^3 mol^{-1} cm^{-1} and 0.003 μg mL^{-1} of Cr^{VI}, respectively. Analyses of certified ores, steels, and pure nickel samples gave results in excellent agreement with the nominal values and with relative standard deviations of $\leq 1.5\%$

Chromium determinations in complicated matrices, such as ores and steels, are important tasks that were achieved by using ICP-MS,[1] NAA,[2] and AAS.[3,4] However, the relatively high costs,[1,2] and high detection limits[1–4] are common features. Therefore, the need for a simple, low-cost, sensitive, and highly selective method is desirable. On the other hand, some chromogenic reagents[5–7] were reported for the spectrophotometric determination of Cr; however, others were recently compared.[8] Of these reagents, diphenylcarbazide[5] is the most popular and a basis of the adopted standard method[9] for Cr determination. However, because the strong interferences of Fe^{III}, V^V, Cu^{II}, Hg^{II}, Mo^{VI}, NO_2^- and amines are very critical, and a direct determination of chromium is difficult, prior separation or extraction techniques were frequently adopted for chromium determination in complicated matrices.[3,4,7–9]

Experimental

Apparatus and Reagents: Unless otherwise stated, these were as described previously.[7]

Samples: Homogenized and finely powdered certified ores were used as received.

Determination of Chromium: To a 10 mL calibrated flask, a portion of a treated sample or the working standard Cr^{VI} solution was transferred and diluted with water to 7.5 mL. Then, 1.5 mL of H_3PO_4 (10 mol dm^{-3}) was added and the mixture shaken. After that 1.0 mL of the working CPH solution (20.0 mmol dm^{-3}) was added and mixed well. A portion of the reacting mixture was transferred to a 50 mm spectrophotometric cell, and the maximum absorbance of the resulting colored species was recorded at 526 nm, against water as a reference.

Results and Discussion

Sulfuric, hydrochloric, phosphoric, and acetic acids were tested as acidic media because in such media oxidizing agents readily react with phenothiazines to give colored species that are believed to be radical cations.[10] The maximum color intensities and stabilities were obtained in sulfuric and phosphoric acid media; however, phosphoric acid was used to provide enhanced selectivity for the proposed method. The absorption spectra of the reaction products of Cr^{VI} with the studied reagents exhibited λ_{max} values of 526, 516, 514, 500, and 526 nm for chlorpromazine-HCl (CPH), promethazine-HCl (PMTH), promazine-HCl (PMH), trifluopromazine-HCl (TFPH), and prochlorperazine dimaleate (PCPM), respectively. The colors developed instantaneously and gave constant absorbances for at least 15 min with all of the reagents, except for PMTH and TFPH, with which the colors were stable for 4 and 10 min, respectively.

The absorbance values increased with the H_3PO_4 concentrations up to 0.7 mol dm^{-3}, and remained almost constant for up to 3.0 mol dm^{-3}. A further increase in the acid concentration resulted in slight decreases of the absorbance values. Therefore, a phosphoric acid concentration of 1.5 mol dm^{-3} was adopted in the recommended procedure. Moreover, the absorbances increased with reagents concentrations of up to 0.4 mmol dm^{-3}; they then remained almost constant up to 3.5 mmol dm^{-3}. Therefore, 2.0 mmol dm^{-3} of the phenothiazine derivative was used in subsequent experiments. On the other hand, added salts, up to 1.5 mol dm^{-3} of $NaNO_3$, Na_2SO_4 or NaCl had almost no effect on the color intensities or stabilities. Also, the method was not sensitive to changing the order of mixing the reagents.

Linear calibration graphs were obtained for chromium determination with all of the tested reagents. The linear dynamic ranges were 0.00–0.33, 0.04–0.41, 0.02–0.56, 0.02–0.37, and 0.00–0.60 μg mL^{-1} of Cr^{VI} for CPH, PMTH, PMH, TFPH, and PCPM, respectively. The molar absorptivities were 3.28, 1.77, 2.70, 2.04, and 2.94×10^4 dm^3 mol^{-1} cm^{-1}, and the Sandell's sensitivity indexes were 0.0016, 0.0029, 0.0019, 0.0026, and 0.0018 μg cm^{-2}, respectively. The detection limits, calculated as three-times the standard deviation of the blank, were 0.003, 0.009, 0.004, 0.006, and 0.004 μg mL^{-1} of Cr^{VI}, respectively. Because these resullts indicated that CPH gave the highest sensitivity, it was used in the recommended procedure. The equation of the calibration graph using CPH as a reagent was $A = 0.022 + 3.140[Cr]$, where [Cr] is the Cr^{VI} concentration in μg mL^{-1}. The small intercept in the calibration equation may be attributed to the presence of a trace oxidizing impurity in the used phosphoric acid, as suggested by the manufacturer's specification sheet. Five replicate determinations of aqueous solutions containing 0.05, 0.1, 0.2, and 0.3 μg mL^{-1} of Cr^{VI} gave quantitative recoveries of ≥ 98.7 with relative standard deviations (RSD) of $\leq 0.9\%$.

In a study of the effects of foreign ions, strong oxidizing or reducing species were expected to interfere by a reaction with CPH or Cr^{VI}, respectively. For example, Fe^{III} was a serious interferent in the absence of phosphoric acid; however, in its presence the method could tolerate 3000 μg mL^{-1} of Fe^{III}.

Table 1. Determination of Chromium in Certified Ores, Steels, and Pure Nickel Samples

	Sample[a)]	Chromium/μg g^{-1}		
No.	Composition	Nominal	Found[b)]	RSD%
1	SiO_2 (52.64); Al_2O_3 (16.50); Fe_2O_3 (0.8); FeO (7.47); MgO (7.50); CaO (11.50); Na_2O (2.46); MnO (0.18); TiO_2 (0.20); CO_2 (0.10); V, 220.	30.00	30.02 ± 0.17	0.6
2	SiO_2 (67.11); Al_2O_3 (11.24); Fe_2O_3 (0.58); CaO (8.90); Na_2O (3.22), K_2O (4.26); TiO_2 (0.10); V, 8.	23.00	22.83 ± 0.27	1.2
3	C, 420; Si, 100; S, 140; P, 30; Mn, 3200; Ni, 170; Mo, 50; Cu, 180; Co, 30; Sn, 60; Al, 690; V, 18; Ti, 9; Nb, 19; Zr, 18.	140.00	139.81 ± 0.91	0.7
4	C, 420; Si, 390; S, 10; P, 20; Mn, 1130; Cu, 80; Fe, 500; Co, 900; Al, 50; V, 10; Ti, 210; B, 33; Pb, 12; Mg, 310; Mo, 10.	10.00	9.98 ± 0.15	1.5

a) Samples No. 1 and 2 are silicate ores (SARM 4 and SARM 48) from MINTEK, Council for Mineral Technology (Randburg, South Africa); No. 3 is a low alloy steel (12 M BS XCCS) from MBH Analytical, Ltd. (Barnet, Herts, England); No. 4 is a high purity nickel sample from MBH (21 M BS 200-2). Sample composition is expressed in wt% (in parenthesis) or in μg g^{-1} (without parenthesis).

b) Average of five replicate determinations ± standard deviation.

Moreover, ≥ 0.01 μg mL^{-1} of V^V was a serious interferent. Extraction with 8-quinolinol[5] completely removed 0–120 μg of V^V from the medium, but resulted in lower Cr^{VI} recoveries of 65–70%, a behavior that may be attributed to a partial reduction of Cr^{VI}. On the other hand, a quantitative co-precipitation of V^V may be achieved in the presence of a collector, such as Mn^{II}, La^{III}, or Fe^{III}.[5,11] However, Fe^{III} was adopted as a collector due to its ability to give a rapid and quantitative co-precipitation[11] and its high tolerability in the developed method. The effects of the different variables affecting the quantitative co-precipitation of V^V were investigated in order to avoid any possible loss of Cr^{VI}. Quantitative recoveries of Cr^{VI} were obtained in the pH range of 4.0–12.0 with a quantitative separation of V^V in the range of 5.8–9.1. Therefore, a pH of 7.0 ± 0.5 was adopted in the procedure. Moreover, collector concentrations in the range of 10–400 μg mL^{-1} of Fe^{III}, in the precipitation vessel, had almost no effect on the recovery of Cr^{VI}. Therefore, a 50 μg mL^{-1} Fe^{III} was adopted in the procedure for samples that might not contain a surfficient Fe^{III} concentration. Thus, the steps of sample preparation, oxidation with $KMnO_4$, and subsequent precipitation described below successfully eliminated the effects of V^V, and most oxidizing and/or reducing species thus rendering the method highly selective for Cr^{VI}. The tolerance limit was taken as the amount that caused an error of ± 5% in the absorbance of 0.15 μg mL^{-1} of Cr^{VI}. It was found to be: (≥ 2000) CyDTA, NH_2NH_3Cl, $(NH_3OH)Cl$, EDTA, $B_4O_7^{2-}$, Br^-, CH_3COO^-, Cl^-, ClO_4^-, F^-, NO_3^-, SO_4^{2-}, Al^{III}, As^V, Be^{II}, Cd^{II}, Ce^{III}, Cu^{II}, Fe^{III}, K^+, Li^+, Mg^{II}, Na^+, NH_4^+, Ni^{II}, Sr^{II}, Sb^V, Tl^I, Zn^{II}; (≥ 1000), phthalic acid, Hg^{II}, Mn^{II}, Sn^{IV}, UO_2^{2+}; (≥ 300) citric acid, oxalic acid, tartaric acid, Cr^{III}, $S_3O_6^{2-}$, $S_2O_3^{2-}$, $S_2O_5^{2-}$, SO_3^{2-}, Co^{II}, La^{III}, Pb^{II}, Mo^{VI}, Nb^V, Th^{IV}, Ti^{IV}, Zn^{IV}; (30) N_3^-, Bi^{III}, Ce^{IV}, Ir^{III}, Mn^{VII}, Rh^{III}, V^V; (10) Au^{III}, Pd^{II}, Pt^{IV}, Re^{VII}, Tl^{III}, W^{VI}; (5) SCN^-, Ag^I, Ir^{IV}, Rh^{IV}.

Applications: Transfer an accurate weight (0.5–2.0 g) of the sample to a 150 mL Teflon beaker and moisten with water. Add 20 mL of H_2SO_4 plus 4 mL of H_3PO_4 (10 mol dm^{-3} each). However, for silicate ore, add 20 mL of HF plus 20 mL of H_2SO_4 (10 mol dm^{-3} each) instead. Warm the beaker slowly on a hot plate until complete dissolution is achieved; add 3 mL of conc. HNO_3 and boil off the oxides of nitrogen, then evaporate to sulfur trioxide fumes. Cool the reacting mixture, dilute with water to about 50 mL, add 1.0 mL of $KMnO_4$ solution (50 mmol dm^{-3}) and boil gently for 5 min. If necessary, add more permanganate to keep the solution purple during boiling. Cool to about 60 °C, add oxalic acid (10 mmol dm^{-3}) drop-wise to reduce the excess permanganate, and after complete decolorization, add 0.2 mL excess of oxalic acid. Add 2.5 mL of the $FeCl_3$ collector solution (20 mmol dm^{-3}) to the sample solution that might not contain sufficient Fe^{III}. Adjust the pH of the resulting solution to 7.0 ± 0.5 using the working NaOH solution (5%), allow for coagulation, and filter off the formed precipitate. Wash the precipitate with three 10 mL portions of water, collect the filtrate and washings, and dilute with water in a 100 mL calibrated flask. Run a blank for this step to avoid any possible introduction of traces of Cr by the used reagents.

Thus, following procedure, the implemented method was successfully applied to certified ores, steels, and pure nickel samples, as shown in Table 1. The obtained data were in excellent agreement with the nominal values.

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