

Selective Determination of Cr(VI) by Indirect Atomic Absorption Spectroscopy

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Summary: A simple, sensitive and rapid indirect method for the determination of chromium(VI) is described. The method is based on the reduction of chromium (VI) to chromium(III) with elemental mercury in sulphuric acid medium. The oxidized mercury in return was determined by atomic absorption spectroscopy and used as a measure of chromium (VI) in the sample. Effects of a number of possible interferences on the determination have been checked and some synthetic and real samples of chromium(VI) have been analysed by the described method as well as by a reference spectrophotometric method.

Introduction

Chromium is one of the micro nutrient elements which are considered essential for human health but exert toxic effects present in excess. A number of experiments made on animals revealed that diets deficient in chromium exhibit impaired capacity to incorporate the amino acids, glycine, serine, and methionine into the protein of their hearts [1,2]. Later, evidence has accumulated that chromium is involved in glucose tolerance in human as well [3]. On the other hand chromium(VI) salts are irritating to mucous membranes, skin and conjunctiva. Allergies and dermatitis are induced through exposure to these

compounds. A higher rate of bronchitis among chromate workers has been reported [4]. For many years it was not realized that chromium compounds could be carcinogenic. However epidemiological studies now have established that chromium(VI) salts can cause pulmonary malignancy [5].

Different types of spectroscopic techniques have been applied successfully to chromium determination. Beyermann *et al.* [6] determined chromium in urine samples at levels of 5ng by X-ray fluorescence spectroscopy. Hambridge [7]

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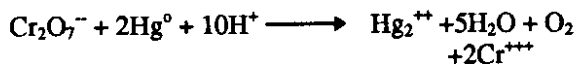
attained an absolute sensitivity of 1 ng in analysis of serum urine and hair with a DC arc spectrograph in a static argon atmosphere. A comprehensive study on the atomic absorption of chromium is made by Feldman and Purdy [8], Roos [9] first time found that chromium(III) exhibited a higher sensitivity than chromium(VI), hence the oxidation state also matters in chromium determination. Kraft and coworkers [10] found that the intensity of the chromium signal bore complex relationship to the oxidation state and the flame temperature. Yanagisawa *et al* [11] separated chromium(III) and chromium(VI) by extraction before determining the two oxidation states by atomic absorption spectroscopy. They used hydroxyquinoline at pH 6 as chelating agent for chromium(III) and diethylthiocarbamate at pH 4 for chromium(VI). Cranston and Murray [12] and also Van Loone *et al.* [13] reported the separate determination in water. De Jong and Brinkmann [14] extracted both oxidation states at different pH values with Aliquat-336, a mixture of methyltri-n-alkylammonium chloride.

To avoid the time consuming and cumbersome step of extraction, an indirect atomic absorption method for the selective determination of chromium(VI) is described in present work. The method is based on the treatment of total chromium sample with elemental mercury in the presence of sulphuric acid which reduced chromium(VI) to chromium(III). The oxidized mercury in return was determined by atomic absorption spectroscopy and used as a measure of chromium(VI) in the sample.

Results and Discussion

Nature of the reaction

In presence of sulphuric acid, chromium(VI) has a standard redox potential of 1.33 volts which is enough to oxidize elemental mercury into mercury(I) ions. In concentrated solutions when chromium(VI) is treated with elemental mercury in presence of concentrated sulphuric acid the appearance of green colour due to chromium(III) is a clear indication of chromium reduction. Most probably the following redox reaction takes place.



Presence of mercury(I) ions was confirmed when yellowish green precipitates of mercury(I) iodide appeared by adding a solution of potassium iodide. Oxidation state of mercury ions was further confirmed by performing a few other tests as well [15].

Effect of concentration and volume of sulphuric acid

This part of the study revealed that the concentration and volume of sulphuric acid were not only crucial for the redox reaction of elemental mercury and chromium(VI) but was also important to dissolve the white precipitate of mercury(I) sulphate which formed during the reaction. Normally concentrated sulphuric acid i.e. 18M is usually used for the oxidation reactions. The same has been found true in present case. The redox reaction between mercury and chromium(VI) took place quantitatively and rapidly in the presence of 18M sulphuric acid.

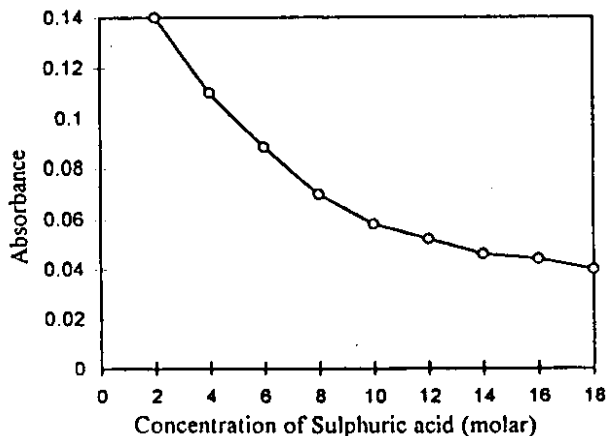


Fig. 1: Effect of sulphuric acid concentration.

On the other hand literature reveals that 1M sulphuric acid has the maximum solubility for mercury(I) sulphate [15]. Hence, for the quantitative and rapid reduction of chromium(VI), the main reaction was carried out in 5 mL of 18M sulphuric acid and then the reaction mixture was diluted to 100 mL to bring the final concentration of sulphuric acid around 1M, so that mercury(I) sulphate should not precipitate.

Effect of temperature

At room temperature the quantitative reduction of chromium(VI) with elemental mercury

in presence of sulphuric acid took 10 to 15 minutes. This time period can be reduced up to five minutes if the reaction is carried out at elevated temperatures. But on the other hand solubility of mercury in sulphuric acid increases by increasing the temperature and the blank shows large values of mercury absorbance. Therefore, the reaction temperature above 40°C is not recommended for the reaction since the blank value tends to increase and affects the results.

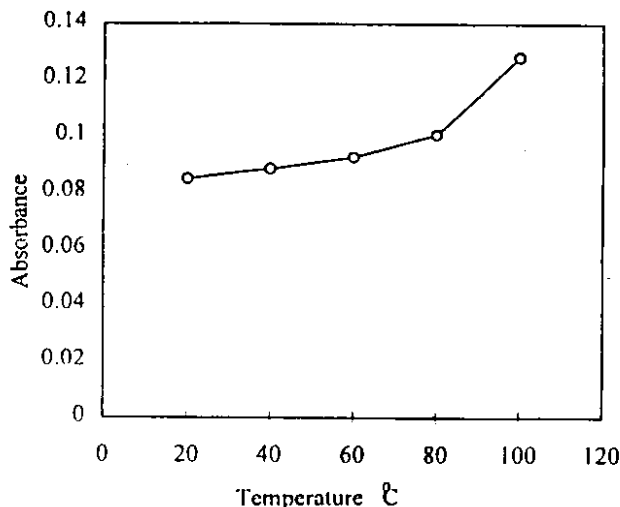


Fig. 2: Effect of temperature

Effect of monochromate and dichromate

Chromium possesses oxidation state 6+ both in chromate as well as in dichromate salts. Moreover in presence of strong acidic media chromate ions should be converted to dichromate ions. Hence principally the same calibration should be obtained by using chromate or dichromate salts. But as shown in Fig. 2, two slightly different calibrations were obtained for the two chromium salts. In this regard literature reveals that under different acidic conditions a number of chromium species co-exist in the solution. Probably the rate of reduction of different species of chromium(VI) with mercury was different. The slight difference found in the two calibrations is probably due to this fact.

Effect of diverse ions

The effect of a number of cations and anions which may interfere the determination, was

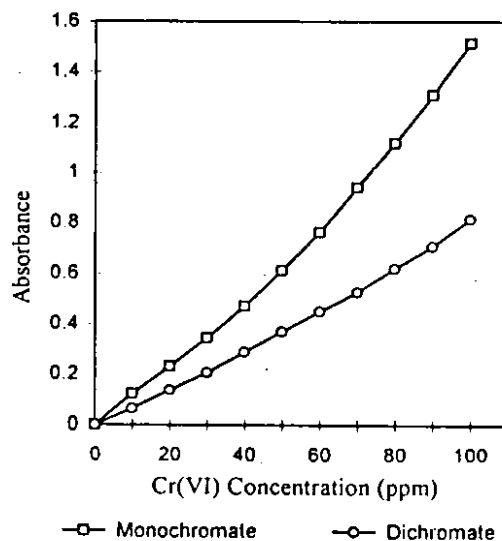


Fig. 3: Effect of monochromate and dichromate salts.

checked by reacting the chromium(VI) with elemental mercury in the presence of ten fold concentration of the concerned ion than that of the chromium and measuring the absorbance of mercury in the final solution.

As shown in Table-1, none of the checked cations caused any considerable interference in the determination. However among the anions, as it was expected, halide ions gave significant negative errors in the chromium determination. This was due to the formation of sparingly soluble mercury halides. A considerable depression in the results caused by thiocyanate and nitric ions is probably due to the fact that these ions themselves reduce chromium(VI) in presence of sulphuric acid and less mercury is oxidized. Hence in order to get the best results the interfering ions should be isolated before determining chromium.

Table-1: Effect of diverse ions

Diverse ions	Added as	Abs.	Deviation
Calcium	carbonate	0.114	-0.004
Nickel	sulphate	0.119	+0.001
Zinc	sulphate	0.112	-0.006
Iron	amm.sulphate	0.123	-0.005
Lead	sulphate	0.122	+0.004
Chloride	sodium	0.072	-0.016
Bromide	sodium	0.079	-0.039
Iodide	potassium	0.083	-0.035
Nitrite	sodium	0.048	-0.070
Thio-cyanate	potassium	0.060	-0.058
Phosphate	sodium	0.112	-0.006

Absorbance without any diverse ions = 0.118

Precision and comparison with a reference method

Precision of the described method was checked by calculating the standard deviation for ten measurements of 2ml. of 1000ppm solution of Cr(VI). The values of standard deviation, relative standard deviation and coefficient of variance obtained were 0.00285, 0.090 and 1.439 respectively. A number of waste water samples from electroplating units, samples of industrial waste water containing corrosion inhibitors and synthetic samples made by dissolving different amounts of dichromates were analysed by the described procedure as well as by standard diphenylcarbazide spectrophotometric method. As shown in Table-2, the results obtained by both the methods are well in agreement with each other.

Table-2: Comparison of Cr(VI) results obtained by the described and reference methods

Samples	Cr(VI) Conc. ppm	
	By the described Method	By Ref. Method
Synthetic-1	25.2	25.5
Synthetic-2	40.5	40.9
Waste Water	82.3	79.8
Recirculating Water	253.4	253.0

Experimental

Equipment and reagents

A Varian 1275 Atomic Absorption Spectrophotometer equipped with an air-acetylene flame and a Varian Hallow Cathode Lamp of mercury was used for absorption studies. Atomic absorption of mercury was measured in a lean flame at 253.7 nm.

Standard solution of chromium (VI) 1000 ppm, was prepared by dissolving 2.829 gm potassium dichromate in 1000 mL water. Working solutions were prepared by appropriate dilution of this solution. Elemental mercury, purified by passing through a column of 2M sulphuric acid, was used.

Calibration procedure

In a set of five 100 mL conical flasks, aliquots of 1000 ppm chromium(VI) solutions in the range of 1 to 5 mL were transferred along with three drops (approximately 1 gm) of mercury

metal. Then 5 mL of concentrated sulphuric acid was added to each flask and the contents were stirred thoroughly for 5 minutes on a magnetic stirrer at room temperature and then diluted by adding roughly 80 mL water. The contents were further stirred for another five minutes and then filtered through a Whatman 42 filter paper into a 100 mL measuring flask. The volume of each flask was made up to the mark with distilled water. A compensatory blank was also prepared by similar manner. Mercury absorbance of each solution was measured at 253.7 nm in a lean air-acetylene flame. Calibration, as shown in Fig. 4, was prepared by plotting mercury absorbance against the chromium(VI) concentration.

Synthetic and real samples of chromium were similarly treated.

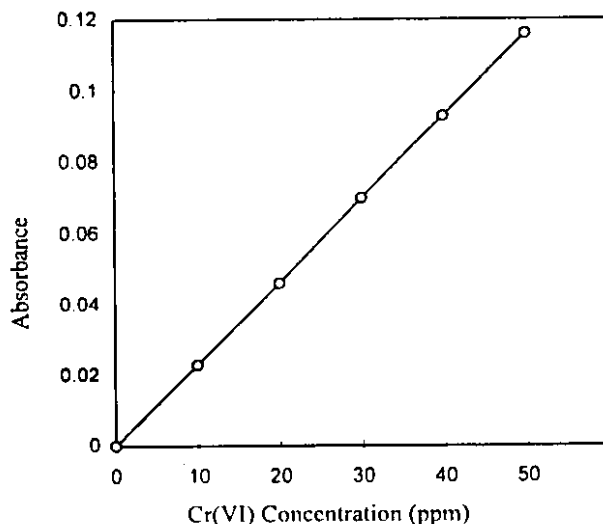


Fig. 4: Calibration curve for chromium (VI)

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