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SIMULTANEOUS DETERMINATION OF Cr (III) AND Cr (VI) IN NATURAL WATERS BY A SOLVENT EXTRACTION BASED ATOMIC ABSORPTION METHOD

M. JAFFAR, SHAHID PERVAIZ AND MASUD AHMAD

Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan

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A new method for the simultaneous determination of Cr(III) and Cr(VI) is proposed employing 1,5-diphenylcarbazide (DPC) to form a colored complex with trace amounts of Cr(VI), followed by solvent extraction of the complex. Total chromium in natural waters is determined by the flame atomic absorption (AAS) method, while Cr(VI) is extracted as a DPC complex with cyclopentanol for colorimetric estimation. The residual Cr (III) in the aqueous phase is directly estimated by AAS and indirectly by colorimetric method after oxidation to Cr (VI) with aqueous ammonium peroxodisulphate. The two Cr (VI) results agree within $\pm 2-3\%$. The extraction equilibrium is quantitatively studied as a function of choice of solvent, pH of medium, equilibration time and concentration of the oxidizing agent. Under optimum extraction conditions, the lower detection limit achieved is 0.005 mg/l Cr (VI). The method is applied to 14 natural waters sampled from open reservoirs, wells and springs. The results show that Cr (VI) content of spring waters is in general greater than that of other waters.

Key words: Cr (III) and Cr (VI) determination, Cr content of water.

Introduction

In recent years serious concern has arisen regarding the levels of chromium in the aquatic environment. Many incidences of chromium poisoning resulting from untreated salines and factory waters have been reported [1,2]. Chromium (VI) compounds are extremely toxic and their carcinogenicity has recently been established [3]. Chromium is frequently present as Cr (VI) in industrial waste waters, metal plating effluents, industrial dyes and inks and is extensively used as a dust inhibitor. The estimation of chromium depends largely upon the nature of the sample. In the case of waste waters, the colorimetric estimation (detection limit = 200 μ g/l) is proposed [4,5]. For total chromium in natural waters, the spectrophotometric method (detection limit = 280 μ g/l) and the graphite furnace based atomic absorption method are reported [6,7]. Catalytic voltametric determination of Cr (VI) in natural waters is also investigated [8]. Among other available methods, the polarographic method [9], the preconcentration based neutron-activation method [10] are worth mentioning besides the complexation method coupled with EC gas chromatography [11]. Solvent extraction based methods are also described [12,13], while an extensive review on these techniques has also appeared [14]. In principle, all these methods are highly specific both in terms of the nature of the sample and the analytical methodology involved.

It was, therefore, imperative to evolve a method of general utility for the simultaneous determination of Cr (III) and Cr (VI) in natural waters of various origins. The present method is based on the determination of total chromium by the flame atomic absorption method. The Cr (VI) in a given water sample is estimated colorimetrically after complexation with 1,5-diphenylcarbazide (DPC) while residual Cr (III) in the

aqueous phase of the sample is oxidized with ammonium peroxodisulphate, followed by solvent extraction and colorimetric estimation of Cr (VI) thus produced. The optimization of experimental variables is achieved in terms of matrix pH, extraction and equilibration times and oxidation conditions. The method is found to be useful for well and spring waters, and is applicable to any water system containing Cr (VI) concentration in excess to 0.005 mg/l.

Experimental

The DPC stock solution was prepared by dissolving 0.250g of the reagent in 100.0 ml acetone. A 50.0 ml aliquot of the water sample was mixed in a 100 ml volumetric flask with 10.0 ml of 0.5M sulphuric acid and 1.0 ml reagent solution. The Cr (VI) complex was extracted from the aqueous phase with 10.0 ml of cyclopentanol. The absorption measurement of the separated organic phase was made at 540 nm against reagent blank prepared by mixing 1.0 ml of the reagent solution and 10.0 ml of 0.5M sulphuric acid with 50.0 ml of deionized water. The Cr (VI) standards were prepared in the range of 0.005 - 0.030 mg/l by dissolving appropriate quantities of potassium dichromate (spectroscopic grade) in deionized water.

To 45.0ml of the separated aqueous phase was added 1.0 ml of 250.0 mg/l ammonium peroxodisulphate aqueous solution to oxidize Cr (III) to Cr (VI). The solution, contained in a glass-stoppered flask, was then heated for 30 min. in a water bath maintained at 80°. The complexation and extraction were then conducted by the procedure outlined above. The remaining part of the unoxidized aqueous phase was directly quantified by flame atomic absorption method. A Hitachi colorimeter, model 100-50, was used to measure the organic

phase absorptions, while a Shimadzu atomic absorption spectrophotometer, model AA-670, was used to determine Cr (III) and total chromium. All reagents used were of AR, spectroscopic grade. Water samples were collected by the procedure given elsewhere [15] during January - May, 1988 from locations indicated in Table 1.

Results and Discussion

Table 1 summarizes the concentrations of Cr (III) and Cr (VI) estimated by the proposed method. The values are averaged for triplicate measurements in each case, with a spread of $\pm 1-2\%$. The relevant absorptometric data appear in Fig. 1 through 4.

The results show that the complexation reaction of Cr (VI) with DPC, being highly selective, and sensitive warrants easy estimation of chromium at a few $\mu\text{g/l}$ level. However, the successful application of the method and the attainment of a lower limit of detection demand a strict

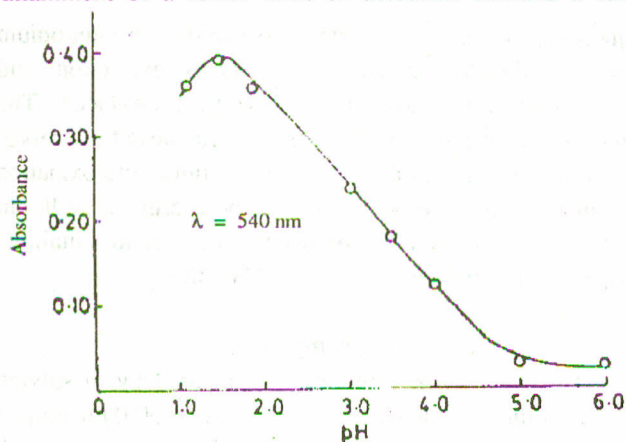


Fig. 1. pH Dependence of absorption of 0.5 mg/l Cr(VI) solution containing 2% (V/V) DPC.

quantitative control on such variables as equilibration time, matrix pH and the amount of the reagent. The choice of the extracting solvent is yet another important consideration, dictated by a large extraction coefficient value. From this viewpoint, two solvents were tried to extract the Cr (VI) complex from the aqueous phase into the organic phase. The comparative data appear in Fig. 5.

Figure 1 shows a critical pH dependence of absorption of a given Cr (VI) solution at constant reagent concentration. It was observed that at the optimum absorption wavelength ($\lambda = 540\text{ nm}$) there existed a small range of pH (from 1.4 to about 1.6) at which the absorption of the complex was maximum.

The oxidation of Cr (III) to Cr (VI) was found to be activated by heating the solutions. Figure 2 illustrates this situation where oxidation of four identical Cr (III) solutions was carried out separately at constant ammonium

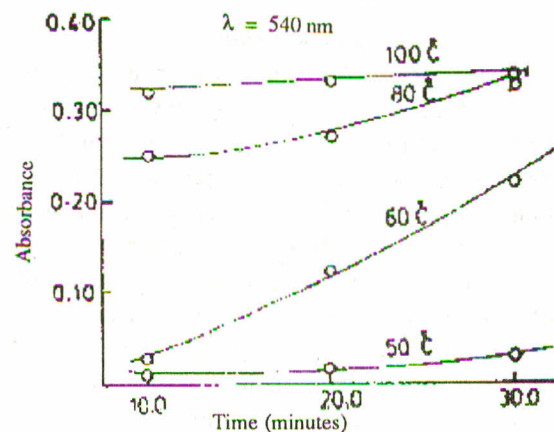


Fig. 2. Dependence of absorption of Cr(VI) chelated complex in aqueous phase on heating time at various temperatures.

TABLE 1. CONCENTRATIONS OF Cr (III) AND Cr (VI) IN VARIOUS NATURAL WATERS.

Sample code	Sample description location	Concentration ($\mu\text{g/l}$)			
		Cr(III) + Cr(VI)	Cr (VI)	Cr(III)/Cr(VI)	Cr(VI) %
S-1	Open reservoir, Punan Wali	59.0	8.8	5.7	14.9
S-2	Water supply scheme, Fatch Jang	60.5	9.2	5.6	15.2
S-3	Spring water, Shehdara Khurd	45.5	7.4	5.1	16.2
S-4	Well water, Saraai Kala	47.9	7.6	5.3	15.7
S-5	Spring water, Barian	59.3	8.4	6.1	14.2
S-6	Spring water, Kherra Galli	59.8	9.0	5.6	15.1
S-7	Spring water, Changa Galli	52.3	16.0	2.3	30.6
S-8	Spring water, Ayubia	52.5	9.8	4.4	18.7
S-9	Well water, Sohawa	51.5	8.5	5.1	16.5
S-10	Deep well water, Bassal	50.5	7.8	5.5	15.4
S-11	Deep well water, Kasral	37.2	5.2	6.1	13.9
S-12	Well water, Kot Fatch Khan	59.2	8.6	5.9	14.5
S-13	Well water, Khunda Moor	55.7	8.4	5.6	15.1
S-14	Well water, Ghor Ghasi	30.6	7.9	2.8	25.8
S-15	Synthetic water sample	60.0	27.4	1.2	45.7

peroxodisulphate concentration as a function of temperature of solutions maintained constant for time intervals ranging from 10-30 min. The data suggested that the temperature region between 50° to 60° was not suitable to yield optimum absorption due largely to incomplete oxidation. A temperature of 80° was found to be suitable towards completion of the reaction as evidenced by higher absorbance. Although at the boiling temperature the oxidation could be swiftly completed, the solution concentration was affected due to drastic volatilization. Hence, as a precaution, the oxidation was conducted by regulating the sample temperature at 80° in a glass-stoppered pyrex flask immersed in a water bath.

The amount of the oxidizing agent to be used with a specific water sample was found to depend on the nature of the sample. Figure 3 shows this dependence. The amount of the oxidizing agent is critical upto 50 mg/l of solution. Any further increase in the oxidant concentration adds only negligibly to the complex formation or the observed absorbance. At about half of this concentration the absorbance of the given solution falls by about 27%. It could be concluded that for a water sample containing about 0.050 mg/l total chromium, the concentration of the oxidizing solution must be about 50 mg/l.

The role of the extracting solvent was also investigated and the relevant data are reported in Fig 5. Cyclopentanol turned out to be a better solvent than cyclohexanol since it afforded easy extraction involving small equilibration time (≈ 10 min.) to produce maximum absorbance. Only a meagre absorption could be obtained with cyclohexanol even at prolonged equilibration time (≈ 1 hr). Hence, a 15-20 min. equilibration time was considered adequate for extraction. The extraction data reported in Table 1 refer to the use of cyclopentanol only.

The present data revealed that Cr (VI) levels in natural waters under investigation ranged between 5.2 -16. $\mu\text{g/l}$, although the variation in total chromium was rather limited. The maximum Cr (VI) content was found in sample S-7 from Changa Gali, having twice as much Cr (VI) as compared, on the average, with other samples. With the exception of this, the rest of the Cr (VI) levels ranged between 13.9-25.8%. The spring waters had, in general, excessive amounts of Cr (VI) compared with the well and open reservoir waters. This could be attributed to such factors as the origin of the waters, underground geology and rock structure of the bed. A 50% Cr (III) + Cr (VI) solution (sample S-15) prepared in deionized water was examined at optimum extraction conditions to check % recoveries in individual cases. The Cr (VI) extraction in this sample corresponded to 91.3% in a single step extraction.

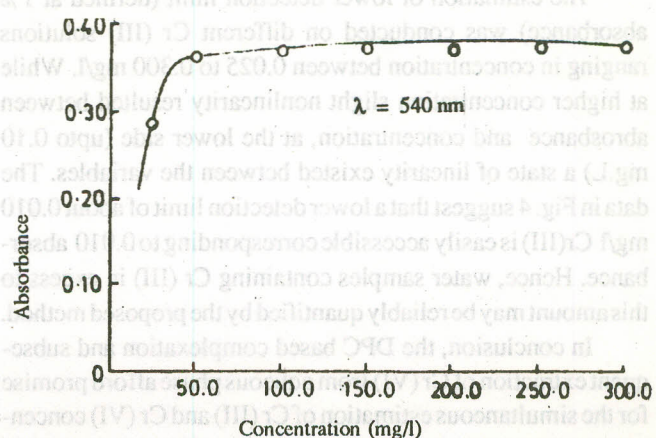


Fig. 3. Absorption of oxidized chromium solutions vs. concentration of ammonium peroxodisulphate.

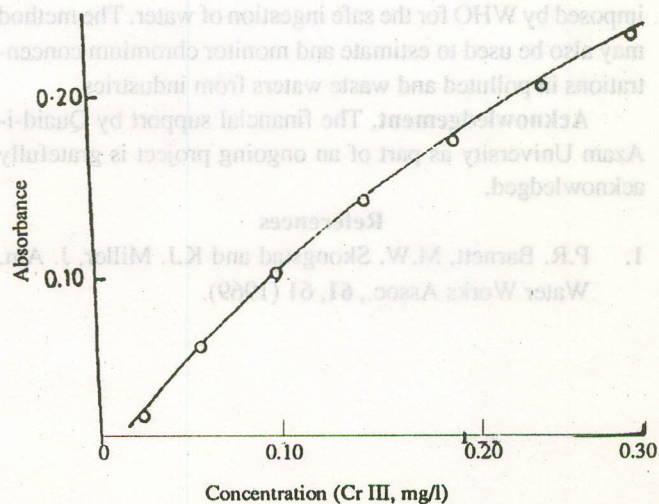


Fig. 4. Estimation of lower detection limit for Cr(III) - Cr(VI) conversion.

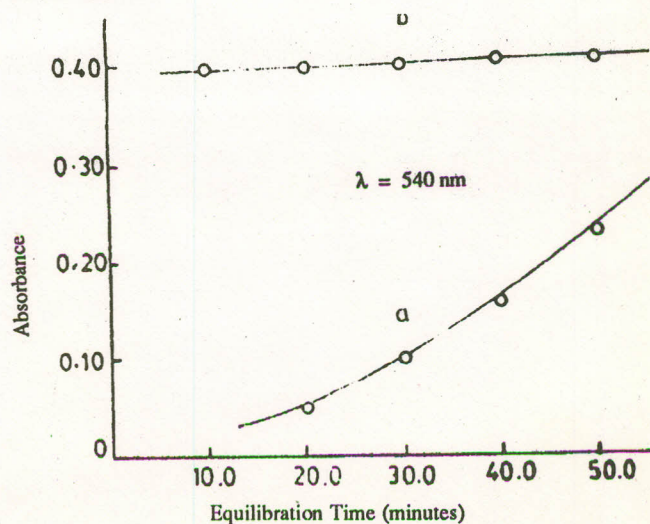


Fig. 5. Suitability check on (a) cyclohexanol and (b) cyclopentanol as a function of absorbance dependence on equilibration time of 0.5 mg/l Cr(VI) solution.

The estimation of lower detection limit (defined at 1% absorbance) was conducted on different Cr (III) solutions ranging in concentration between 0.025 to 0.300 mg/l. While at higher concentration slight nonlinearity resulted between absorbance and concentration, at the lower side (upto 0.10 mg/L) a state of linearity existed between the variables. The data in Fig. 4 suggest that a lower detection limit of about 0.010 mg/l Cr(III) is easily accessible corresponding to 0.010 absorbance. Hence, water samples containing Cr (III) in excess to this amount may be reliably quantified by the proposed method.

In conclusion, the DPC based complexation and subsequent extraction of Cr (VI) from aqueous phase afford promise for the simultaneous estimation of Cr (III) and Cr (VI) concentrations in natural waters of varied types. The present work was restricted to natural waters containing elevated chromium content [15] in excess to the threshold limit of 0.050 mg/l imposed by WHO for the safe ingestion of water. The method may also be used to estimate and monitor chromium concentrations in polluted and waste waters from industries.

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