Determination of ultra trace amount Chromium in water samples with the 1-(2-PyridylAzo)-2-Naphthol, (PAN) by the bromate ion in sulfuric acid with kinetic spectrophotometric method

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ABSTRACT

A new kinetic spectrophotometic method for the determination of trace amount Chromium (III) in Tea real samples has been described based on it s the catalytic effect on the oxidations of 1 - (2 – PyridylAzo) - 2 - Naphthol, (PAN), by potassium bromated in sulfuric acid. The reaction is followed spec- trophotometrically by measuring the decrease in the absorbance at 469 nm. Under the optimum conditions of0.2 molL^{-1} sulfuric acid, 1.0×10^{-4} molL^{-1}, 1- (2 -PyridylAzo) - 2 - Naphthol, (PAN), 0.01 molL^{-1} potassium bromate at 35°C, calibration graph in the rang of 0.001-0.06 ngL^{-1} Chromium (III). Concentration was obtained with detection limit of 0.2303 g mL^{-1} by the fixed-time method of 5.5 min. The relative standard deviation for 0.05ngL^{-1} Chromium (III) is %90. No serious interference was identified. The applicability of the method was demonstrated by the determination of the Chromium (III) in Water, Vegetables and blood samples.

Keywords: Chromium (III); Kinetic; 1-(2-PyridylAzo)-2-Naphthol, (PAN); Determination; Spectrophotometic

INTRODUCTION

Chromium is a major water pollutant, usually as a result of some industrial pollution including tanning factories, steel work, dyeing or chromium plating, wood preservation, and artificial fertilizers [1]. For this reason, determination ion of chromium in environmental samples and natural water, waste water samples and soil samples has become very important. The USEPA has set concentration 0.1ng/L of total chromium for drinking water as "maximum contaminant level goals" WHO states that the guideline value of 50μg/L of chromium (VI) because of these importance of chromium species, their accurate and facile determinations are in important in the chemistry [2]. The sophisticated techniques, such as inductively coupled plasma- mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), electrochemical analysis, spectrophotometry, neutron activation analysis and atomic absorption spectrophotometry (AAS), been adopted for sensitive assays for both oxidation

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states of chromium. These methods have disadvantage of cost and instruments used in regular analysis. AAS often has low sensitivity due to thematrix effect of samples such as salinity [3]. Environmental samples at low levels and has matrix effects with detection limit of lead[4]. The traditional methods of spectrophotometers are employed with separation from matrix elements. Extractive and micellar sensitized spectrophotometer with ability to separate and preconcentrat of chromium solve these problems and lead to a higher confidence level and easy determination of the trace elements by less sensitive, but more accessible instrumentation such as spectrophotometer. For this purpose various preconcentration method of chromium in micellar media are used [5]. The spectrophotometric and extraction method based on co-ordination with different ligands have been described for chromium determination [6-9]. Hence, sensitive and selective methods for determination of Chromiumin foodstuffs, drinking waters and drinks are of great interes. There have been numerous spectrophotometric methods for the determination of Chromium. The oxidation of Chromiumto permanganate and a measurement of the absorption of the charge-transfe band of permanganate at 558 nm has long been used as a standard method for Chromium determination this method suffers from low sensitivity. Spectrophotometric methods based on complex formation with chromogenic reagents provide good sensitivity, but have showed serious interferences from many cations and anions despite the high detection limit of 0.05 ng mL^{-1} [10, 11]. Numerous kinetic methods have been reported based on the catalytic effect of Cr^{3+} on the oxidation of organic compounds with suitable oxidants. Although these methods have shown good

sensitivity, they are time consuming and irreproducible, since it is difficult to control the timing of the reaction, which is variable from one experiment to another [12– 16], Some recent enhancements of the method using a flow injection tech- nique have been reported [17 – 19], However, if the reaction time is longer than the flow rate, the method will not be efficient and still irreproducible. Several efforts in crease the reaction rate by temperature have been re- ported; however, either the sample degrades or airbubbles will develop that hinder the flow rate [20-26]. The azo-dye PAN (1-[2-pyridylazo]-2-naphthol) is a well-known metallochromic indicator for the quantitative and qualitative determination of variety of metal ions. PAN has many characteristics required an ionophore. This ionophore reacts highly colored complexes. The complexes can be reversed to form again the ionophore over a large number of repetitions [27]. In this work, the catalytic effect of Chromium(III) on the oxidation of barium die phenyl amino sulfunate with potassium bromide in the presence of 1-(2-PyridylAzo)-2-Naphthol, (PAN), was investigated. A catalytic kinetic Spectrophotometric method for the determination of Chromium (III) was developed [28, 29]. The proposed method is extremely sensitive, with higher selectivity and is a simpler procedure than the three methods mentioned above. The method was applied successfully to the determination of total Chromium (III) in Water, Vegetables and blood samples.

EXPERIMENTAL
Apparatus
All the determinations of the analytes were carried out using a Sens AA GBC double beam atomic absorption spectrometer (AAS) equipped with deuterium background corrector. Hollow cathode lamps were used as radiation sources and the operational conditions of the

equipment were established according to the manufacturer's recommendations for each element. An adjustable capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomizations. The UV/Vis spectra were obtained from a Perkin-Elmer, model Lambda2 spectrophotometer. A Genway model 3510 pH/Ion meter with a combined glass electrode was used for pH measurements. Laboratory glassware was kept overnight in 10% nitric acid solution. A NBE ultrathermostat (VEB Prufgerate – Werk Medingen, Germany) was used to control the temperature.

Reagents and materials
All chemicals, except barium die phenyl aminosulfunate, were prepared of the analytical grade purchased from Merck Company, solution (Merck, Darmstadt, Germany). The solutions were prepared with doubly distilled water. The concentrations of the stock solutions were as follows: 1-(2-PyridylAzo)-2-Naphthol, (PAN), 1.0×10^{-4} molL^{-1}, potassium bromide, 0.1 molL^{-1} sulfuric acid, 0.2molL^{-1}Chromium (III) sulphate, 1000.

Pretreatment of real samples
Water samples
Analysis of water samples for determination of Cr (III) ion content was performed as following: 200 mL of sample was poured in a beaker and 8 ml concentrated HNO$_3$ and 3 ml of H$_2$O$_2$ of (30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. After adjustment of samples pH to desired value the were performed according to general described procedure [30].

Blood sample
Homogenized blood sample 20 mL was weighed accurately and in a 200 mL

beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO$_3$ and 2 mL HClO$_4$ 70 % was added and heated for 1 h. The content of beaker was filtered through a Whatman No. 42 filter paper into a 250 mL calibrated flask and its pH was adjusted to desired value and diluted to mark with de-ionized water. In all of real and synthetic sample amount of Cr (III) ion was found by standard addition method [31].

Vegetable sample
Spinach sample was bought from Shiraz, Iran. Afterwards, they were taken in small mesh. A 40 g sample was heated in silica crucible for 3 hours on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 mL concentrated nitric acid and3mL 30% H$_2$O$_2$ again kept in furnace for2 hours at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL hydrochloric acid and 2-4 mL70% perchloricacid and evaporated to fumes, so all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 7.0 made up to 15 mL by addition of KOH [32].

Procedure
A typical kinetic Spectrophotometric method experiment required the following steps: 1 ml of manganese solution equated to 0.01 ml grams was added to the 10 ml volumetric flask. Than 1 ml gram of potassium bromide (0.1 mol L^{-1}) and 1 ml of sulfuric acid solution (0.2 mol L^{-1}) was added. By adding the first drop of 1 ml 1-(2-PyridylAzo)-2-Naphthol, (PAN) 1.0×10^{-4} mol L^{-1}, to the volumetric flask, the time of the reaction beginning is recorded, after 5 sec the solution is mixed for 30 sec, and then it is volume by adding the distilled water, a sufficient amount of

the solution was added to a 1 cm cell, the difference between the quantities of the absorption in a wavelength equal to 469 nm in a time interval equalto 1-5.5 min was measured by mean of spectrophotometer (A As). All these steps would be repeated for a non catalytic reaction without the presence of manganese as the catalyst element (AAb), finally (AA) AAblank-AAsample is calculated. 1-(2-PyridylAzo)-2-Naphthol, (PAN), oxidation is traced in the acidic medium by potassium bromide, which its wavelength is 469 nm. The absorption spectra in an aqueous solution are shown in figures 1 and 2.
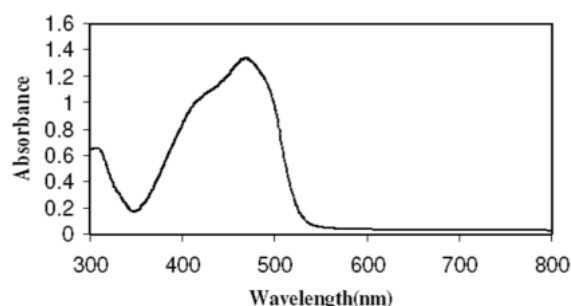
Fig. 1. The absorption spectra oxidation of product 1-(2-PyridylAzo)-2-Naphthol, (PAN).
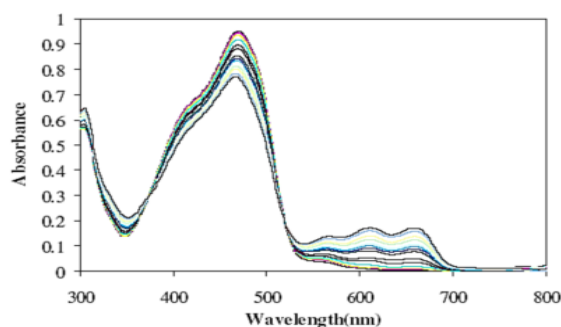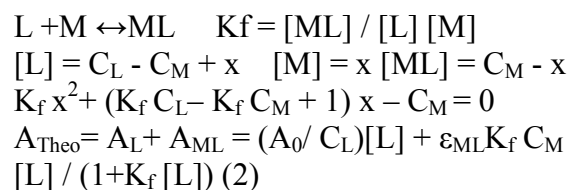

Fig. 2. The absorption spectra oxidation of product 1-(2-PyridylAzo)-2-Naphthol, (PAN), 20min mg L^{-1}.

RESULTS AND DISCUSSION
### *Investigation of ligand complexation with metal ions*
The complexation studies between the ligand and Cr(III) ion were carried out to determine the stoichiometry of the metals - ligand reactions as well as the formation constants and the molar absorptivities of these complexes. The stoichiometry between the ligand and each of the metal ions were determined from the absorbance-mole ratio data. The plots at 469 nm (Figure 3), clearly show a 1:1 (ligand to metal) stoichiometry for all themetal complexes. The formation constants, K_f, and the molar absorptivities, ε_{ML}, of the resulting complexes were then evaluated from the absorbance-mole ratio data and with the aid of a nonlinear curve fitting of the theoretical absorbance, A_{Theo}, to the experimental absorbance, A_{Exp}, using Microsoft Excel Solver program [33]. When known concentrations of metal, C_M, is mixed with a constant concentration of ligand and ML complexes are formed, the following equations can be written;

$$L + M \leftrightarrow ML \quad Kf = [ML] / [L] [M]$$
$$[L] = C_L - C_M + x \quad [M] = x \quad [ML] = C_M - x$$
$$K_f x^2 + (K_f C_L - K_f C_M + 1) x - C_M = 0$$
$$A_{Theo} = A_L + A_{ML} = (A_0 / C_L)[L] + \varepsilon_{ML} K_f C_M [L] / (1 + K_f [L]) \quad (2)$$

where A_0 is the initial absorbance of the ligand with concentration of C_L before any metal ions addition. Also, x is a reversed amount of ligand or metal reproduced from decomposition of ML at equilibrium which is equal to [M] value under $C_M \geq C_L$ condition. The procedure actually consists of two mutual steps. First, by initial guessing for K_f and solving Equation (1), x value is obtained which yields [L] parameter from $[L] = C_L - C_M + x$ then A_{Theo} is calculated by the substitution of [L] in Equation (2) (C_L, C_M and A_0 are known parameters). In the second step, for fitting the curve of A_{Theo} to that of A_{Exp}, minimization of SSR, sum of squared of residual, is performed by the Excel Solver program and two adjustable parameters K_f

and ε_{ML} are found. The results, which are summarized in (Table 1), show the values of formation constants for the considered metal complexes.
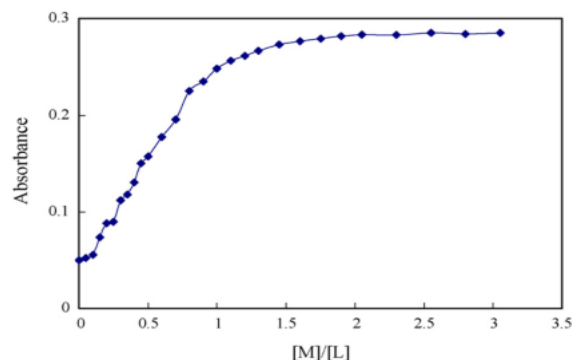
Fig. 3. Absorbance-mole ratio plot for Cr-PANcomplexes at [M] = 469 nm, [PAN] = 1.0×10^{-4} mol/L in Methanol.

**Table 1.** Formation constants and molar absorptivities of the metal complexes

Type of complex	K_f	ε_{ML}	SSR[a]
Cd—FPDHQO	1.02×10^{-4}	2.71×10^{-3}	1.22×10^{-3}

[a]SSR = $\sum (A_{Exp} - A_{Theo})2$

Effect of time on the reaction rate
As it was expressed in the method, to obtain optimum time of the reaction, 1 ml Cr (III) 0.01 mg L^{-1} solution, 1 ml potassium bromide 0.1 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml 1-(2-PyridylAzo)-2-Naphthol, (PAN), 1.0×10^{-4} mol $L^{-1}$are added to the volumetric flask 10 ml and by adding distilled water. Absorption of so lutions was measured in the 0-11 min interval of time. The above mentioned operation was repeated for biank solution (the solution without Cr (III). Changes in absorption based on the time at 30 centigrade degrees temperature are shown in figure 4. 5.5 min was selected as the optimum time.
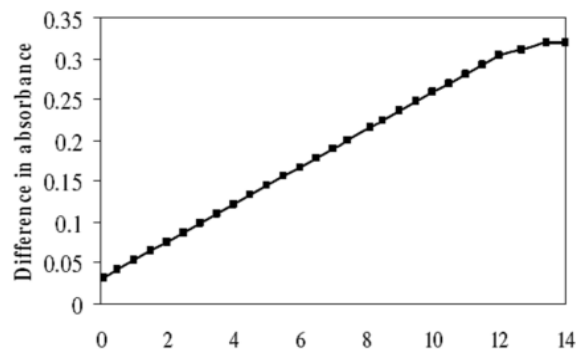
Fig. 4. The effect of time on the reaction rate.

### Effect of sulfuric acid concentration on the rate of reaction
As it was expressed in the method, to obtain optimum sulfuric acid concentration of the reaction, 1 ml Cr (III) mgL^{-1} solution, 1 ml potassium bromide 0.2 mol L^{-1}, 1 ml sulfuric acid solution 0.1 to 10 mol L^{-1} and 1 ml, 1-(2-PyridylAzo)-2-Naphthol, (PAN), 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 5.5 min. The above mentioned operation was repeated for biank solution (the solution without Cr (III)). As it is shown in figure 5, the o.2 molar concentration of sulfuric acid has the most changes in the absorption, so that, it was selected as the optimum concentration of the acid.
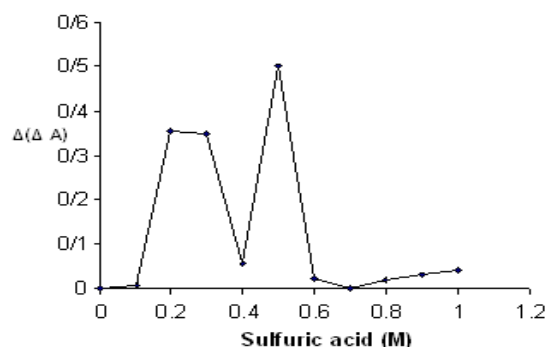
Fig. 5. The effect of sulfuric acid concentration on the rate of reaction.

Effect of 1-(2-PyridylAzo)-2-Naphthol, (PAN) on the reaction rate

To inspecting The effect of 1-(2-PyridylAzo)-2-Naphthol, (PAN), on the reaction rate, 1 ml Cr (III) 0.01 mg L^{-1} solution, 1 ml potassium bromide 0.1 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml, 1-(2-PyridylAzo)-2-Naphthol, (PAN), 1.56×10^{-5} to 2.5×10^{-3} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 5.5 min. The above mentioned operation was repeated for biank solution (the solution without Cr (III)). The results are shown in and figure 5, based on those results 1.0×10^{-4} mol L^{-1} was selected as the desired concentration.
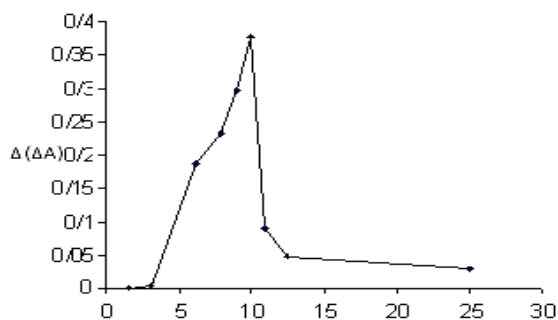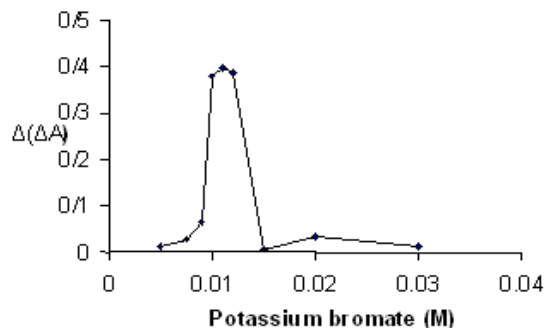

Fig. 5. The effect of 1-(2-PyridylAzo)-2-Naphthol, (PAN), on the reaction rate.

Effect of potassium bromide concentration on the reaction rate

To inspecting the effect of potassium bromide concentration, 1 ml Cr(III)0.01 mg L^{-1} solution, 1 ml potassium bromide at different concentration 0.05 to 0.3 molL^{-1}, 1 ml sulfuric acid solution 0.2mol L^{-1} and 1 ml 1-(2-PyridylAzo)-2-Naphthol, (PAN), 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 5.5 min. The above mentioned operation was repeated for blank solution (the solution without Cr (III)). Results are shown in figure 6, based on that results, potassium bromide at a

concentration of 0.011 molL^{-1} was selected as the desired concentration.

Fig. 6. The effect of 1-(2-PyridylAzo)-2-Naphthol, (PAN), on the reaction rate.

### Effect of temperature on the reaction rate

At first put the cells including: Cr (III), potassium bromide, 1-(2-PyridylAzo)-2-Naphthol, (PAN), distilled water and volumetric 10 ml flasks in the thermostat to reach to the desired temperature. After they go to the equilibrium temperature, 1 ml Cr (III) 0.01 mg L^{-1} solution, 1 ml sulfuric acid solution 0.2mol L^{-1} and 1 ml 1-(2-PyridylAzo)-2-Naphthol, (PAN), 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 5.5 min. The above mentioned operation was repeated for blank solution (the solution without Cr (III)). As it is shown in figure 7, 35 centigrade degree was selected as the desired temperature.
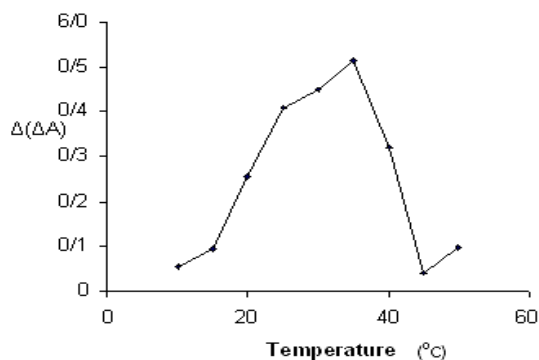
Fig. 7. The effect of temperature on the reaction rate.

Effect of ionic power of the medium was also

Inspected; potassium bromide and potassium nitrate were used for this purpose. 1 ml Cr(III)0.01 mg l-1 solution, 1 ml potassium bromide 0.1 mol L^{-1}, 1 ml sulfuric acid solution 0.2mol L^{-1} and 1 ml 1-(2-PyridylAzo)-2-Naphthol, (PAN), 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 5.5 min. as we can see in figure 8 results show that the effect of ionic power on the reaction rate is neglectible, and can be ignored.
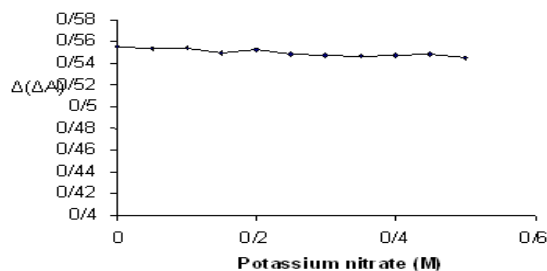
**Fig. 8.** The effect of Ionic power on the reaction rate.

Calibration graph and reproducibility

Reaching to the standard curve of Cr (III) in the reaction, the system went into the desired condition. So different volumes of Cr (III) (100 ng mL^{-1}), 1 ml potassium bromide 0.1 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml 1-(2-PyridylAzo)-2- aphthol, (PAN), 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 5.5 min. the above mentioned operation was repeated for blank solutions. The examination/test was done at 35 centigrade degrees. Results are shown figure 9.

Effect of foreign ions

The accuracy and reliability of this method was evaluated by comparing the results obtained for the same samples by an AAS method. The results estimated by AAS and spectrophotometry are shown in Table 4. The results estimated by spectrophotometry are much less as compare to results obtain by AAS. It may be attributed to the interference of foreign ions in the determination of chromium. The interfering ions. These ions may interfere with chromium (III).In order to assess the potential analytical applications of the proposed kinetic reaction, the influence offoregn ions on the determination of nickel was investigated [34-36]. The tolerated limits for the ions assayed are shown in Table2, (was relative errors less than 5%). As can be seen, the proposed method is highly selective.
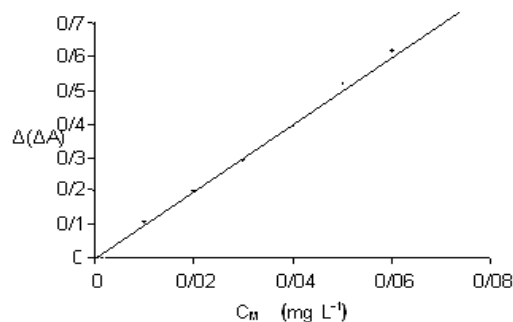
Fig. 9. Calibration graph for Cr (III).

Application

To assess the applicability of the method to real samples withdifferent matrices, containing various amounts of diverse ionswereused. For accuracy and reliability of proposed method, spikingexperiments and independent analysis were used. The proposed method was applied to the determination of total Chromium(III) in water, blood, and Vegetables samples. In Table3 the results obtained are shown, and compared with those obtained by atomic absorption spectrophotometry. Thelevel of the analyteions were found below the detection limit ofrelated element.The results of replicate three analyses of each sample showthat the ions recoveries are almost quantitative with a low RSD.The

recovery of spiked samples is satisfactory reasonable and wasconfirmed using standard addition method, which indicate

thecapability of the proposed method for the determination of traceamounts of these elements in different samples.

Table 2. Effects of the matrix ions on the recoveries of the examined Chromium (III) ion (N=6)

Ion	Added As	Tolerance Limit, mg L^{-1}
Cl^-, K^+, Na^+	KCl, NaCl	1000
Mg^{2+}, Ca^{2+}	chloride salts	800
Cu^{2+}	Nitrate salts	700
HCO_3^-	$NaHCO_3$	1000
SCN^-	KSCN	1000
PO_4^{3-}	Na_3PO_4	400
Fe^{3+}	Nitrate salts	300
CO_3^{2-}	Na_2CO_3	500
Mn^{2+}	Nitrate salts	150
Cd^{2+}	Nitrate salts	250

Table 3. Recovery of trace Chromium (III) from water, vegetables and blood sample afterapplication of presented procedure (N=6)

sample	Added (ngL^{-1})	Founded (ngL^{-1})	RSD %	Recovery %
Tap water	0	103.3	1.1	---
	100	161.9	1.8	103
River water	0	61.8	1.1	---
	100	164.3	1.3	95.3
Vegetable	0	67.4	1.7	---
	100	228.2	2.7	100.8
Blood	0	64.1	1.9	---
	100	169.6	2.3	102

CONCLUSION
The proposed method is very simple, highly selective, sensivite and reproducible for the determination of Chromium (III). The method also exploits low–cost instrumentation and overcomes the problems associated with previously reported spectrophotometric method for the determination of Chromium [37-40]. The methodis simple, accurate can be applied for the determination of analytesin environmental samples [41, 42].

ACKNOWLEDGEMENTS

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