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# Utilization of 2-Amino-6-(1,3-thiazol-2yldiazenyl)phenol for Chromium Speciation in Environmental Samples Spectrophotometrically

**Alaa S. Amin,[1,*] Ragaa El-Sheikh,[2] and Mohamed I. Shaltout[2]**

[1] *Chemistry Department, Faculty of Science, Benha University, Benha, Egypt*
[2] *Chemistry Department, Faculty of Science, Zagazig University, 44519, Egypt*

[*] *Corresponding Author: Email: asamin2005@hotmail.com Tel: +20552350996*

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**Abstract:** Due to the toxicity of chromium, species depend on their chemical properties and bioavailabilities, speciation of chromium are very important in environmental samples. A speciation procedure for chromium(III), chromium (VI) and total chromium in environmental samples is presented in this work, prior to Cr(III) complexation with new reagent 2-amino-6-(1,3-thiazol-2- yldiazenyl)phenol (ATDP) at the optimum conditions and measured spectrophotometrically. After reduction of Cr(VI) by 0.05 M sodium sulfite, the system was applied to the total chromium. Cr(VI) was calculated as the difference between the total Cr content and the Cr(III) concentration. The influences of the analytical parameters including pH of the aqueous solution and its amounts, reagent concentration, time and temperature were investigated. The complex gives a maximum absorption at 503 nm with a molar absorptivity coefficient of $1.04 \times 10^6$ L $mol^{-1}$ $cm^{-1}$. The linear range for Cr(III) determination is 10–400 ng/mL. No considerable interferences have been observed from other investigated anions and cations on the chromium speciation. The proposed method was applied to the speciation of chromium in environmental samples including natural waters and total chromium in digested tobacco, coffee, tea, and soil samples, comparing the results simultaneously with those obtained using an atomic absorption spectrophotometer, whereby the validity of the method has been tested.

**Keywords:** Chromium speciation; Spectrophotometry; Thiazolylazo dyes; Environmental analysis.

## 1. INTRODUCTION

In environmental samples, chromium is one of the pollutants. Chromium exists in the environment as chromium(III) and chromium(VI) oxidation states. As oxidation states, the chemical properties of these species are different. Chromium is an indispensable nutrient element for the carbohydrates and lipids metabolism. While chromium(III) is considered to be essential nutrition and for the maintenance of normal glucose tolerance, chromium(VI) can have acute and chronic toxic, including carcinogenic effect [1,2]. Chromium is a major water pollutant, usually as a result of some industrial pollution including tanning factories, steel works, dyeing or chromium plating, wood preservation, etc. and artificial fertilizers [3,4]. For this reason, determination of chromium in environmental samples as natural water, waste water samples and soil samples has become very important. The US EPA has set the concentration of 0.1 mg/L of

total chromium for drinking water as “maximum contaminant level goals”. WHO states that the guideline values of 50 µg/L of Cr(VI) [5]. Because of the importance of the chromium species, their accurate and facile determinations are an important point in the chemistry.

For the specified reasons, the determination of chromium in environmental and biological samples has assumed great significance. Determination of Cr(VI) in micro quantities is of interest to Analytical Chemists. Although AAS is the most common method of chromium detection, a number of other methods have been reported for Cr(VI) determination such as Neutron Activation Analysis (NAA), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) [5–8]. Moreover, such techniques are usually not available in most laboratories. Due to the expensive nature of the above instruments, most researchers still pursue colorimetric and spectrophotometric methods [9–12]. Pyrocatechol has been used as an indicator to determine Cr(VI) spectrophotometrically [13]. Andruch, et al., [14] described a procedure for Cr(VI) extraction and spectrophotometric determination using the dye 2-[2-(4-methoxy-phenyl-amino)-vinyl]-1,3,3-trimethyl-3H-indoliumchloride. Vanasidd-appa and Kumar [15] proposed a method for the spectrophotometric determination of Cr(VI) by using trifluoperazine hydrochloride (TFPH). This method is based on the oxidation of TFPH. Similarly, a number of extractive spectrophotometric methods have been employed for the determination of Cr(VI) by various researchers [16–18]. El-Shahat [10] proposed a method for the direct determination of Cr(VI). Other reagents have been suggested for the spectrophotometric determination of Cr(VI) using phenylarsenazo [19], citrazinic acid [20] and leucoxylenecyanol FF [21].

Various analytical techniques have been used for determination of chromium including Photometric and fluorimetric [22,23], atomic absorption spectrometry (AAS) [24], inductively coupled plasma atomic emission spectrometry (ICP-AES [23–25], and high performance liquid chromatography [26,27], etc. Due to the levels of chromium species in the natural and waste water samples are generally at µg/L and high matrix contents of the samples, a separation/preconcentration technique is necessary, prior to determine chromium by an instrumental technique [28–31] .

In the present work, a new reagent, 2-amino-6-(1,3-thiazol-2yldiazenyl) phenol (ATDP) was synthesized, characterized and used for spectrophotometric determination of total chromium using optimum conditions for complexation in Triton X-114 as surfactant. The proposed method was also applied to the determination of chromium in food, water and biological samples.

## 2. EXPERIMENTAL

### 2.1. Instrument

All absorption spectra were made using JASCO V-670 UV/Vis spectrophotometer (Japan) with a scanning speed of 200 nm/min and a band width of 2.0 nm, equipped with 10 mm matched quartz cells. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A Perkin Elmer atomic absorption spectrometry model AAnalyst 300 was used for all GFAAS measurements.

### 2.2. Reagents and solution

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Double deionized water (Milli-Q Millipore 18.2 MΩ/cm, resistivety) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO3 (1 + 9) and were rinsed with distilled water prior to use. Stock solutions of diverse elements were prepared from high purity compounds
Chromium(VI) and chromium(III) working standard solutions were all prepared by appropriate dilution of, respectively, 1000 mg/L $K_2Cr_2O_7$ (Merck) and 1000 mg/L $CrCl_3.6H_2O$ (Vetec) stock solutions. Reduction of

Cr(VI) to Cr(III) was carried out using sodium sulfite as the reducing reagent (Vetec). The stock solution of 0.05 M sodium sulfite was prepared by dissolving 630.2 mg of the chemical in water to give a final volume of 100 mL. Series of phosphate buffer solutions of pH = 2.9–11.2, were prepared by following the standard methods [32].

### 2.3. Preparation of ligand

The ligand, 2-amino-6-(1,3-thiazol-2yldiazenyl) phenol (ATDP) was prepared according to the procedure reported previously [33]. A solutions of 0.01 mole (10.013 g) of 2-aminothiazol was prepared in 1:1 HCl and cooled to – 5.0 ºC. to this solution a cold sodium nitrite solution of 0.01 mole (6.903 g) was added and mixed with stirring and kept in an ice bath of – 5.0 ºC for 20 min. The cooled diazonium salt solution was used for coupling with cold solution of 0.01 mole o-nitrophenol in 10 % NaOH. The azo compound formed was kept for 30 min in an ice bath of – 5.0 ºC, then filtered off, washed by water and dried. The crude material was recrystallized using dimethylformamide. The chemical structure was confirmed by elemental analysis, C, H, N, FTIR, and $^{1}$H-NMR spectra was investigated. Stock solution of ATDP was prepared by dissolving appropriated weighed amounts of solid reagent in least amount of DMF and competed to the mark in a 100 mL measuring flask.

### 2.4. General procedure

To aliquot containing 0.1–4.0 μg/mL of Cr(III), 2.0 mL of $1 \times 10^{-3}$ M ATDP solution, and 2.5 mL of phosphate buffer of pH 6.1 were added. The solution was transferred to a 10 mL measuring flask. The solution was taken up to the mark with bidistilled water and allowed to stand for 2.0 min at room temperature. The absorbance of the solution was measured at 503 nm, against the reagent blank solution prepared similarly.

### 2.5. Stoichiometric relationship

The stoichiometric ratios of the complex formed between Cr(III) ion and ATDP was determined by applying the continuous variation [34] and the molar ratio [35] methods at the wavelengths of maximum absorbance. In continuous variation method, equimolar solutions were employed: $5.0 \times 10^{-4}$ M standard solutions of Cr(III) ion and $5.0 \times 10^{-4}$ M solutions of ATDP were used. A series of solutions was prepared in which the total volume of Cr(III) ion and ATDP was kept at 1.0 mL. The Cr(III) ion and ATDP were mixed in various complementary proportions (0 : 1, 0.1 : 0.9, 0.2 : 0.8,. . ., 1 : 0, inclusive) and completed to volume in a 10 mL measuring flask as described in the above mentioned procedure. In the molar ratio method, the concentrations of Cr(III) ion is kept constant (0.5 mL of $5.0 \times 10^{-4}$ M) while that of and ATDP ($5.0 \times 10^{-4}$ M) is regularly varied (0.1–2.4 mL). The absorbance of the prepared solutions is measured at optimum condition complex.

### 2.6. Analysis of the real samples

The water samples analyzed were collected in pre-washed (with detergent, doubly deionized distilled water, dilute $HNO_3$ and doubly deionized distilled water, respectively) polyethylene bottles. The samples were filtered through a Millipore cellulose membrane of pore size 0.45 μm. The samples were stored in 1.0 L polyethylene bottles and acidified to 1.0 % with nitric acid and were subsequently stored at 4.0 $^{o}$C in a refrigerator. In order to eliminate the chlorine in tap water, the samples were treated for 5.0 min with 5.0 g of activated charcoal and filtered before being transferred into a polyethylene bottle. Before the analysis, the pH`s of the samples were adjusted to 6.1.

For solid samples analyzed, tobacco, coffee, tea, and soil sample from Benha City were also microwave digested. Digestion conditions for microwave system for the samples were applied as 2 min for 250 W, 2.0 min for 0 W, 6.0 min for 250 W, 5.0 min for 400 W, 8 min for 550W, vent: 8 min, respectively [36,37].

Tobacco, coffee and tea samples (1.0 g) were digested with 6.0 mL of HNO3 (65 %), 2.0 mL of H2O2 (30 %) in microwave digestion system and diluted to 50 mL with deionized water. Soil sample (1.0 g) were digested with 6.0 mL of HCl (37 %), 2.0 mL $HNO_3$ (65 %) in microwave digestion system and diluted to 50 mL with deionized water. After microwave digestion, the volume of the sample was made up to 25 mL with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample.

### 2.7. Procedure for determination of Cr(VI) by AAS

To the real sample solutions one drop of $H_2SO_4$ and one drop of 0.01% KMnO4 solutions were added and heated gently (5.0 min) for the oxidation of Cr(III) to Cr(VI). After cooling, one drop of 2.0 M HCl was added to destroy the excess of permanganate [38] After oxidation, the sample was used for the analysis of Cr(VI) by AAS and absorbance was measured at 357.9 nm. The amount of Cr(VI) can be calculated from the calibrated plot which was drawn by taking the standard Cr(VI) solution.

## 3. RESULTS AND DISCUSSION

Complex of Cr(III) with ATDP in aqueous media has a maximum absorbance at 503 nm. The absorption spectrum of the complex shows a maximum absorbance at 503 nm against a reagent blank as the reference. (Fig. 1).

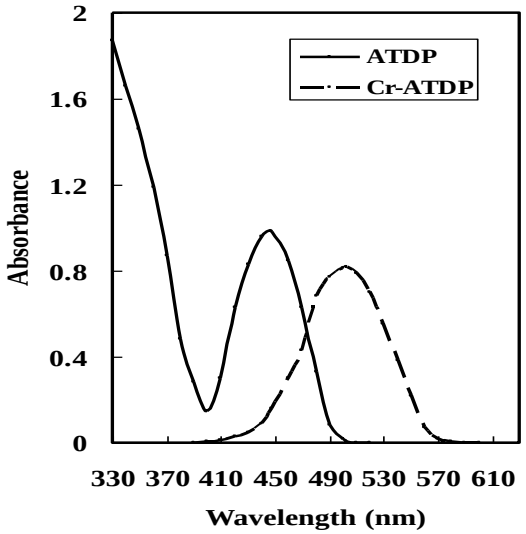


**Fig. 1.** Absorption spectra for 2 x $10^{-4}$ M ATDP complexed with 400 ng/mL Cr(III) ion at the optimum conditions

### 3.1. Optimization of the system

To take full advantage of the procedure, the reaction conditions must be optimized. Various experimental parameters were studied in order to obtain optimum conditions. These parameters were optimized by setting all parameters to be constant and optimizing one each time.

The effect of pH on the absorbance at a constant concentration of complex was investigated in the range of 2.9–11.2. The absorbance of the Cu(II)– ATDP at 503 nm was studied against the reagent blank. The absorbance was nearly constant in the pH range of 5.9–6.3. Therefore, pH 6.1 was selected as optimal [Fig. 2]. Moreover the amount of pH 6.1 was studied to select the optimum volume. A 2.0–3.0 mL of pH 6.1 gave the highest absorbance value. Therefore 2.5 mL of pH 6.1 per 10 mL was selected for all further studies.

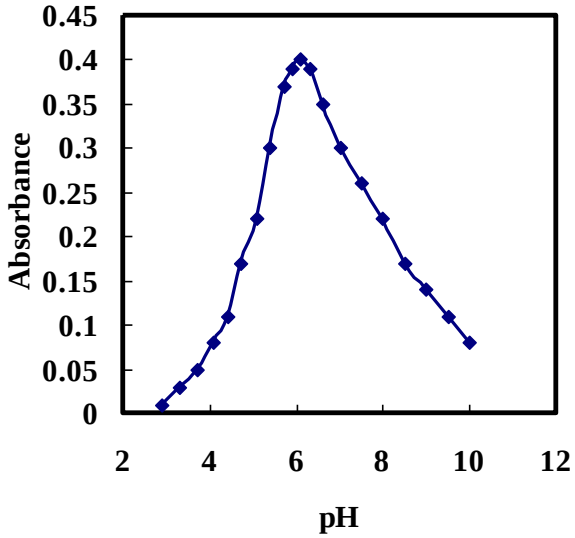


**Fig. 2.** Effect of pH on the complexation of 200 ng/mL of Cr(III) using ATDP at the optimum conditions

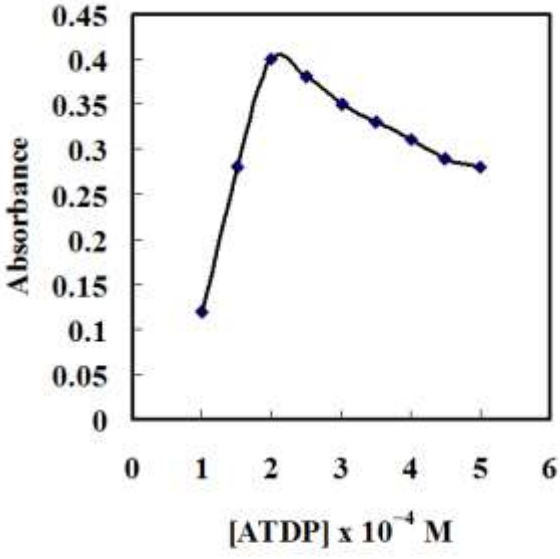


**Fig. 3.** Effect of [ATDP] on complexation of 200 ng/mL of Cr(III) at the optimum conditions.

Effect of ATDP concentration on determination of Cr(III) was investigated in the range of 1.0–5.0 × $10^{-4}$ M. The sensitivity of the method increased by increasing ATDP concentration up to 2.0 × $10^{-4}$ M [Fig. 3] and decreased at higher concentrations. It was expected that increasing ATDP causes an increase in the absorbance of complex, because increasing in ATDP concentration caused an increase in concentration of the complex. At concentrations higher than 2.0 × $10^{-4}$ M, the concentration of uncomplexed ATDP increases significantly. Therefore, much probably decrease of absorbance change at concentrations higher than 2.0 × $10^{-4}$ M is due to this fact that the free ATDP competes with the complexes. A concentration of 2.0 × $10^{-4}$ M of ATDP was selected as the optimum.

In order to investigate the effect of time and temperature, the optimum reaction conditions were used at various time and temperature. The results showed that complexation reaction was completed in 2.0 min. Raising the temperature upto 60 ºC has no effect on the complex formation.

### 3.2. Stoichiometric relationship stability constant

The stoichiometric ratio between Cr(III) ion and ATDP in the formed complex was determined by the continuous variations and molar ratio methods. Job's method of continuous variation of equimolar solutions was employed: a 5.0 × $10^{-4}$ M standard solution of Cr(III) ion and ATDP, were used. A series of solutions was prepared in which the total volume of Cr(III) ion and NTDP was kept at 1.0 mL. The absorbance was measured at the optimum wavelength. The results indicate that 1 : 1 (Cr(III) : ATDP) complex is formed.

The stability of the complexes was evaluated. The formation of the complexes was rapid and the orange color was stable at least for 15 h without any change in color intensity and with the maximum absorbance at room temperature. The conditional stability constant of the complex was calculated from the continuous variation data using the Harvey equation [39]. The conditional stability constant was found to be 6.06.

### 3.3. Effects of foreign ions

Various salts and metal ions were added individually to a solution containing Cr(III) and the proposed procedure was applied. The tolerance limit was set, as the diverse ion amount require causing ± 5.0 % error in the determination of Cr(III). The results obtained are given in Table 1. Under these optimized conditions, most of the probable concomitant cations and anions do not interfere. The tolerable levels of the some heavy metal ions are suitable for the analyte ions in the real samples examined in present study, because of the levels of transition metals in these samples are lower than their interferic level. The influences of Cr(VI) as concomitant ion were also investigated. As can be seen in Table 1, the recoveries of Cr(III) were not influenced till 100 µg/mL of Cr(VI).

### 3.4. Determination of total chromium

In order to determine total chromium, model solutions that contain different amounts Cr(VI) and Cr(III) were prepared. Then reduction of Cr(VI) ions to Cr(III) in the model solutions were performed by adding 2.0 mL of 0.05 M sodium sulfite solution. Then the procedure presented was applied to these solutions. The results are given in Table 2. The results show that the proposed method could be applied for the determination of total chromium.

**Table 1.** Influences of some ions on the recoveries of 2.0 µg/mL Cr(III)

| Ions | Added as | Concentration (µg/mL) | Recovery of $Cr^{3+}$ (%)[a] |
|---|---|---|---|
| $K^+$ | KCl | 10000 | 98.75 ± 0.75 |
| $Na^+$ | NaCl | 8000 | 99.00 ± 0.90 |
| $Mg^{2+}$ | $MgCl_2$ | 7500 | 101.67 ± 0.81 |
| $Ca^{2+}$ | $CaCl_2$ | 6000 | 101.16 ± 0.85 |
| $Cl^-$ | NaCl | 6000 | 101.33 ± 1.00 |
| $SO_4^{2-}$ | $Na_2SO_4$ | 5000 | 98.25 ± 1.01 |
| $PO_4^{3-}$ | $Na_3PO_4$ | 4500 | 100.50 ± 0.96 |
| $NO_3^-$ | $KNO_3$ | 4000 | 98.25 ± 0.77 |
| $F^-$ | NaF | 3000 | 102.40 ± 0.69 |
| borate | Na borate | 2500 | 101.67 ± 0.95 |
| Succinate | Na succinate | 2000 | 98.50 ± 1.07 |
| $Ag^+$ | $AgNO_3$ | 1250 | 98.25 ± 0.88 |
| $Cu^{2+}$ | $CuSO_4$ | 800 | 98.00 ± 1.10 |
| $Ni^{2+}$ | $NiSO_4$ | 650 | 101.33 ± 0.80 |
| $Cd^{2+}$ | $Cd(NO_3)_2$ | 600 | 101.67 ± 1.15 |
| $Al^{3+}$ | $Al_2(SO_4)_3$ | 500 | 98.50 ± 0.93 |
| $Fe^{3+}$ | $FeCl_3$ | 350 | 97.00 ± 0.81 |
| $Mn^{2+}$ | $MnSO_4$ | 250 | 103.50 ± 1.09 |
| $Co^{2+}$ | $CoSO_4$ | 200 | 102.50 ± 0.84 |
| $Zn^{2+}$ | $ZnSO_4$ | 150 | 97.50 ± 0.69 |
| $Pb^{2+}$ | $Pb(NO_3)_2$ | 120 | 97.25 ± 1.05 |
| $Cr^{6+}$ | $K_2Cr_2O_7$ | 100 | 97.00 ± 0.86 |

[a] Mean ± standard deviation.

### 3.5. Analytical characteristics

Table 3 summarizes the analytical characteristics of the optimized method, including regression equation, linear range and limit of detection. The limit of detection, defined as $CL = 3S_B/m$ (where $CL$, $S_B$, and $m$ are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 30 ng/mL. The relative standard deviation (RSD) and relative error for six replicate measurements of 2.0 µg/mL of Cr(III) was 0.86% and 1. 74% and for 4.0 µg/mL of Cr(III) was 1.33% and 1.14%, respectively.

**Table 2.** Determination of total chromium in spiked test solutions ($N$ = 5)

| Added (µg) | | Found [a] (µg) | | | Recovery (%)[a] | | |
|---|---|---|---|---|---|---|---|
| Cr(III) | Cr(VI) | Cr(III) | Cr(VI) | Total chromium | Cr(III) | Cr(VI) | Total chromium |
| 0.00 | 2.00 | 0.00 | 1.98 | 1.98 | -- | 99.00 | 99.00 |
| 0.50 | 1.50 | 0.49 | 1.52 | 2.01 | 98.00 | 101.33 | 100.50 |
| 1.00 | 1.00 | 1.01 | 1.01 | 2.02 | 101.00 | 101.00 | 101.00 |
| 1.50 | 0.50 | 1.48 | 0.49 | 1.97 | 98.67 | 98.00 | 98.50 |
| 2.00 | 0.00 | 2.01 | 0.00 | 2.01 | 100.50 | --- | 100.50 |
| 2.25 | 0.75 | 2.27 | 0.76 | 3.03 | 100.89 | 101.33 | 101.00 |
| 3.00 | 0.00 | 2.99 | 0.00 | 2.99 | 99.67 | ---- | 99.67 |

[a]: Average of six determinations

The sensitivities expressed as molar absorptivities, of the proposed methods are compared in Table 4 with those of published spectrophotometric methods. The higher sensitivity of the proposed method is notable, greater even than that of the all methods by at least eight times [40-46].

### 3.6. Analytical applications

The method was applied to the speciation of Cr(III) from Cr(VI) in natural water samples from a tap water from Benha City, a Nile river water from Shobra Al-Keima and a sea water sample from Raas el-Bare. Chromium species were also spiked to these samples. The results are given in Table 5. A good agreement was obtained between the added and measured analyte amounts. These results confirm the validity of the proposed method. The method could be applied successfully for speciation of trace amounts of chromium in both spiked and water samples. The relative standard deviations for water samples for Cr(III) and Cr(VI) were in the range of 1.3–3.7 % and 2.1–4.3%. Also the application of the proposed procedure for total chromium was performed to the microwave digested samples given in Table 6. The relative standard deviations for solid samples were in the range of 3.5–8.0%.

**Table 3.** Analytical features of the proposed method

| Parameters | Proposed method | Parameters | Proposed method |
|---|---|---|---|
| Amount of DMF | 0.5 | Regression equation [a] | |
| pH | 6.1 | Intercept | 0.004 |
| Optimum [ATDP] M | $2.0 \times 10^{-4}$ | Slope (µg/mL) | 2.0 |
| Reaction time (min) | 2.0 | intercept | - 0.005 |
| Beer's range (ng/mL) | 10 – 400 | Correlation coefficient (*r*) | 0.9992 |
| Ringbom range (µg/mL) | 0.3 – 3.70 | RSD [a] (%) | 0.87 |
| Molar absorptivity (L $mol^{-1}$ $cm^{-1}$) | $1.04 \times 10^{6}$ | Detection limits (ng/mL) | 3.0 |
| Sandell sensitivity (ng/cm) | 5.1 | Quantification limits (ng/mL) | 98.0 |

[a] A = a + bC, where C is the concentration in µg/mL and A is the absorbance units.

**Table 4.** comparative analysis with previously spectrophotometric methods of the chromium determination

| Reagent | Organic phase | $\lambda_{max}$ (nm) | $\varepsilon \times 10^{-4}$ L $mol^{-1}cm^{-1}$ | Interference | Ref |
|---|---|---|---|---|---|
| Diphenylcarbazid | – | 546 | 4.17 | Fe, Mo, V, Cu, Hg | [40] |
| Methyl violet | Benzene | 608 | 2.60 | – | [41] |
| Crystal violet | Butyl acetate | 598 | 8.00 | Oxidants | [42] |
| Pentamethylen- bis (triphenyl phosphonium) | Dichlorethane | 365 | 0.14 | W, Mo, Mn, $ClO_4$ | [43] |
| Triphenyl tetrazolium chloride | Dichlorethane | 250 | 3.03 | Hg | [44] |
| Iodnitrotetrazolium chloride | Dichlorethane | 250 | 8.8 | Hg | [45] |
| Tetrazol violet | Dichlorethane | 230 | 12.2 | Hg | [45] |
| Nitro bluetetrazolon chloride | Dichlorethane | 260 | 8.2 | Hg | [46] |
| hydroxylamine | pH 4.0 | 390 | 5.41 | W, Mo, Mn | [47] |
| 1,5-diphenylcarbazide | -- | 654 | 1.40 | Hg, Mo,Mn | [48] |
| 2-hydroxy-3-methoxy benz-aldehyde thiosemicarbazone | DMF | 385 | 0.120 | Fe, Pd, In | [49] |
| ATDP | Aqueous | 503 | 104.0 | | PM |

PM: Proposed method

**Table 5.** Determination Cr(III), Cr(VI) and total chromium in some natural water samples (*N*=5)

| Samples | Added (µg) | | Found (µg) | | | Recovery (%) | | |
|---|---|---|---|---|---|---|---|---|
| | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) | Total | Cr(III) | Cr(VI) | Total |
| Tap water from Benha City, Egypt | --- | --- | 0.22 | 0.40 | 0.62 | --- | --- | --- |
| | 0.3 | 0.5 | 0.522 | 0.91 | 1.432 | 100.38 | 101.11 | 100.85 |
| | 0.5 | 0.30 | 0.72 | 0.695 | 1.415 | 100.00 | 99.29 | 99.65 |
| | 0.4 | 0.4 | 0.616 | 0.81 | 1.426 | 99.35 | 101.25 | 100.42 |
| River water from Shobra AlKeima, Egypt | --- | --- | 0.43 | 0.88 | 1.31 | --- | --- | --- |
| | 0.5 | 0.75 | 0.925 | 1.627 | 2.552 | 99.46 | 99.82 | 99.69 |
| | 0.75 | 0.50 | 1.17 | 1.37 | 2.54 | 99.15 | 99.28 | 99.22 |
| | 0.6 | 0.6 | 1.02 | 1.48 | 2.50 | 99.03 | 100.00 | 99.60 |
| Sea water from Raas ElBare, Egypt | 0.2 | 0.3 | 0.51 | 1.13 | 1.64 | --- | --- | --- |
| | 0.30 | 0.20 | 0.818 | 1.333 | 2.151 | 100.99 | 100.23 | 100.51 |
| | 0.25 | 0.25 | 0.755 | 1.37 | 2.125 | 99.34 | 99.28 | 99.30 |
| | 0.20 | 0.30 | 0.717 | 1.433 | 2.15 | 100.99 | 100.21 | 100.47 |

**Table 6.** The level of total chromium in some real samples after application of the presented and GF-AAS procedures (*N*=5)

| Sample | Concentration (µg/g) | RSD (%) | t-test[a] | F-value[a] | GF-AAS |
|---|---|---|---|---|---|
| Tobacco | 1.48 | 2.74 | 1.34 | 2.87 | 1.45 |
| Coffee | 0.27 | 3.15 | 1.58 | 3.21 | 0.26 |
| Red tea | 0.18 | 2.48 | 1.21 | 2.58 | 0.18 |
| Green tea | 0.15 | 3.27 | 1.77 | 3.43 | 0.16 |
| Soil from Benha City | 24.7 | 1.98 | 0.84 | 2.46 | 24.5 |

[a]: The theoretical values of t- and F- at P = 0.05 are 2.57 and 5.05, respectively

The performance of the proposed method was assessed by calculation of the *t*-test (for accuracy) and *F*-value (for precision) [50] compared with AAS method. The results showed that the calculated values (Table 6) did not exceed the theoretical values. A wider range of determination, higher accuracy, and more stability and less time consumption shows the advantage of the proposed method over other methods. Also, there is no need for extraction or heating in the present method**.**

## 4. CONCLUSION

Chromium speciation can be determined efficiently with ATDP. The proposed methods have been applied to determine chromium in natural waters and total chromium in microwave digested tobacco, coffee, tea, and soil samples, with good results. The proposed method is simple and more sensitive than other methods commonly used at microgram level, in addition to lower tolerance limits.

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