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A new turn-on fluorimetric method for the rapid speciation of Cr(III)/Cr(VI) species in tea samples with rhodamine-based fluorescent reagent

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Abstract

A new fluorimetric method with rhodamine-based fluorescent agent was developed for the rapid speciation of Cr(III)/Cr(VI) in tea, soil and water samples. The system, which utilizes a fluorescent reagent, was used for the first time after synthesis/characterization of 3',6'-bis(diethylamino)-2-{[(1E)-(2,4-dimethoxyphenyl)methylene] amino}spiro[isoindole-1,9'-xanthen]-3(2H)-one (BDAS). The reagent responds instantaneously at room temperature in a 1:1 stoichiometric manner to the amount of Cr(III). The selectivity of this system for Cr(III) over other metal ions is remarkably high, and its sensitivity is below 0.01 mg L^{-1} in aqueous solutions which enables a simplification without any pretreatment of the real sample. The method has a wide linear range of 0.1-10 mg L^{-1} and a detection limit of 0.15 µg L^{-1} for Cr(III) while the relative standard deviation was 0.1% for 0.1 mg L^{-1} Cr(III) concentration. The results of detection and recovery experiments for Cr(III) in tea, soil and water were satisfactory, indicating that the method has better feasibility and application potential in the routine determination and speciation of Cr(III)/Cr(VI). The results of analysis of the certified reference material (INCT-TL-1 tea sample and CWW-TM-D waste water) are in good agreement with the certified value.

Keywords: Fluorescence reagent; Direct determination; Chromium speciation; Tea samples

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1. Introduction

Heavy metals are defined as metallic elements that have a relatively high density compared to water. With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids that are able to induce toxicity at a low level of exposure [1]. Heavy metal ion pollution poses severe risks for human health and the environment [2]. For this reason, the demand for fast, reliable analytical methods for determining different species of an element in real samples has rapidly increased because in most cases the different biological, nutritional or toxicological properties depend critically on chemical form or oxidation state [3-4].

Chromium (Cr) is a naturally occurring element present in the earth's crust, with oxidation states (or valence states) ranging from chromium (II) to chromium (VI) [5]. Chromium compounds are stable in the trivalent [Cr(III)] form and occur in nature in this state in ores, such as ferrochromite. The hexavalent [Cr(VI)] form is the second most stable state [6]. Elemental chromium [Cr(0)] does not occur naturally. Known to exist in all oxidation states from 0 to VI, Cr(III) and Cr(VI) are the forms most commonly found [7]. There are a number of predominant chromium species which may exist depending on solution pH [7-8].

Chromium contamination is widespread and occurs in a variety of industrial processes such as in the metallurgical, and chemical industries, electroplating, refractories, pigments, tanning industries, oxidative dying and cooling water towers [9]. Chromium is a "paradox" since it is classified as both biologically important and also as a toxic industrial hazard depending upon its oxidation state. Cr(III) is known to be an essential trace nutrient involved in the mechanism of action of the pancreatic hormone insulin and glucose metabolism [10]. No minimum daily requirement of chromium has yet been established, but 50-200 µg per day is considered adequate. Cr(III) is found in fruits, vegetables, meats, cereals and various other foods. A deficiency of this nutrient may lead to glucose intolerance [11].

Conversely, Cr(VI) is known to be carcinogenic and mutagenic. Unlike Cr(III), Cr(VI) may cross cellular membranes by way of non-specific anion carriers [12], causing skin ulcerations, nasal perforations, and lung cancer [13-14]. The subsequent reduction of Cr(VI) to intermediates such as Cr(IV) and Cr(V) is thought to play a role in its toxicity [15]. However, it is necessary to control the level of Cr(VI) in drinking water, where typical concentrations of total chromium are in the range 0.1–0.5 μg L^{-1} [14–17]. These facts show that speciation analysis of Cr, as well as its determination, is very important for its biological, food and also environmental evaluations.

There are a wide variety of techniques available for the speciation of dissolved chromium in real samples. They can be broadly divided into a number of categories, namely chromatography [16] ion-exchange [17], spectrometry [18-22], solvent extraction [20,23], voltammetry [24], and coprecipitation [25]. Most techniques have been found to give good recoveries in spiked samples of natural waters where the presence of interfering substances is likely to be minimal.

For the above reasons, a novel fluorescence analysis method for detecting Cr(III)/Cr(VI) was proposed in real samples without any preconcentration/separation step. The novel method for the determination of Cr(III) using the fluorogenic ligand 3',6'-bis(diethylamino)-2-{[(1E)-(2,4-dimethoxyphenyl)methylene] amino}spiro[isoindole-1,9'-xanthen]-3(2H)-one (BDAS) was used for the first time determination of Cr(III) using a home-made fluorimetry system and also the Cr(III)-binding properties of BDAS, a water-soluble, turn-on fluorescence-based reagent that exhibits high selectivity and sensitivity for Cr(III). The conditions of speciation and determination in the food samples were optimized; ion interference, detection limit, recovery experiments and real sample detections were conducted to evaluate the feasibility of the method.

2. Materials and methods

2.1. Apparatus

Fluorescence measurements were carried out in a home-made fluorimetry system equipped with a violet laser lamp. Instrumental parameters were controlled with a software program (Fig. 1) [26-27]. A Nel Electronic PH900 Model pH meter (Istanbul, Turkey) was used to measure pH values in the sample solutions. IR spectra (400–4000 cm−1) of the molecule was recorded on a Perkin Elmer Model 298 spectrophotometer. The ^{1}H and ^{13}C-NMR spectra were measured with a Bruker Avance III 400 MHz (Billerica, MA). The chemical shifts (δ ppm) were recorded in parts per million (ppm) down field from TMS (assigned as zero ppm). The purity of the tested compound was determined by combustion elemental analyses with a Leco-932 CHNS-O elemental analyzer (Kalamazoo, MI).

2.2. Reagents and standard solutions

All the reagents used were of the highest available purity and were used without further purification (Merck, Darmstadt, Germany). Cr(III) stock solutions (1000 mg L^{-1}) were purchased from Sigma. Deionized pure water was used for the preparation of the stock solutions. Working solutions were prepared from these stock solutions on a daily basis using 1.0 mol L^{-1} of HNO_3. Hydrochloric acid, sulfuric acid, ethanol and other chemical compounds were purchased from Merck. BDAS was firstly synthesized/characterized and used as a fluorescence reagent for the analysis of Cr(III). A solution of BDAS was prepared by dissolving 0.1 mg of the reagent in a 100-mL volumetric flask with ethanol. Throughout the study, the following acid solutions were prepared to adjust the sample acidity: hydrochloric, nitric and sulfuric acid (0.1-4 mol L^{-1}).

2.3. Synthesis of fluoresence reagent

2.3.1. Synthesis of compound 2-amino-3',6'-bis(diethylamino)spiro[isoindole-1,9'-xanthen]-3(2H)-one (RH)

To a 250-mL flask, rhodamine B (1.25 g, 2.5 mmol) was dissolved in 50 mL of ethanol. Next, 2.5 mL of 80% hydrazine hydrate was dissolved in 50 mL ethanol and added dropwise to the above 250-mL flask with vigorous stirring. The stirred mixture was refluxed until the solution became light orange. The mixture was then cooled, and the solvent was removed with a rotary evaporator. Next, 1 mol L^{-1} HCl (50 mL) was added to the solid in the flask to generate a clear red solution, and then 1 mol L^{-1} NaOH (55 mL) was added slowly with stirring until the pH of the solution reached 9–10. The pink precipitate was collected by filtration and washed three times with 25 mL of water. After drying in a vacuum oven, the reaction afforded 1.14 g (93.6%) of RH. [28-29]. The reaction scheme is shown in Fig. 2.

2.3.2. Synthesis of fluorescence reagent BDAS

A mixture of compound RH (1.14 g, 2.5 mmol) and 2,4-dimethoxybenzaldehyde (0.40 g, 2.5 mmol) in absolute ethanol (60 mL) was refluxed for 24 hours to obtain a pink-red precipitate. Next, the precipitate was filtered and washed three times with plenty of ethanol. The residue was dried to give the compound BDAS in 80% yield (1.20 g). M.p.: 178-179 oC. Anal. Calc. For C37H40N4O4: C, 73.49; H, 6.67; N, 9.28. Found: C, 73.24; H, 6.50; N, 9.10.

1H NMR (400 MHz, DMSO-d6): δ (ppm) = 9.00 (s, 1H, N=CH), 7.87-6.41 (m, 7H, Ar-H), 6.36 (dd, 6H, Xanthene-H), 3.74, 3.72 (s, 6H, OCH3), 3.34 (q, 8H, NCH2CH3), 1.06 (t, 12H, NCH2CH3). 13C NMR (100 MHz, DMSO-d6): δ (ppm) = 163.80, 163.00, 159.66, 153.15, 151.66, 148.82, 144.45, 133.96, 129.61, 129.09, 128.09, 126.36, 124.19, 123.23, 116.02, 108.39, 106.94, 106.02, 98.67, 97.71, 65.74, 56.19, 55.86, 44.10, 31.41, 14.69, 14.42, 12.85.

IR (ATR, cm-1): 2969-2835 (arom. and aliph. C-H), 1684 (C=O), 1614 (C=N), 1548, 1515 (C=C).

2.4. Synthesis and Characterization of Cr(III)-BDAS complex

The Cr(III)-BDAS complex was prepared by optimized conditions of BDAS reagent and Cr(III) using 1 mol L^{-1} of HNO_3. A solution of Cr(III) (1 mg L^{-1}) dissolved in EtOH (2 mL) was added dropwise to a solution of BDAS (3 mL 0.1% in EtOH) at room temperature. The purple solution was put aside so that the solvent would slowly evaporate. A purple product was formed within a few days and to eliminate the impurities on the Cr(III)-BDAS complex it was washed with deionized water and dried in the open air. The complex was characterized by FT-IR study. The reaction scheme is shown in Fig. 3

As can be seen from Fig. 3, the FT-IR study revealed that the characteristic stretching frequency of the amidic "C=O" of the rhodamine moiety at 1684 cm^{-1} is shifted to a lower wavenumber (1666 cm^{-1}) in the presence of 1 equiv. of Cr(III). This shift signifies a strong polarization of the C=O bond upon efficient binding to the Cr(III) ion, and in fact indicates cleavage of this bond. This indicates that the opening of the spirolactam ring in BDAS occurred in the presence of Cr(III). A possible mechanism of interaction between Cr(III) and BDAS is depicted in Fig. 3.

Cr(III)-BDAS in ethanol was based on optimum conditions and the stoichiometry of the synthesized complex was determined by the Job's plot method. The BDAS reagent gives the maximum fluorescence at 510.4 nm when using the new-home made fluorometric system while the Cr(III)-BDAS complex gives the maximum absorbance at 596.2 nm and the complex is pink in color. The reagent blank does not show any absorbance at this wavelength. The fluorescence intensity of the complex against the mole fraction of Cr(III) gave a graph that indicates the formation of the complex having a Cr(III) : BDAS ratio of exactly 1-1, which was assumed by using the mole-ratio method (see Fig. 3).

2.5. Preparation of the real samples

Real samples which included five different types of water namely tap water from Erciyes University and Bozok University campus, sea water from the Mediterranean and Black Sea (Alanya and Zonguldak) and storage water (Yozgat), were collected in clean amber bottles. The water samples were filtered, except for tap water, before analyses.

The presented procedure for the speciation of Cr(III) and Cr(VI) species based on the fluorimetric method was applied to various real samples. The tap water, sea water and storage water, soil, and also various tea samples were used as real samples. The tap water samples were collected from Erciyes University and Bozok University campus laboratory and analyzed without pretreatment. The sea water samples from the Mediterranean and Black Sea (Alanya and Zonguldak) and storage water (Yozgat), were collected in prewashed polyethylene bottles. All the other water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 m pore size except for tap water and analyzed as given in Section 2.6.

A 0.1-g aliquot from each of the tea and soil samples was treated with 10 mL of concentrated HNO_3 and then heated until a clear solution was obtained. The process continued until complete evaporation and 10 mL of concentrated HNO_3 was added once more to the moist residue. Afterwards the mixture was completely evaporated and then 2 mL of concentrated H_2O_2 was added to it. After completing the dissolution process, the sample solution was filtered through a cellulose filter paper. The filter paper was washed with 1–2 mL of 0.1 mol L^{-1} HNO_3. The filtrate was diluted to 25 mL with 0.1 mol L^{-1} of HNO_3. These sample solutions were treated by the proposed procedure described below. The final measurement volume of the sample solutions was 5 mL. A blank digest was carried out in the same way.

From the certified reference material (INCT-TL-1 tea leaves), a 0.1-g amount of tea leaves was dissolved in a mixture of 10 mL of concentrated HNO_3 and 2 mL of concentrated H_2O_2 on a hot plate. After completing the dissolution process, all the sample solutions became clear. The volume of the samples was diluted to 25 mL with 0.1 mol L^{-1} of HNO_3. These sample

solutions were analyzed by using the proposed procedure described in *Section 2.6 and 2.7*. The final measurement volume of the sample solutions was 5 mL. The concentration of the investigated Cr(III)/Cr(VI) in the final measurement solution was determined by the home-made fluorimetry system.

2.6. General procedure for Cr(III)

The method was tested firstly by using model solutions, prior to application to the real samples. Under the optimized experimental conditions, aliquots of 5 mL of sample solution, which were adjusted to the optimum 0.1 mol L^{-1} HNO_3, containing 0.1 mg L^{-1} Cr(III) were placed into 15-mL test tubes. Then 2.5 mL of 0.1% BDAS fluorescence reagent in ethanol solution and 1 mL of 0.25% (w/w) sodium dodecyl sulfate (SDS) solution were added to the sample solution. A pink colored Cr(III)-BDAS complex solution was formed in the test tube. In this step, Cr(III) reacted with the BDAS reagent and the complex formed. Then, the sample volume was diluted up to 5 mL using 0.1 mol L^{-1} HNO_3. In order to determine the Cr(III) in the solution, the complex was introduced to the home-made fluorometry system. The Cr(III) signals were measured in the peak height mode utilizing the instrument software. The calibration graph was constructed against aqueous standards by using to the same procedure. Blank determinations were carried out in exactly the same way as the measurements made for the sample and calibration standards. All the experiments were performed in at least triplicate (n = 3) or more.

2.7. Determination of total chromium

In order to determine the total chromium, test solutions containing 0.1 mg L^{-1} each of Cr(III) and Cr(VI) were prepared. In order to reduce Cr(VI) ions to Cr(III) ions in the test solutions, 0.25 mL of 1 mol L^{-1} HNO_3 and then 1 mL of 0.1% (w/v) hydroxylamine hydrochloride were added to the test solution. The solution was allowed to stand at room

temperature for 10 min. After the reduction of Cr(VI) to Cr(III), the acidty of the sample was adjusted to 1.0 using HNO_3 and the volume of the solution made up to 5 mL with HNO_3. The described procedure was applied and total chromium was determined by the fluorimetric method. The concentration of Cr(VI) in samples was calculated by subtracting the concentration of Cr(III) from the total chromium concentration.

3. Results and discussion

3.1. Effect of acidity

In order to evaluate the effect of acidity on the fluorescence signal of the Cr(III)/Cr(VI)-BDAS complex, the effect of acidity was studied. For this reason, sample solutions were acidified from 0.5 to 3 mol L^{-1} with HNO_3, HCl and H_2SO_4, and processed according to the recommended procedure.

The fluorescence intensity of Cr(III) was maximum at around 0.1 mol L^{-1} of HNO_3,while Cr(VI) did not give any signal for the BDAS reagent. These results show that both the chromium species could be determined quantitatively at 0.1 mol L^{-1} of HNO_3. In all subsequent studies for the separation/speciation of Cr(III)/Cr(VI) ions, 0.1 mol L^{-1} of HNO_3 was used as optimum. Therefore, the acidity of the system that would give the maximum complex formation was studied by measuring the fluorescence intensity of Cr(III)/Cr(VI)-BDAS in 0.1 mol L^{-1} of HNO_3. As can be seen from Fig. 4, 0.1 mol L^{-1} of HNO_3 was chosen as the optimum concentration for further studies.

3.2. Effect of the surfactant

The surfactant, sodium dodecyl sulfate (SDS), was used to shift the fluorescence intensity of the Cr(III)-BDAS complex. It was observed that SDS shifted the maximum fluorescence peak of the BDAS alone when compared to the complex. The shifts may account for the greater

solubilization of the BDAS in the presence of SDS compared to the complex. These results indicate that favorable solubilization is brought about by non-ionic surfactants. Throughout the study, the SDS amount used was 1 mL of 0.25% SDS.

3.3. Effect of the time on the complexation

The influence of complexation time in the fluorimetric method of Cr(III) and Cr(VI) using the BDAS reagent was also studied. The effect of complexation time was studied over the range of 0–180 min, while the other experimental conditions remained constant. The obtained results indicated that complexation time had no significant impact on complexation efficiency. The complexation of Cr(III) with BDAS is a very fast reaction, showing a high luminescence signal, while Cr(VI) did not give any signal with BDAS. The optimum complexation time was assigned as 0.5 min in is study. Therefore, this method is time independent, which is its most important advantage. In this method, the most time-consuming step is the centrifuging of the sample solution during the process.

3.4. Effect of the amount of the BDAS

The effect of the amount of complex-forming fluorescence reagent (BDAS) 0.1% (w/v) on the recovery efficiency of the fluorimetric method for the determination of Cr(III) and Cr(VI) was investigated for amounts of reagent varying from 0.0 to 4.0 mg. The results showed that the Cr(III) signals sharply increased up to 2.5 mg of the reagent and gave the maximum peak around 2.5 mg BDAS. Then the Cr (III) signal sharply decreased after 2.5 mg while Cr(VI) did not give any signal for any concentrations of BDAS. Therefore, a selected amount of the BDAS (2.5 mg) was used because of satisfying Cr(III) recoveries (see Fig. 5).

3.5. Effect of temperature on complexation

The effect of temperature (range: 0–50°C) on the Cr(III)–BDAS complex formation was also investigated. Increasing the reaction temperature from 0 to 10°C did not significantly affect the signal; unlike at temperatures higher than 20°C, decreased fuorescence intensity was observed in the sample solutions (Fig. 6). This negative effect caused by temperature may be perhaps due to the thermo-coagulation of the sample solution, with the formation of a precipitate which could incorporate the complex, interfering with it in the sample medium. As can be seen in Figure 8, the optimum temperature was chosen as 10°C.

3.6. Effect of interferences

The effect of interferences on the determination of the two chromium species (Cr(III)/Cr(VI)) was investigated using the optimized fluorimetric method -speciation procedure. The possible interfering metal ions were added individually to the model solutions containing 0.5 mg $L^{-1}$from both Cr(III) and Cr(VI) ions and then the proposed procedure was applied. The effect of each interfering species was considered as interference when the analytical signal in the presence of the species resulted in an absorbance deviation of more than ±5%. The results are shown in Table 1. The results indicate that various substances commonly present in water and/or waste water samples do not interfere in the analysis of these two chromium species under the experimental conditions.

3.7. Analytical features

Under the optimum experimental conditions, a linear relationship between the fluorescence intensity and Cr(III) concentration was obtained in the range of 0.1–10 mg L^{-1}. The calibration equation was $I = 158.86C + 0.579$ with a correlation coefficient (R^2) of 0.9998. The reproducibility of the method was checked by measuring a 0.1 mg L^{-1} chromium(III) standard ten

times, and relative standard deviation values of 0.1% were obtained. The detection limit according to the signal-to-noise ratio of 3Sb/m, where Sb is the signal of the blank (n = 21) and m is the slope, was 0.15 μg L^{-1}. The quantification limit, according to the signal-to-noise ratio of 10Sb/m, was about 1.5 μg L^{-1}.

3.8. Analytical application

The proposed was successfully applied to the determination of total chromium in some tea samples, soil and coffee samples (Table 2).

The proposed method was also applied for the determination of Cr(III) and Cr(VI) in some water samples. Preparation of the samples to be analyzed was performed as described above in *Section 2.5*. The results are shown in Table 3.

The recovery studies for chromium(III) were performed in storage water samples. The known amounts of chromium(III) were spiked to the sample solutions in order to estimate the accuracy of the presented procedure (Table 4). Good agreement was obtained between the added and found the Cr(III) contents using the recommended procedure. As shown in Table 4, all of the samples gave recoveries ranging from 95 to 100%.

The validation of our proposed method was conducted by analyzing a certified standard (INCT-TL-1 tea sample and CWW-TMD waste water) (Table 4). The results in this study demonstrate that the novel fluorescence reagent called BDAS can be used for the speciation without any separation and preconcentration determination of μg L^{-1} levels of Cr(III) in samples with high salt contents.

4. Conclusion

The development of a simple, sensitive and selective fluorimetric method for the determination of Cr(III)/Cr(VI) ions based on their complexation with BDAS has been described

herein. The complex was monitored at λem = 596.2 nm and λex = 405 nm. The proposed method was applied for the analysis of chromium ions in various tea, soil and water samples and was found to exhibit a low detection limit. The data from the presented method have been compared with those of recently reported methods on speciation of chromium (Table 5). Some parameters obtained are comparable to those presented by the other methods. The robustness of this method was checked by analyzing a certified chromium standard material, whereby excellent agreement was observed. The advantage of using BDAS as a fluorogenic ligand for the analysis of chromium is that it exhibits attractive luminescence properties. We firstly designed and developed a novel fluorescence reagent which has functional nitrogen and carbonyl groups with donor centers and receptors acting as binding sites for Cr(III). It absorbs and emit slight at relatively long wavelengths and hence will be advantageous in eliminating matrix interference from short emitting species in real samples.

Above all, this new home-made fluorimetric system minimizes the analysis time and manpower needed in laboratories compared to other off-line and on-line systems. The proposed method could be used for routine analyses in clinical laboratories for accurate determination of Cr(III) in aqueous or biological fluids.

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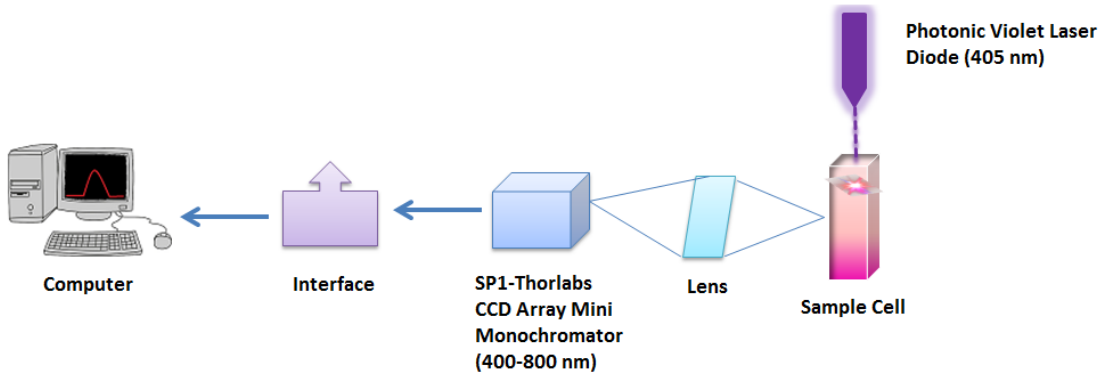


Fig. 1. Home-made fluorimetry system and its operation steps.

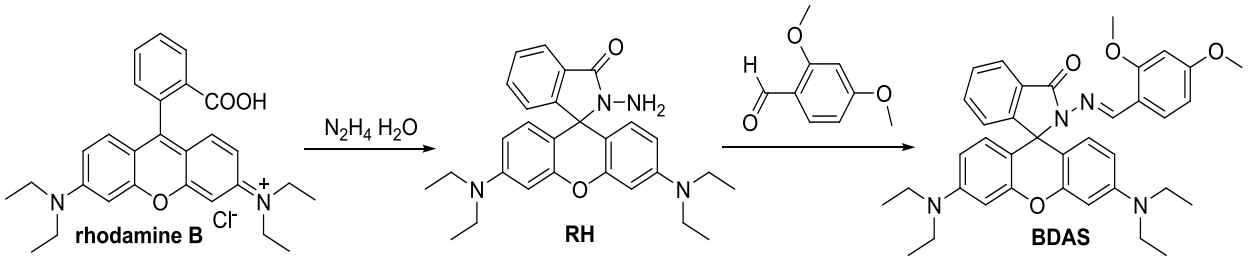


Figure 2. Chemical structure of the BDAS reagent

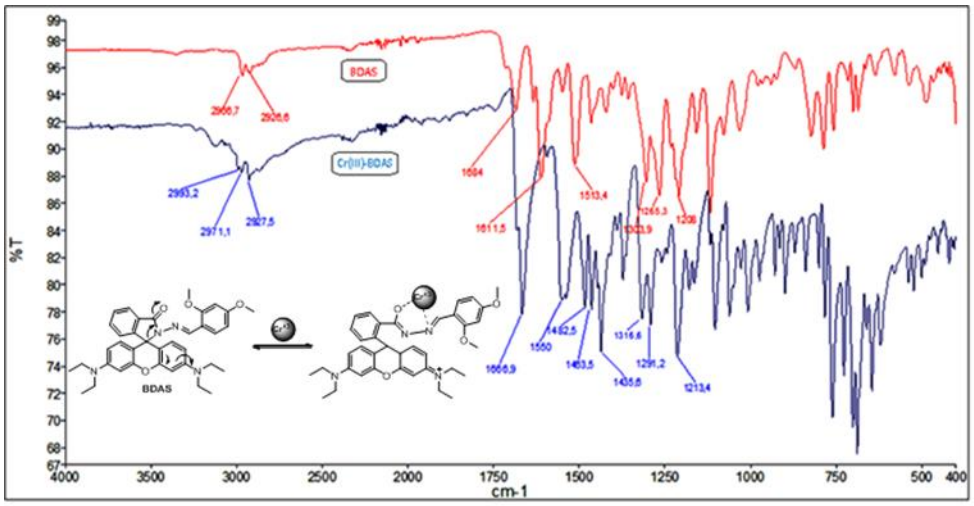


Figure 3. The IR spectra of the BDAS and the Cr(III)-BDAS complex.

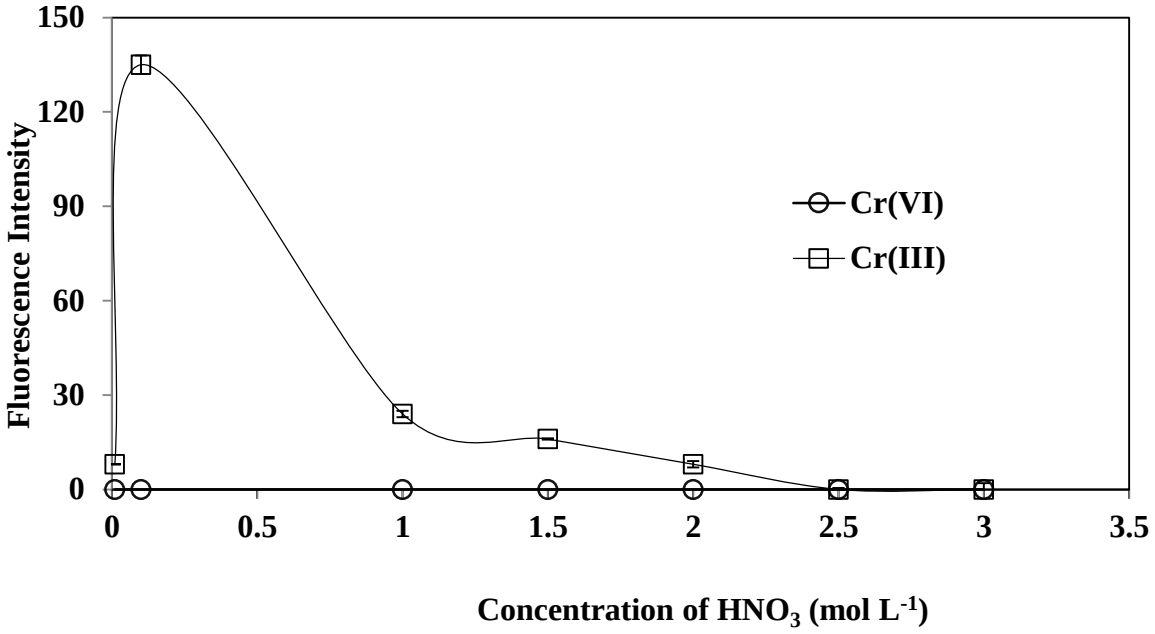


Figure 4. Effect of acidity on Cr(III) and Cr(VI) signal (n = 3).

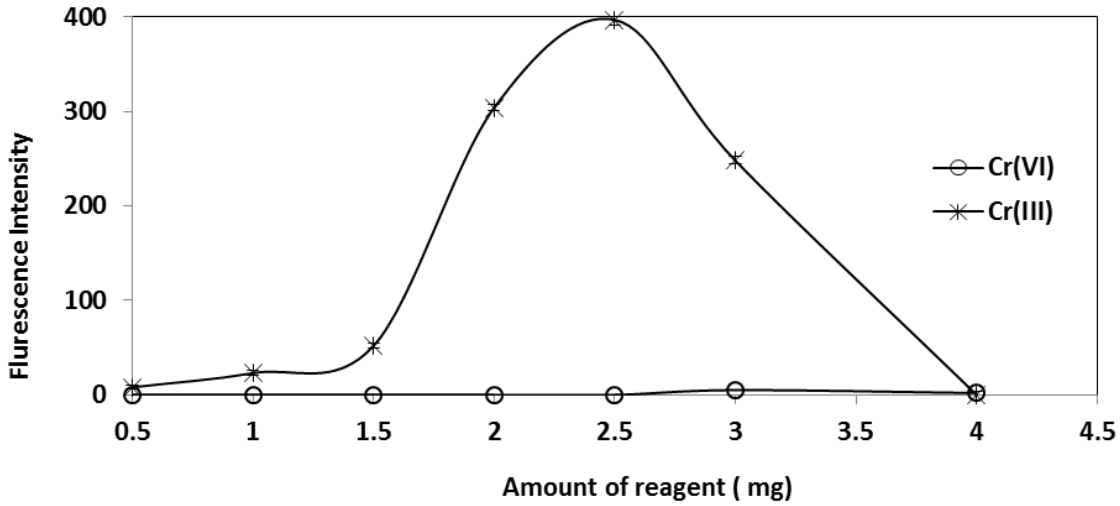


Fig. 5. Effects of the amount of the BDAS on the Cr(III) and Cr(VI) ions (n = 3)

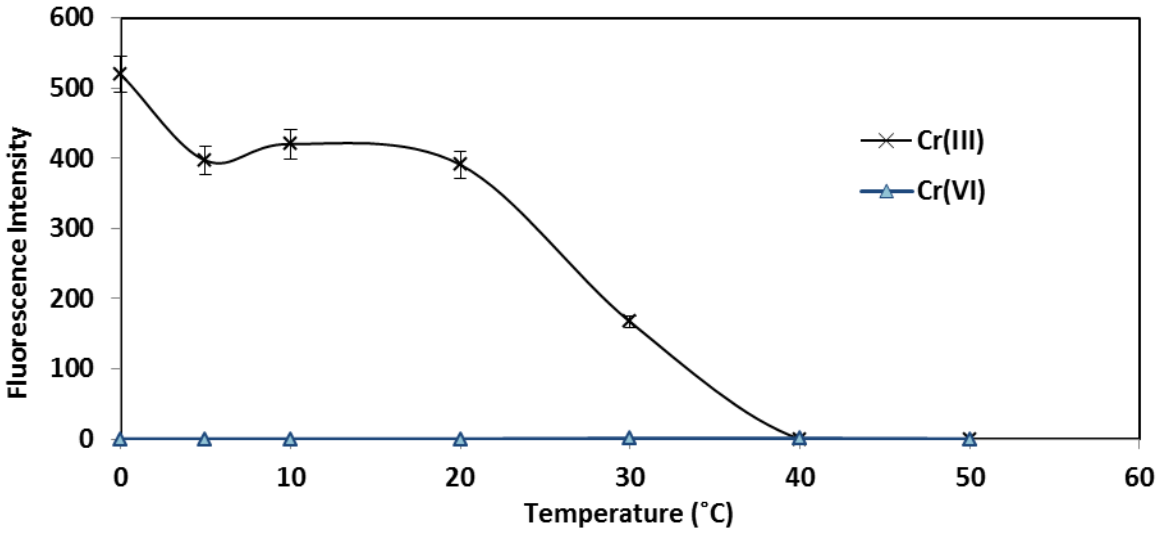


Fig. 6. Effect of the temperature on the Cr(III)/Cr(VI) signals (n = 3).

Table 1.

The effect of interfering substances on the recovery of Cr(III) ions (n = 3).

Matrix ions	Added as	Concentration (mg L^{-1})	Recovery (%)
Na^+	NaCl	750	99 ± 1[a]
K^+	KNO_3	1500	96 ± 2
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	6000	100 ± 1
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	1600	98 ± 2
SO_4^{2-}	Na_2SO_4	400	102 ± 2
Cl^-	NaCl	7000	97 ± 1
Mg^{2+}	$Mg(NO_3).6H_2O$	1600	98 ± 2

[a]Average of three measurements ± standard deviation.

Table 2.

Conecentration of total chromium in some tea, coffee and soil samples (n = 3)

Sample	Total chromium (mg kg^{-1})
Mate leaf tea	0.09 ± 0.02[a]
Package mate tea	0.60 ± 0.10
Rosehip tea	0.52 ± 0.21
Package rosehip tea	0.73 ± 0.25
Camomile	1.21 ± 0.50
Package camomile tea	-
Linden tea	0.71 ± 0.20
Package linden tea	-
Fennel tea	0.96 ± 0.20
Package fennel tea	0.45 ± 0.10
Nettle tea	0.71 ± 0.20
Package nettle tea	0.54 ± 0.10
Form tea	0.96 ± 0.15
Cinnamon tea	0.05 ± 0.01
Lioness tea	1.24 ± 0.60
Thyme tea	0.09 ± 0.02
Processed black tea	0.23 ± 0.01
Unprocessed tea leaf	0.36 ± 0.15
Black cabbage	-
Turkish caffee	0.15 ± 0.09
Artificial fertilized soil	0.20 ± 0.06
Natural fertile soil	-

[a]Average of three measurements ± standard deviation.

Table 3.

Speciation of Cr(III), Cr(VI) and total chromium in various water samples (mg L^{-1}, n = 3).

Water samples	Cr(III)	Cr(VI)	Total chromium
Tap water[1]	0.75 ± 0.3[a]	0.50 ± 0.08	0.8 ± 0.2
Tap water[2]	0.75 ± 0.3	-[b]	0.75 ± 0.3
Sea water (Alanya)	0.5 ± 0.1	0.17 ± 0.05	0.67 ± 0.3
Sea water (Zonguldak)	0.6 ± 0.3	0.12 ± 0.06	0.72 ± 0.4
Storage water	0.85 ± 0.5	0.17 ± 0.03	1.02 ± 0.4

[1]Bozok University

[2]Erciyes University

[a]Average ± standard deviation.

[b] Below the detection limit.

Table 4.

The determination of Cr(III) in various water samples after the application of the presented procedure (n = 3).

Sample	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
Storage water	-	0.85 ± 0.3	
	0.1	0.95 ± 0.2	95 ± 3
	-	0.85 ± 0.3	
	0.2	1.04 ± 0.6	95 ± 2
	-	0.85 ± 0.3	
	0.5	1.34 ± 0.5	98 ± 2
	-	0.85 ± 0.3	
	1.0	1.8 ± 0.6	95 ± 3

Sample	Certified value (mg kg^{-1})	Found (mg kg^{-1})	Recovery (%)
INCT-TL-1 tea sample	1.91 ± 0.22	1.899 ± 0.2	99 ± 1

Sample	Certified value (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
CWW-TMD Wastewater	1.00 ± 0.05	0.997 ± 0.3	100 ± 3

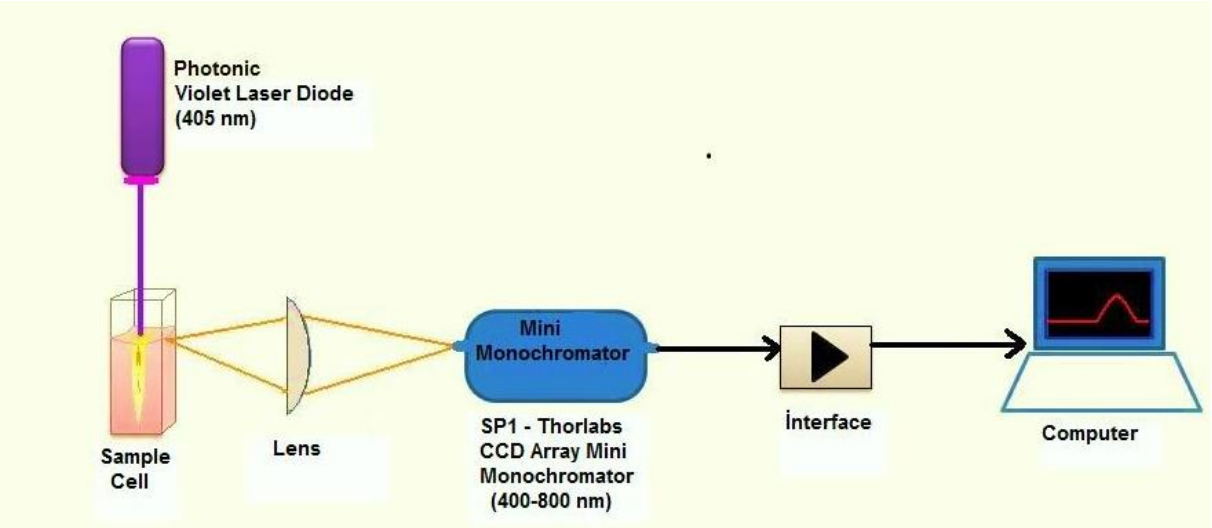
[a]Average of three measurements ± standard deviation.

Table 5

Comparison of the results of the proposed method with the other published works for the determination of chromium species.

Method/ Technique	Samples	Reagent	Detection limit (mg L^{-1})	RSD / (%)	PF[a]	Reference
Electrothermal atomic absorption spectrometry (ETAAS)	Tap water, well water, mineral water, urine samples.	1-undecanol containing 2-thenoyltrifluoroacetone	6	5.1	333	30
On-line flow injection-Flame atomic absorption spectrometry	Tannery and plating-bath effluents	C18 bonded silica gel	0.02	3.5-5.1	90/100	31
On-line flow injection (FI) preconcentration-(ETAAS)	Drinking water samples	Activated carbon	3000	4	-	32
Flame atomic absorption spectrometry	Natural water sample	Ammonium pyrrolidine dithiocarbamate	0.9	9	100	33
Solid Phase Extraction-HPLC	Standard reference water sample	Ammonium pyrrolidine dithiocarbamate	0.5	5	50	34
Direct determination/ Fluorimetry method	Tea samples	BDAS	0.15 (µg L^{-1})	0.1	-	This work

[a]PF = Preconcentration factor



Graphical abstract

Highlights

A new fluorogenic ligand was firstly used for the determination of Cr(III)/Cr(VI) using the a home-made fluorimetry system. > The system was firstly used. > The method was applied for the determination of some food samples without preconcentration/separation.