Technical paper

A New Method for Indirect Determination of Iodide and Thiosulfate in Table Salt and Milk Based on a Combination of Solid-Phase Extraction and Flame Atomic Absorption Spectrometry

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Abstract

A new indirect method for the determination of iodide and thiosulfate ions in table salt and milk by flame atomic absorption spectrometry was described. This method is based on the reduction of chromium (VI) to chromium(III) with the reducing action of iodide and/or thiosulfate, separation of unreacted Cr(VI) as its 1,5-diphenilcarbazide complex on a column filled with Amberlite XAD-16, elution of the complex by 10 mL of 0.05 mol L^{-1} H_2SO_4 in methanol and determination by flame atomic absorption spectrometry. Amount of the analytes were calculated from the amount of Cr(VI) reacted with the analytes. The optimum conditions for the determination of iodide and thiosulfate ions, including pH and volume of sample solution were examined. The effect of interfering species on the recovery of the iodide and thiosulfate ions was also investigated. The precision of the proposed method is good as it provides relative standard deviation value of 3.5% for thiosulfate and 4.5% for iodide during five replicate determinations of 10 μg mL^{-1} of thiosulfate and 15 μg mL^{-1} of iodide, respectively. The accuracy of the procedure was tested by analyzing spiked real samples and certified reference sample (BCR 150 Milk powder). The procedure described was successfully applied for the determination of iodide in table salt and milk and, thiosulfate in table salt. Iodide and thiosulfate ions have been determined in real samples with relative error below 15%.

Keyword: Iodide, thiosulfide, flame atomic absorption spectrometry, Amberlite XAD-16, indirect determination

1. Introduction

Iodine exists mainly as iodide and iodate along with a small fraction of organic iodine compounds in foods, seawater etc. Iodine was used first commercially in the form of potassium iodide as remedy for goiter, and as a iodoform, which was used as disinfectants for cuts and for sanitation.[1] Iodine is widely used in catalysis as a catalyst, in some manufacturing processes as stabilizer, in foods as additives (iodization of salt and mineral mixtures). Addition of iodine to table salts is part of a preventive program for iodine deficiency disorder in many countries. Salts are commonly iodized with potassium iodide. The average iodine level of liver oil, soil, drinking water and seawater is about 69000 mg kg^{-1}, 2.8 mg kg^{-1}, 8–11 μg L^{-1} and 50 μg L^{-1}, respectively.[1] Iodine is a biologically essential element as a constituent of thyroid hormones and its deficiency in the human body causes goitre and other malfunctions. The normative daily iodine requirement of adult men was found to be 1 ng g^{-1} body weight.[1] Iodine is ingested into an organism in food, hence monitoring of iodine intake from this resource is important.[2] Iodized salt, milk, eggs, dairy products and marine fish are the main sources of iodine to food chain. The above sources supply 74% of iodine intake, while 16% is supplied by vegetable food and 10% by beverages.[1] The iodination of industrially used salt raised the iodine content of industrial foods such as bread and sausage. The greatest contributors of iodine to humans are animal foodstuffs (75%) and vegetable foodstuffs (15%).

The detection and quantitative determination of iodine in high concentrations is possible by precipitation of AgI, PdI_2 and HgI_2 or by Volhard method. However, in lower concentrations these methods are insufficient. In biological materials, iodine determinations have been carried

out on the basis of Sandell-Kolthoff technique during the past 60 years.[1–3] This technique is based on the reaction of Ce(IV) and As(III) catalyzed by iodide anion and spectrophotometric measurement. Nowadays, iodine is determined by using inductively coupled plasma mass spectrometry (ICP-MS),[4] inductively coupled plasma optical emission spectrometry (ICP-OES),[2–5] energy dispersive X-ray fluorescence analysis,[6] chromatographic methods,[7,8] electrochemical methods,[9,10] spectrophotometric methods,[11,12] neutron activation analysis[13] are also used for the determination of iodine.

Thiosulfate is an oxyanion of sulfur produced by the reaction of sulfite ions with elemental sulfur in boiling water. Thiosulfate occurs naturally in hot springs and geysers, and is produced by biochemical processes. Thiosulfates are stable only in neutral or alkaline solutions, but not in acidic solutions, due to decomposition to sulfite and sulfur. Thiosulfate is used in paper industry to halt bleaching, in leather industry, in textile industry to set dye, in photography to dissolve the silver salts from photographic film and in various chemical processes as chlorine-removing agent. The determination of thiosulfate, sulfite and sulfide in their mixtures is difficult because they are labile and participate in complex equilibria with other sulfur compounds formed by their auto-redox reactions.[14] Unfortunately, there are few measurement methods available at or below μg g^{-1} levels for simultaneous determination of these compounds, especially in complex matrices. Various instrumental methods, such as spectrophotometry,[15,16] amperometry,[17] voltammetry,[18] polarography,[19] ion-exclusion chromatography,[20] capillary electrophoresis,[21] ion chromatography[22] and high performance liquid chromatography[23] have been proposed for the determination of thiosulfate.

The above mentioned methods are sensitive to the determination of both iodide and thiosulfate. However, some of them have disadvantages such as their high cost, often tedious, complicated and/or time-consuming, and proneness to interferences. Recently, indirect determinations of thiosulfate and especially iodine by atomic absorption spectrometry are widely used.[24–28] It is recognized that flame atomic absorption spectrometry (FAAS) should be preferred to above methods if both of these methods can be applied for any sample due to some advantages of this method such as low cost, short time of analysis, and simplicity. Atomic absorption spectrometer is analytical instrument available in most analytical laboratories. This technique has been proved as suitable tool for the indirect determination of organic compounds, increasing the range of species accessible with such spectrometers. Bermejo-Barrera et al. proposed an indirect method for the determination of iodide.[25] In that study, the iodide contained in the sample is oxidized to iodine, which is distilled by means of microwave energy and reduced back to iodide. This iodide is combined with Hg(II) and 2,2'-dipyridyl to give an ion pair, which is selectively extracted into isobutylmethylketone (IBMK). Mercury is determined in the extract by electrothermal atomic absorption spectrometry (ETAAS) in order to determine iodide. In another study, a method to determine iodide is developed, based on the formation of an ion pair between 1, 10-phenanthroline, mercury(II) and iodide that can be selectively extracted into IBMK. IBMK layer was analyzed by ETAAS for mercury and then iodide was quantified.[26] Haase and Broekaert used the interference caused by iodide in the determination of mercury by FI-CVAAS for indirect determination of iodide.[28] Yebra and Cespon proposed an indirect flow injection atomic absorption spectrometric method for the determination of iodide in tap and sea water based on the reduction of Cr(VI) to Cr(III) in acid medium.[29,30] The Cr(III) formed was retained online, proportional to the iodide concentration in the sample, on a poly(aminophosphonic acid) chelating resin, which is only selective for this oxidation state. Reduced Cr(III) was preconcentrated on the column, eluted with HCl solution and determined by FAAS. The proposed method allows the determination of iodide in the 6–220 μg L^{-1} range with a relative standard deviation of 2.7%.[29]

This paper describes a new method for the indirect determination of thiosulfate and iodide in table salt and milk based on a combination of solid-phase extraction and flame atomic absorption spectrometry. It was based on the reduction of a known excess amount of Cr(VI) by iodide and thiosulfate followed by the separation of non-reduced Cr(VI) from product of Cr(III) by a column solid phase extraction as its diphenylcarbazide (DPC) complex and determination of the non-reduced amount of Cr(VI) in the eluent by FAAS. Separation and speciation of Cr(VI) and Cr(III) by solid phase extraction on a column filled with Amberlite XAD-16 had been optimized in our previous study.[31] Here, various analytical parameters such as sample volume, flow rate and pH were optimized. The proposed method has already been applied to the indirect determination of ascorbic acid in some drug and fruit juice samples successfully before.[32] In this study, the developed chromium speciation method was adapted for the determination of iodide and thiosulfate and optimum experimental conditions were investigated. The developed method was applied for the determination of iodide in table salt and milk, and thiosulfate in table salt.

2. Experimental

2. 1. Instrumentation

A Philips PU 9285 model atomic absorption spectrometer equipped with deuterium lamp background corrector and with an air acetylene burner was used for the analysis under the conditions suggested by the manufacturer. Chromium hollow cathode lamp was used to measure the absorbance of chromium. The operating conditions

were as follows: Wavelength, 357.9 nm; lamp current, 12 mA; bandpass, 0.5 nm and fuel flow rate, 1.4 L min^{-1}. Deuterium lamp background correction was used. All pH measurements were made with a Consort digital pH meter and a combined glass electrode.

2. 2. Reagents

All solutions were prepared using analytical reagent grade chemicals unless otherwise specified and doubly distilled deionized water. Standard solutions of iodide and thiosulfate ions, 1000 μg mL^{-1}, were prepared daily by dissolving 0.1307 g of KI (Merck) and 0.2214 g of $Na_2S_2O_3.5H_2O$, respectively in water and diluted to 100 mL with water in a volumetric flask. 1,5-diphenylcarbazide (DPC) solution (0.01 mol L^{-1}) was prepared daily by dissolving appropriate amount of DPC (Merck) in 5 mL of acetone (Merck) and diluting to 25 mL with water. The solution was kept in an amber-glass bottle. A solutions of 1000 μg mL^{-1} Cr(VI) was prepared by dissolving 0.2829 g of $K_2Cr_2O_7$ (Merck) in water and diluted to 100 mL with water in a volumetric flask. H_2SO_4 (95–98%, Merck) and methanol (Merck) were used. Amberlite XAD-16 Resin (Room and Hass; surface area, 800 m^2 g^{-1}; wet mesh size, 20–60 mesh) was used after washing with methanol, 1 mol L^{-1} HCl solution and water, respectively and dried for 2 h at 60 °C.

2. 3. Column Preparation

A glass column (150 mm length 10 mm i.d) with a glass-wool over its stopcock was used as a mini column. A total of 300 mg of Amberlite XAD-16 resin was added in water and then the slurry obtained was placed into the column to obtain a bed height of about 1.5 cm. A small amount of glass-wool was placed on top to avoid disturbance of adsorbent during sample passage. The column was preconditioned by passing a blank solution having same pH with the sample solution prior to use. After each use, the resin in the column was washed with dilute HCl and with water, respectively and stored in water for the next experiment.

2. 4. Preparation of Samples

Commercially available table salt was used as sample. As it was known that table salt contains both iodide and thiosulfate, sample solution was prepared in two different ways: (1) 5.000 ± 0.001 g of salt sample was weighed in 50 mL volumetric flask, and 20 mL of deionized water and 5 mL of 1 mol L^{-1} H_2SO_4 were added to dissolve the sample. The solution was diluted to 50 mL with water to obtain 0.1 mol L^{-1} H_2SO_4. This sample was used for thiosulfate determination. (2) 5.000 ± 0.001 g of salt sample was weighed in 50 mL volumetric flask, and 20 mL of deionized water and 2.7 mL of concentrated H_2SO_4 (d = 1.84 g mL^{-1}, 98% m/m) were added to dissolve the sample. It was diluted to 50 mL with water to obtain 1 mol L^{-1} H_2SO_4. This sample was used for the determination of total content of iodide and thiosulfate.

Two packages of pasteurized milk (totally 2 L of milk) were purchased from the local market. Then, two packages of milk was poured into a 2 L beaker and mixed thoroughly. 200 mL of milk sample was taken into a 250 mL beaker and 10 mL of concentrated HCl was added to the sample to precipitate proteins. After the precipitations completed, the obtained mixture was filtered through Schwarzband filter paper (Carl Schleicher & Schüll). The filtrate was evaporated until the volume decreased to about 50 mL. By adding concentrated sulfuric acid to the filtrate, concentration of sulfuric acid was adjusted to about 1 mol L^{-1}. This sample was used for the determination of iodide by the procedure given below.

Accurately weighted (about 5 g) amount of certified reference material (BCR 15 Milk powder) was treated with 4 mL of water and 0.5 mL of concentrated HCl to precipitate proteins. Then, the obtained mixture was filtered through Schwarzband filter paper (Carl Schleicher & Schüll). By adding concentrated sulfuric acid to the filtrate, concentration of sulfuric acid was adjusted to about 1 mol/L. This sample was used for the determination of iodide by the procedure given below.

2. 5. Procedure

In order to prepare synthetic spiked sample solution, 1.2 mL of 100 μg mL^{-1} Cr(VI), 10 mL of 15 μg mL^{-1} iodide (or 10 mL of 10 μg mL^{-1} thiosulfate) and 1 mL of 0.01 mol L^{-1} DPC solution were added into a 100 mL volumetric flask and the volume is adjusted to 100 mL with water. For the analysis of real samples, 10 mL of prepared sample solutions was taken instead of the solution of iodide and/or thiosulfate ions. Then, pH of the sample solution was adjusted to the desired value (pH = 1) at which the recovery of Cr(VI) is the highest with sulfuric acid. The resulting solution was passed through the column at the desired flow rate (1.5 mL min^{-1}). The retained chromium (VI)-DPC complex on the column was eluted with 10 mL of 0.05 mol L^{-1} H_2SO_4 solution in methanol. Chromium content in the eluate was determined by FAAS. Iodide and thiosulfate content were calculated by using stoichiometric relationship between Cr(VI) and iodide and thiosulfate ions (1 g of Cr(VI) is equivalent to 7.33 and 3.23 g of iodide and thiosulfate ions, respectively). The reaction schemes are as follows:

$$Cr_2O_7^{2-} + 6\ I^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 3\ I_2 + 7\ H_2O$$

$$Cr_2O_7^{2-} + 3\ S_2O_3^{2-} + 14\ H^+ \rightarrow 2\ Cr^{3+} + 3\ SO_4^{2-} + 3S + 7\ H_2O$$

$$\text{Non-reduced } Cr_2O_7^{2-} + \text{DPC} \rightarrow \text{Cr-DPC complex}$$

Cr-DPC complex + Amberlite XAD-16 →
Adsorbed Cr-DPC onto Amberlite XAD-16

Cr-DPC onto Amberlite XAD-16 + Eluent H_2SO_4 →
Elution solution containing Cr(VI)

3. Results and Discussion

3. 1. Optimization of Column solid Phase Extraction of Chromium Species

Optimization of the parameters such as pH of the sample solution, eluent type, sample volume, amount of adsorbent, flow rate of sample solution effecting the column solid phase extraction of chromium species (Cr(III) and Cr(VI)) were investigated and reported in our previous paper.[31] Quantitative recovery (> 95%) was found at the pH 1 with Cr(VI) while the recovery of Cr(III) is rather low (< 5%). This could make it possible to separate Cr(VI) from Cr(III).[31] Optimum values found for the determination of Cr(VI) was given in Table 1. The linearity of this system was evaluated for chromium concentration ranging from 1 to 5 mg L^{-1} under the experimental condition mentioned above. The calibration graph was found to be linear up to 5 mg L^{-1} with regression coefficient above 0.99. The detection limit, as the concentration corresponding to three times the standard deviation of the blank signal (n = 12) was 45 μg L^{-1} for Cr(VI).[31]

Table 1 Optimum conditions for preconcentration/separation of Cr(VI) by the Amberlite XAD-16[32]

Parameter	Value
pH	1
Eluent (0.05 mol L^{-1} H_2SO_4 solution in methanol) volume, mL	10
Amount of adsorbent (mg)	300
Flow rate of the sample solution (mL min^{-1})	1.5
Volume of the applicable sample solution (mL) (Containing 10 μg Cr(VI))	250
Acidity of redox reactions[a] (H_2SO_4), mol L^{-1}	0.1–1.0

[a] Determined experimentally in this study

3. 2. Effect of Acidity

The proposed procedure of indirect determination of iodide and thiosulfate was based on its reducing action on Cr(VI) in acidic medium and following the atomic absorption spectrometric determination of the remaining Cr(VI) after separating the Cr(VI) from Cr(III) by a column solid phase extraction of Cr(VI) as its DPC complex onto Amberlite XAD-16. Amberlite XAD-16 resin is selective only for Cr(VI). The dependence of the redox reaction between Cr(VI) and iodide or thiosulfate on the acidity of the solution is one of the important parameters that can have a significant influence on the over-all performance of the indirect method. Oxidation of both iodide and thiosulfate with Cr(VI) is quantitative in the medium of 1 mol L^{-1} H_2SO_4. However, in 0.1 mol L^{-1} H_2SO_4, only thiosulfate can be oxidized by Cr(VI). Therefore, optimum acidity of medium of the redox reactions was adjusted to 0.1 mol L^{-1} H_2SO_4 for thiosulfate determination and 1 mol L^{-1} H_2SO_4 for iodide and/or total iodide and thiosulfade determination. After the redox reaction was completed, pH of the mixture was adjusted to the range of 1.0–1.5 using diluted sulfuric acid which was found as optimum pH for solid phase extraction of chromium species before.[31]

3. 3. Effect of Volume of Sample Solution (Analyte Concentration)

The effect of changes in the volume of sample solution passed through the column on the recovery of iodide and thiosulfate was investigated in order to determine an applicable sample volume or a minimum iodide and thiosulfate concentration. For that purpose, 10, 25, 50 and 100 mL of sample solutions containing fixed amount of iodide and thiosulfate (150 μg and 100 μg, respectively) corresponding to 15, 6, 3 and 1.5 μg mL^{-1} for iodide and 10, 4, 2 and 1 μg mL^{-1} for thiosulfate, respectively, were passed through the column under the optimum conditions determined experimentally. It was found that iodide and thiosulfate could be recovered up to 50 mL of sample solution with a relative error of about 10 % (Table 2). At higher sample volumes, the recoveries decreased and the relative error increased gradually with increasing volume of sample. It can be concluded that 3 μg mL^{-1} iodide and 2 μg mL^{-1} thiosulfate could be determined by this method for 50 mL sample volume.

Table 2 Effect of sample volume on the determination of iodide and thiosulfate

Analyte	Volume of sample solution mL	Added μg mL^{-1}	Found* μg mL^{-1}	Relative error, %
Iodide	10	15	14.3 ± 0.8	–4,7
	25	6	5.8 ± 0.2	–3.3
	50	3	2.7 ± 0.2	–10
	100	1,5	0.60 ± 0.02	–60
Thiosulfate	10	10	9.3 ± 0.4	–7
	25	4	3.8 ± 0.1	–5
	50	2	1.80 ± 0.01	–10
	100	1	0.68 ± 0.04	–32

[a] Mean of five determinations at 95% confidence level $(\bar{x} \pm \frac{t \cdot s}{\sqrt{N}})$

3. 4. Interference Studies

To assess the validity of the method, a study of interference for iodide and thiosulfate determination was also performed. The cations in the sample would not interfere

with the determination of iodide and thiosulfate because they are not adsorbed by Amberlite XAD-16 resin column. The interfering effect of the cations on the separation and determination of Cr(VI) had been investigated in our previous study.[31] Recovery of Cr(VI) was quantitative when the ratio of interfering ions to chromium (VI) was 10 for Fe(III), 25 for Pb(II) and Al(III), 50 for Cu(II), Ni(II), Mn(II), Co(II) and 100 for Zn(II), Cd(II), Na(I), K(I), Mg(II) and Ca(II).[31] The interfering effect of chloride, bromide, glucose, citric acid, ascorbic acid that are commonly found in the samples analyzed were investigated by adding different amount of other species to a solution containing 15 μg mL^{-1} iodide and 10 μg mL^{-1} thiosulfate. The interference effect of analytes to each other was also studied. The results are listed in Tables 3 and 4. According to this work, no interferences were observed in iodide determination for glucose and citric acid up to 30 μg mL^{-1}, for bromide up to 750 μg mL^{-1} and for chloride up to 15000 μg mL^{-1} (relative error < 10%). However, ascorbic acid and thiosulfate interfered with determination of iodide above 10 μg mL^{-1}. In thiosulfate determination, iodide also interfered with the determination above 100 μg mL^{-1}. It was concluded that from these results, iodide can not be determined accurately in the samples containing ascorbic acid and/or thiosulfate. Both of the iodide and ascorbic acid and/or thiosulfate are oxidized by Cr(VI) in given experimental conditions (1 mol L^{-1} H_2SO_4). As can be seen in our previous study, ascorbic acid can also be oxidized in 0.1 mol L^{-1} H_2SO_4 medium[32] and at that condition iodide does not oxidize and therefore does not interfere with the determination of ascorbic acid. In order to overcome the ascorbic acid and thiosulfate interferences, two different experimental conditions (1 mol L^{-1} H_2SO_4 and 0.1 mol L^{-1} H_2SO_4) should be applied. While at the presence of 1 mol L^{-1} H_2SO_4, total Cr(VI) content reacted with ascorbic acid, thiosulfate and iodide is determined, at the presence of 0.1 mol L^{-1} H_2SO_4, Cr(VI) content reacted with only ascorbic acid and thiosulfate is determined. The difference in Cr(VI) contents corresponds the Cr(VI) reacted with iodide. Results obtained for different experimental conditions were given in Table 5.

Table 3 The effect of some species on the recovery of iodide (pH, 1; eluent, 10 mL of 0.05 mol L^{-1} H_2SO_4 solution in methanol; sample volume, 10 mL; amount of the iodide, 100 μg)

Interferent	Concentration species of interfering μg mL^{-1}	Added μg mL^{-1}	Found[a] μg mL^{-1}	Relative error %
Chloride	–	15	14.3 ± 0.8	–4.7
	150	15	15.2 ± 0.3	+1.3
	750	15	14.5 ± 0.4	–3.7
	1500	15	16.1 ± 0.4	+7.3
	7500	15	15.7 ± 0.5	+4.7
	15000	15	16.5 ± 0.2	+10
Bromide	–	15	14.3 ± 0.8	–4.7
	150	15	15.7 ± 0.7	+4.7
	750	15	16.0 ±0.2	+6.7
	1500	15	16.4 ± 0.3	+9.3
	7500	15	20 ± 1	+33
Ascorbic acid	–	15	14.3 ± 0.8	–4.7
	12	15	31.7 ± 0.9	111
Glucose	–	15	14.3 ± 0.8	–4.7
	15	15	14.9 ± 0.6	–1
	30	15	14.6 ± 0.6	–4.0
Citric acid	–	15	14.3 ± 0.8	–4.7
	30	15	14.6 ± 0.3	+4.0
	15	15	16.5 ± 0.4	+10
Tiosulfate	–	15	14.3 ± 0.8	–4.7
	15	15	48 ± 2	+220

[a] Mean of five determinations at 95% confidence level $(\bar{x} \pm \frac{t \cdot s}{\sqrt{N}})$

Table 4 The effect of some species on the recovery of thiosulfate (pH, 1; eluent, 10 mL of 0.05 mol L^{-1} H_2SO_4 solution in methanol; sample volume, 10 mL; amount of the thiosulfate, 100 μg)

Interferent	Concentration species of interfering μg mL^{-1}	Added μg mL^{-1}	Found[a] μg mL^{-1}	Relative error %
Chloride	–	10	9.7 ± 0.8	–3
	100	10	10.2 ± 0.3	+2
	1000	10	10.5 ± 0.4	+5
	10000	10	10.1 ± 0.4	+1
Bromide	–	10	9.3 ± 0.4	–7
	100	10	9.2 ± 0.1	–8
	1000	10	9.4 ± 0.3	–6
	10000	10	9.3 ± 0.3	–7
Iodide	–	10	9.3 ± 0.4	–7
	100	10	9.3 ± 0.3	–3
	1000	10	11.8 ± 0.2	+18

[a] Mean of five determinations at 95% confidence level $(\bar{x} \pm \frac{t \cdot s}{\sqrt{N}})$

3. 5. Precision and Accuracy of the Method

In order to investigate the precision of the method, the general procedure given above was applied to the determination of iodide and thiosulfate in synthetic sample solution containing 15 μg mL^{-1} iodide and 10 μg mL^{-1} thiosulfate, separately. Results of successive determinations were given in Table 6. The precision of the proposed method is good as it provides relative standard deviation value of 4.5% and 3.5% during five replicate determinations of 15 μg mL^{-1} of iodide and 10 μg mL^{-1} thiosulfate, respectively. The accuracy of the method was also checked by calculating relative error (< 7%).

In order to check the accuracy of the proposed method, iodide has been determined in certified reference material (BCR 150 Milk powder) by the proposed method. Four determinations have been performed on the four sample portions by applying dissolution and test procedure given above. Good agreement was obtained between

Table 5 Determination of iodide and thiosulfate in synthetic sample

Anions (Condition)	Reacted Cr(VI) μg mL^{-1}	Thiosulfate, μg g^{-1} Labeled	Found*	Relative error, %	Iodide, μg g^{-1} Labeled	Found*	Relative error, %
$S_2O_3^{2-}$ + I^- (1 mol L^{-1} H_2SO_4)	6.13 ± 0.06						
$S_2O_3^{2-}$ (0.1 mol L^{-1} H_2SO_4)	4.25 ± 0.06	15	13.72 ± 0.3	–8.7	15	13.7±0.4	–8.7
I^-	1.88 ± 0.06						

[a] Mean of five determinations at 95% confidence level $(\bar{x} \pm \frac{t \cdot s}{\sqrt{N}})$

the estimated content by the proposed method and the certified values for the iodide. It was found that there is no significant difference between the results found by the proposed method (1.10 ± 0.08 μg g^{-1}) as the mean of four determinations at 95% confidence level and the certified values (1.29 ± 0.09 μg g^{-1}) according to the *t*-test. It can be concluded that there is no systematic error in the determination at 95 % confidence level (the relative errors are below 15%). The relative error is acceptable level for quantitative trace analysis. These results also indicate that the developed method is not affected by potential interferences from the major matrix elements of the analyzed reference material.

Table 6 Accuracy and precision of the method of iodide and thiosulfate determination in synthetic sample

	Added μg mL^{-1}	Found[a] μg mL^{-1}	RSD, %	Relative error, %
Iodide	15	14.3 ± 0.8	4.5	–4.7
Thiosulfate	10	9.3 ± 0.4	3.5	–7.0

[a] Mean of five determinations at 95% confidence level $(\bar{x} \pm \frac{t \cdot s}{\sqrt{N}})$

3. 6. Application

To investigate the applicability to real samples, the proposed method has been applied to the determination of iodide in table salt and milk, and thiosulfate in table salt (Tables 7 and 8). As shown in the Tables, the recoveries of iodide and thiosulfate added to table salt and milk were all close to 100%. The results of recovery test are very good. No interference was found in view of the presence of a very complex matrix of the samples (especially milk) as indicated by the good recovery of iodide (about 90%). The proposed method could be applied to determination of iodide in iodized salt and milk, and thiosulfate in iodized salt without interference from other constituents of samples encountered.

Table 7 Iodide and thiosulfate determination in table salt

Anions (Condition)	Reacted Cr(VI) μg mL^{-1}	Thiosulfate, μg g^{-1} Labeled	Found*	Relative error, %	Iodide, μg g^{-1} Labeled	Found*	Relative error, %
$S_2O_3^{2-}$ + I^- (1 mol L^{-1} H_2SO_4)	3.76 ± 0.06						
$S_2O_3^{2-}$ (0.1 mol L^{-1} H_2SO_4)	3.16 ± 0.06	100	102 ± 4	+2	46	43.7±0.6	–5
I^-	0.60 ± 0.04						

[a] Mean of five determinations at 95% confidence level $(\bar{x} \pm \frac{t \cdot s}{\sqrt{N}})$

Table 8 Determination of iodide in milk

Sample	Added, μg mL^{-1}	Found*, μg mL^{-1}	RSD, %	Relative error, %
Milk	–	0.86 ± 0.07	6	–
	1.0	1.66 ± 0.07	4	–11

[a] Mean of five determinations at 95% confidence level $(\bar{x} \pm \frac{t \cdot s}{\sqrt{N}})$

4. Conclusions

The proposed method, using the reaction between iodide and thiosulfate and Cr(VI), is based on the off-line preconcentration/separation by column solid phase extraction and flame atomic absorption spectrometric indirect determination of iodide and thiosulfate. This method provides interference free determination of iodide and thiosulfate due to prior separation of Cr(VI) from the interfering species. The proposed method could be applied to the analysis of table salts containing different amount of iodide and thiosulfate without interference from other constituents encountered. The method is sensitive, selective and suitable for laboratory rutin control. Repeated use of column is possible.

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Povzetek

Opisana je nova metoda določevanja jodida in tiosulfata v kuhinjski soli in mleku s plamensko atomsko absorpcijsko spektrometrijo. Osnovana je na redukciji Cr(VI) v Cr(III) zaradi prisotnosti jodida in/ali tiosulfata, reakciji presežnega Cr(VI) z 1,5-difenilkarbazidom in njegovi ločbi na koloni polnjeni z ionsko izmenjalno smolo Amberlite XAD-16. Po spiranju kolone z 10 mL 0,05 M H_2SO_4 v metanolu določimo koncentracijo presežnega Cr(VI) s plamensko atomsko absorpcijsko spektrometrijo. V prispevku so podani optimalni pogoji za določevanje jodida in tiosulfata, kot so pH, volumen vzorca in vpliv motečih ionov. Relativni standardni odmik petih meritev vzorcev s koncentracijo tiosulfata 10 μg mL^{-1} in koncentracijo jodida 15 μg mL^{-1} je 3,5 % oziroma 4,5 %. Točnost metode je bila preverjena z analizo referenčnega vzorca (BCR mleko v prahu) in realnih vzorcev kuhinjske soli in mleka v prahu. Relativne napake meritev so bile v vseh primerih manjše od 15 %.