J. Braz. Chem. Soc., Vol. 20, No. 8, 1535-1540, 2009.
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0103 - 5053 $6.00+0.00

Micelle-mediated Extraction and Determination of Tin in Soft Drink and Water Samples

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Desenvolveu-se a pré-concentração em fase micelar de traços de estanho na determinação de Sn(IV) por espectrofotometria baseada na extração no ponto de nuvem (CPE) do complexo de Sn(IV) com violeta de pirocatecol em um meio surfactante. Violeta de pirocatecol (PCV) foi usado como agente quelante e brometo de cetiltrimetilamônio (CTAB) como agente surfactante catiônico. Foram estudadas as condições da reação e otimização da extração do elemento, ou seja, a concentração do surfactante, concentração do reagente, influência do pH e tempo de reação/extração. As figuras de mérito do método (limite de detecção, linearidade e fator de pré-concentração) foram estabelecidas. A linearidade se encontra na faixa de 0,30-175,00 ng mL^{-1} ($2,0 \times 10^{-9}$ a $1,5 \times 10^{-6}$ mol L^{-1}) de Sn(IV). O limite de detecção do método (LOD) foi de 0,16 ng mL^{-1} ($1,3 \times 10^{-9}$ mol L^{-1}) de Sn(IV). O desvio padrão relativo (R.S.D.) e o erro relativo para 5 replicatas foi de 0,71% e 2,9% para a concentração de 30,00 ng mL^{-1} Sn(IV) e de 1,6% e 3,4% para a concentração de 50,00 ng mL^{-1} de Sn(IV) respectivamente. O efeito de interferência de alguns cátions e ânions também foi avaliado e o método foi aplicado na determinação de estanho em amostras de sucos em conserva e amostras de água com resultados satisfatórios.

A micelle-mediated phase preconcentration of trace quantities of Sn(IV) as a prior step to its determination by spectrophotometry has been developed, based on cloud point extraction (CPE) of the complex of Sn(IV) with pyrocatechol violet complex in surfactant media. Pyrocatechol violet (PCV) and cetyltrimethylammonium bromide (CTAB) were used as chelating agent and cationic surfactant, respectively. The optimal extraction and reaction conditions (e.g. surfactant concentration, reagent concentration and the effects of pH and time) were studied and the analytical characteristics of the method (e.g., limit of detection, linear range and preconcentration factor) were obtained. Linearity was obeyed in the range of 0.30-175.00 ng mL^{-1} (2.0×10^{-9} to 1.5×10^{-6} mol L^{-1}) of Sn(IV). The detection limit (LOD) of the method was 0.16 ng mL^{-1} (1.3×10^{-9} mol L^{-1}) of Sn(IV). The relative standard deviation (R.S.D.) and relative error for five replicate measurements of 30.00 ng mL^{-1} Sn(IV) were 0.71% and 2.9%, and for 50.00 ng mL^{-1} of Sn(IV) were 1.6% and 3.4%, respectively. The interference effect of some anions and cations was also tested. The method was applied to the determination of tin in soft drinks (canned juices) and water samples, with satisfactory results.

Keywords: tin, pyrocatechol violet, specrtophotometry, cloud point extraction

Introduction

Tin is a toxic metal which could gather in a human body and animal tissue.[1] There are mainly two chemical species of inorganic tin (Sn(II) and Sn(IV)) in environmental samples. Sn(II) seems to be more toxic than Sn(IV).[2] High concentrations of tin brings serious interference to the metabolism of zinc.[3] Tin is extensively used as a coating element for steels and also as an alloying agent in a wide variety of metal compositions. Tinplate is widely used in food industry and for the production of beverage cans. The use of tinplate for food and beverage packaging may result in some tin dissolving into the food content.[4] Differential toxicities of the different forms of an element have required an increasing development and use of analytical determination of the chemical species. The behavior of inorganic tin as a moderately corrosion-resistant metal is of considerable interest due to its important applications in food and electronic industries.[4] Therefore, the analysis and monitoring of inorganic tin species in environmental samples is extremely important. For the determination of inorganic tin, the separation methods reported in the literature are usually based on solvent extraction,[5] liquid

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chromatography,[6] gas chromatography[7] and solid phase extraction.[8]

Cloud point extraction (CPE) has become one of the most preferred preconcentration steps for enhancing the sensitivity in inorganic analysis and it has been applied to the separation of environmental and biological samples with a complicated matrix.[9-13] CPE is an outstanding alternative to conventional solvent extraction because it produces high extraction efficiencies and preconcentration factors, and uses inexpensive, non-toxic reagents. Several methods have also been reported for the FAAS and GFAAS determination of Sn after cloud point extraction.[14-16] This paper proposes a method for preconcentration and determination of tin by spectrophotometry based on cloud point extraction (CPE) of the complex of Sn(IV) with pyrocatechol violet complex in surfactant media.

Experimental

Apparatus

A Perkin-Elmer Lambda 45 UV/Vis spectrometer was used for recording absorbance spectra. Absorption measurements at fixed wavelength were performed using a Shimadzu UV-mini-1240 V spectrophotometer with 1 cm quartz cell (0.5 mL). A Metrohm pHmeter (model 713) with a combined glass electrode was used for pH measurements. A centrifuge with 10 mL calibrated centrifuge tubes (Superior, Germany) were used to speed up the phase separation process.

Reagents

The surfactant, cethyltrimethylammounium bromide (CTAB), (Sigma Company) was used without further purification. Stock solution of Sn(IV) at a concentration of 1000 μg mL^{-1} was prepared by dissolving appropriate amount of $SnCl_4.5H_2O$ salt (Fluka) in triply distilled water. Working standard solutions were obtained by appropriate dilution of the stock solution. A solution of 1.30×10^{-3} mol L^{-1} of pyrocathechol violet (PCV), (Merck) was prepared by dissolving appropriate amounts of this reagent in triply distilled water. The solution pH of 3.0 ± 0.1 was adjusted with glycine/hydrochloric acid buffer. N,N-dimethylformamide (DMF) solvent and potassium iodide salt were purchased from Merck.

Procedure

An aliquot of a Sn(IV) standard solution was transferred to a 10 mL centrifuge tube, 0.6 mL of the 1.3×10^{-3} mol L^{-1} PCV solution and 2.0 mL of pH 3.0 buffer solution were added. This was followed by the addition of 0.4 mL of 2.74×10^{-3} mol L^{-1} surfactant CTAB solution and 2.0 mL of 0.4 mol L^{-1} of KI solution. The solution was made up to the mark with triply distilled water and allowed to stand for 10 min at room temperature. Clouding of the solution took place without heating. Separation of the aqueous and surfactant- rich phase was accomplished by centrifugation for 15 min at 3,800 rpm. Then, the aqueous phase could be separated by inverting the tube. The surfactant rich phase of this procedure was dissolved and diluted to 0.5 mL with DMF and transferred into a 0.5 mL quartz cell. The absorbance of the solution was measured at 576 nm. The blank solution was submitted to the same procedure and its absorbance was measured at 576 nm.

Determination of tin in canned juice samples

A 10 mL sample (canned pineapple) was transferred to a 100 mL conical flask, and 2.5 mL of concentrated nitric acid was added. The sample was then carefully heated and evaporated to near dryness. After cooling, the pH of the digested sample was adjusted to 4.0 by adding sodium hydroxide solution. Then the solution was transferred and diluted to 10 mL using water.[4] The tin content of canned juices was determined with proposed method.

Results and Discussion

Pyrocatechol violet (pyrocatechol sulfonaphthalein or 3,3’,4’-trihydrooxyfuchsone-2’-sulfonic acid, PCV) has been applied as a sensitive reagent for colorimetric determination of tin. Pyrocatechol violet forms at least two complexes with Sn(IV).[17] The absorption spectra of PCV in the presence of two different amounts of Sn(IV) show that at low ratios of Sn(IV):PCV the predominant form of the complex is a 1:2 Sn(IV):L complex, with a λ_{max} at 550 nm, while at high ratios of Sn(IV):PCV both the 1:1 and 2:1 Sn(IV):L complexes are present in the solution.[18] The addition of surfactant improves the selectivity and sensitivity of the metal determinations due to the batho- and hyperchromic effects. The reaction of Sn(IV) with pyrocatechol violet in surfactant media has been studied.[19] Pyrocatechol violet forms a red-colored complex with quadrivalent tin at pH 2.5. Apparently bivalent tin does not form a colored complex with pyrocatechol violet under the condition used for development of Sn(IV) complex, but is readily oxidized to the higher oxidation state and is included in the measurement of Sn(IV).[20] Complex of Sn(IV) with PCV in the presence of CTAB in aqueous media has a maximum absorbance at 660 nm. Addition of the iodide ion caused turbidity of the solution. Therefore the ternary complex of Sn(IV)-PCV-CTAB can be extracted by CPE method. The absorption spectrum of the ternary complex in surfactant-rich phase shows a maximum absorbance at 576 nm (Figure 1). After separation of surfactant-rich phase, the absorbance was measured at 576 nm against a reagent blank as the reference.

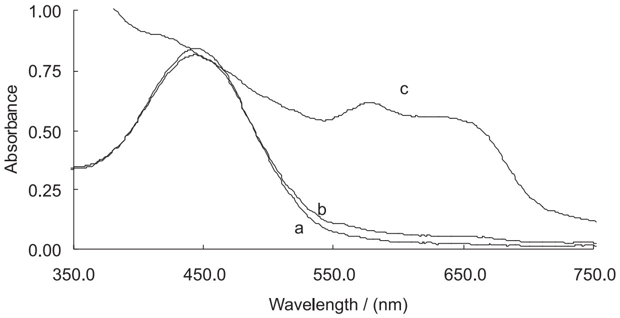

Figure 1. Absorption spectra for PCV in the presence of CTAB (a), its complex with Sn (IV) in aqueous media (b) and its complex after extraction in surfactant rich phase (c). Conditions in surfactant rich phase: Sn(IV), 0.1 µg mL^{-1}; [PCV] = 7.7×10^{-5} mol L^{-1}; [CTAB] = 1.1×10^{-4} mol L^{-1}; [KI] = 8.0×10^{-2} mol L^{-1}; pH 3.0.

Optimization of the system

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

The effect of pH on the extraction and determination of Sn(IV) was investigated in the range 1.0-7.5. The pH was adjusted using HCl and NaOH. The absorbance of the Sn(IV)-PCV-CTAB system at 576 nm in surfactant-rich phase was studied against the reagent blank. Maximum absorbance was obtained at pH 2.5-3.5. In more acidic or more alkaline solutions, the absorbance decreased because of incomplete complex formation and/or incomplete extraction of the complex. Therefore pH 3.0 was selected as optimum pH. Different buffer solutions of pH 3.0, including acetate, phosphate and glycine/HCl were tested, and glycine/HCl buffer solution was found as the best.

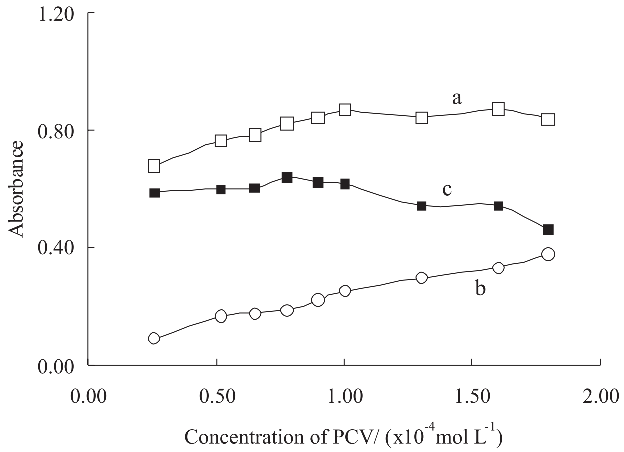

Figure 2. Effect of PCV concentration on the extraction and determination of Sn(IV); sample (a), blank (b), and their difference (c). Conditions: Sn(IV), 0.1 µg mL^{-1}; [KI] = 0.02 mol L^{-1}; [CTAB] = 4.9×10^{-4} mol L^{-1}; pH 3.0.

Effect of PCV concentration on the extraction and determination of Sn(IV) was investigated in the range 1.3×10^{-5} to 1.8×10^{-4} mol L^{-1}. The results are shown in Figure 2. The sensitivity of the method increased by increasing PCV concentration up to 7.8×10^{-5} mol L^{-1} and decreased at higher concentrations. At concentrations higher than 7.8×10^{-5} mol L^{-1} the concentration of complex did not change significantly but the concentration of uncomplexed PCV increased significantly. Therefore, probably the decrease of absorbance at concentrations higher than 7.8×10^{-5} mol L^{-1} is due to the fact that the free PCV competes with the complexes in extraction to surfactant rich phase. A concentration of 7.8×10^{-5} mol L^{-1} of PCV was selected as the optimum.

Effect of CTAB concentration on the extraction and determination of Sn(IV) was investigated in the range 2.7×10^{-5} to 2.7×10^{-4} mol L^{-1}. The results are shown in Figure 3. The absorbance increased by increase in CTAB concentration up to 1.1×10^{-4} mol L^{-1}. The blank signal also increased slowly by increasing CTAB concentration. But the difference between the sample and blank signals (at 576 nm) increased by increasing CTAB concentration up to 1.1×10^{-4} mol L^{-1} and decreased slowly at higher concentrations. Therefore, 1.1×10^{-4} mol L^{-1} of CTAB was chosen as the optimum.

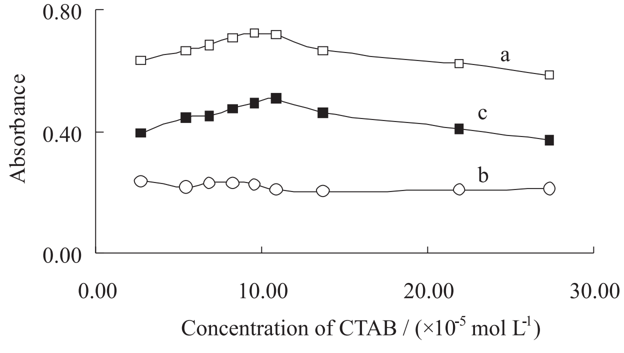

Figure 3. Effect of CTAB concentration on the extraction and determination of tin (IV); sample (a), blank (b) and their difference (c). Conditions: tin (IV), 0.1 µg mL^{-1}; [KI] = 0.02 mol L^{-1}; [PCV] = 7.8×10^{-5} mol L^{-1}; pH 3.0.

Addition of proper inorganic salts can cause cationic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases and causes clouding of the solution at room temperature. Several inorganic salts including NaCl, NaF, KNO_3, KBr and KI, were tested and KI was found as the best. Therefore, iodide was added to induce micellar growth and extraction of complex. The effect of iodide concentration was studied in the range 0.01-0.20 mol $L^{-1.}$ The results show that addition of 0.08 mol L^{-1} iodide was suitable for maximum extraction of the complex. A concentration of 0.08 mol L^{-1} iodide was selected for further experiments.

Effect of time on the reaction and also on the CPE procedure was investigated. The results showed that complexation reaction was completed in 10 min. Also a 15 min centrifugation at 3,800 rpm was found to be adequate for successful phase separation.

In order to select the proper dilution solvent for the precipitated surfactant rich phase, different solvents (DMF, DMSO, ethanol and acetonitrile) were tried so as to select the one producing the best sensitivity. DMF gave the best results due to its high sensitivity and solubility. Therefore, DMF was chosen to have an appropriate amount of sample for transferring and measuring the sample absorbance. Finally, surfactant rich phase was dissolved and diluted to 0.5 mL with the DMF.

Analytical characteristic

A calibration graph was constructed by measuring the difference between sample and blank absorbance (ΔA) for surfactant-rich phase as a function of Sn(IV) concentration at fixed wavelength of 576 nm. The analytical characteristics of the optimized method, including regression equation, linear range, limit of detection, and preconcentration factor are given in Table 1. The limit of detection, defined as $C_L = 3S_B/m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 0.16 ng mL^{-1}. Because the amount of Sn(IV) in 10 mL of sample solution is measured after preconcentration by CPE in a final volume of 0.5 mL of DMF, the maximum preconcentration factor is 20.

Table 1. Analytical features of the proposed method

Regression equation (n = 15)	ΔA = 0.0047C - 0.0045, r = 0.9995
Linear range (ng mL^{-1})	0.30 - 175.00,[a] (0.24 - 1.42 μg mL^{-1})
Limit of detection (ng mL^{-1}) (n=5)	0.16[a] (10)
Maximum preconcentration factor	20

[a] Linear range before preconcentration

In order to obtain the accuracy and precision of the method, two different concentrations of Sn(IV) were analyzed using the proposed method. The relative standard deviation (R.S.D) and relative error for five replicate measurements of 30.00 ng mL^{-1} of Sn(IV) were 0.71% and 2.9% and for 50.00 ng mL^{-1} of Sn(IV) was 1.6% and 3.4%, respectively.

Interference study

The effects of different ions on the preconcentration and determination of 0.1 μg mL^{-1} Sn(IV) by the proposed method under the optimum conditions were tested. The results are summarized in Table 2. The tolerance limit was defined as the concentration of added ion that caused less than ± 5% relative error. Most of the cations and anions examined did not interfere with the extraction and determination of Sn(IV). Ag^+ interfered at 3.0 μg mL^{-1} and Cu^{2+} interfered at 1.0 μg mL^{-1}. The interfering effects of Ag^+ and Cu^{2+} up to 15.0 and 10.0 μg mL^{-1} were removed by the addition of 4.2×10^{-5} mol L^{-1} EDTA, and the interfering effects of Fe^{3+} up to 2.5 μg mL^{-1} was removed by the addition of 4.2×10^{-4} mol L^{-1} ascorbic acid to the solution.

Table 2. Tolerance ratios of diverse ions on the determination of 0.1 μg mL^{-1} of Sn(IV) using the proposed method.

Ion	Tolerance ratio, foreign ion/Sn, w/w
SiO_4^{4-}, Cr^{3+}, Co^{2+}, Na^+, NO_3^-, Ni^{2+}, Mg^{2+}, K^+	1000
$H_2BO_3^-$	500
Hg^{2+}	200
Bi^{3+}, Ca^{2+}, Cd^{2+}, Mn^{2+}	100
Fe^{2+}	50
Zn^{2+}, Ba^{2+} Pb^{2+}, F^-	25
Ag^+	30 (150)[a]
Cu^{2+}	10 (100)[a]
CN^-	10
Fe^{3+}	1 (25)[b]
$Cr_2O_7^{2-}$, Sn^{2+}, Al^{3+},VO_3^-, Sb^{3+}	1

[a] after addition of 4.2×10^{-5} mol L^{-1} EDTA

[b] after addition of 4.2×10^{-4} mol L^{-1} ascorbic acid

Application

Determination of tin in water samples

The proposed method was successfully applied to the determination of tin ions in water samples. River water sample was taken from a river in the city of Hamadan (Iran). The sample was filtered on-site through nitrocellulose membrane (0.45 µm, Sartorius, Germany). The sample was adjusted to the respective pH and spiked with Sn(IV). The results are shown in Table 3. The recoveries are close to 100% and indicate that the proposed method is applicable for the determination of tin in water samples.

Table 3. Determination of Sn in water samples by the proposed method

Sample	Amount of Sn, (µg L^{-1})		Recovery
	Added (as Sn(IV))	Found [a]	
Tap water	-	2.38 ± 0.02	-
	10.00	12.16 ± 0.08	97.8
	40.00	43.05 ± 0.12	101.7
	100.00	105.30 ± 0.09	102.9
Mineral water	-	1.72 ± 0.07	-
	5.00	7.03 ± 0.10	106.2
	30.00	31.08 ± 0.14	97.9
	85.00	86.51 ± 0.52	99.8
River water	-	1.10 ± 0.06	-
	3.00	4.10 ± 0.11	100.0
	30.00	32.58 ± 0.23	104.9
	100.00	96.10 ± 0.72	95.0
Well water	-	n.d.[b]	-
	5.00	5.06 ± 0.01	101.2
	40.00	38.50 ± 0.10	96.2
	125.00	125.70 ± 1.23	100.6

[a]average of three determinations ± standard deviation, [b] not detected

Determination of tin in canned juice samples

The accuracy and applicability of the proposed method was applied to the determination of tin in canned juice samples. The results are given in Table 4 and indicate the successful applicability of the proposed method for the determination of tin in such samples.

Table 4. Determination of Sn in canned juice samples by the proposed method.

Sample	Sn (µg L^{-1})		Recovery(%)
	Added (as Sn(IV))	Found	
1	-	55.90 ± 0.32	-
2	30.00	86.39 ± 0.57	101.6
3	50.00	106.42 ± 1.36	101.0

As Sn(II) is readily oxidized to Sn(IV), the obtained results for the amounts of tin in water and canned juice samples may be considered as the total amounts of Sn(II) and Sn(IV).

Comparison of the proposed method with other methods

A comparison between the proposed method with the previously reported methods for preconcentration and determination of Sn(IV) (Table 5) indicates that this method provides a lower detection limit and/or wider linear range for the determination of trace quantities of Sn(IV) and total Sn in real samples.[14,15,21-23]

Conclusions

The preconcentration and determination of Sn(IV) and total Sn using PCV and CTAB reagents and cloud point extraction shows interesting features. This combination resulted in a simple, sensitive and inexpensive analytical procedure successfully used to tin preconcentration and determination in real samples. The procedure is very economical, because it consists of much low equipment and running costs and shows also simplicity in apparatus and manipulation.

Table 5. Comparison of the proposed method with some preconcentration methods

Sorbent/reagent	Analytical method	Detection Limits (µg L^{-1})	Linear range (µg L^{-1})	Sample	Ref
Pyrocatechol violet	[a]FI-SPE	0.3	2.0-40.0	Fruit	21
Pentahydroxyflavone	SPE	60.0	Up to 1.2 (µg mL^{-1})	Zinc material	22
8-HQ/Triton X-114	[b]CPE-GFAAS	0.012	0.05-2.00	Water	15
PAN	CPE-GFAAS	0.51	0.0-5.0 (µg mL^{-1})	Water	14
Saccharomyces cerevisiae	[c]SPE-ICP-OES	1.1	40-200	Water	23
PCV/CTAB	CPE	0.16	0.30-175.00	Water, sheep liver, canned juices	This work

[a] Flow injection –solid phase extraction, [b] cloud point extraction – graphite furnace atomic absorption spectrometry, [c] solid phase extraction- inductively coupled plasma – optical emisson spectrometry

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Received: January 3, 2009
Web Release Date: August 28, 2009