Trace determination and separation of tin (II) by floatation-spectrophotometric using kalmagyte and CTAB

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Abstract

A novel floatation-spectrophotometric extraction method was developed for the recovery of tin (II) from aqueous samples prior to determination by UV spectrophotometric detection. The method is based on the formation of a complex between tin (II) and kalmagyte in pH=8. The complex is floated in the interface of *n*-hexane and aqueous phases. After removing the aqueous phase, the floated particles are dissolved in methanol and the absorbance is measured at 637 nm. Different parameters of the floatation-spectrophotometric technique such as reagent concentration, pH, surfactant, standing time and interfering ions were studied and optimized to obtain the best extraction results with the minimum interference from other compounds. Under these conditions, the extraction of the target compound was almost complete (mean values of recovery was more than 92.6%) in a short time (6 min). The optimized method demonstrated good linearity ($r^2 > 0.9991$) in the range of 4-350 ng/mL, sensitivity (limit of detection for tin (II), 1.7 ng/mL), accuracy (0.19–7.35%) and precision (3.66%, 4.21%). The applicability of the proposed method was demonstrated by extraction of tin(II) from different water samples.

Keywords: Floatation-spectrophotometric, tin (II), kalmagyte, water samples.

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Introduction

Tin (II) is a volatile and toxic element that can be harmful to the environment and health of body [1,2]. In industry, tin (II) is widely used in various applications such as tin (II) plating (II), alloys, biocidal agents, antifouling paints, and as a heat and light stabilizer for plastics [3-6]. Therefore, tin (II) is one of the important contaminants in waste-water due to their wide uses in many industrial processes. Many techniques have been developed for the determination of tin (II) in different matrix. These include high performance liquid chromatography [7,8], atomic absorption spectrometry [9–12] and spectrophotometry of its complexes [13-15], titrimetric methods [16, 17], and electrochemical methods based on polarography [18–21] or stripping Voltammetry [22–24], inductively coupled plasma-mass spectrometry [25] and neutron activation analysis [26]. In some of these techniques, analysis time is long, the detection limit is sometimes poor, and in others, special pretreatment is required before analysis [27].

The procedures which were described provide a more sensitive, fast, and simple method for the measurement of tin (II) in different water samples by flotation-spectrophotometric based on its complex formation with kalmagyte in basic media. In this method a complex between tin(II) and kalmagyte was formed; then, it was floated into the interface between aqueous and *n*-hexane phase and, afterwards, they were extracted into methanol solvent and its absorbance is measured at 637 nm. In order to show the performances of the proposed method, determination of tin (II) as a case study in water samples by UV spectrophotometric were investigated.

Experimental

Instruments and reagents

The spectrophotometer UV-Vis (model 1245, shimadzu, Japane) was used for all the *absorbance* measurements with a 10 mm quartz cell. pH measurements were made with a 827 pH meter (Metrohm, Switzerland) equipped with a combine Ag/AgCl glass electrode.

Methanol and *n*-hexane were obtained from Merck, Germany. Double distilled water was used in all of our experiments. Other reagents were of analytical grade and were purchased from Merck, Germany. Individual stock solutions of each tin (II) 10μg/mL, kalmagyte 1×10^{-4} molL^{-1}, and CTAB 1×10^{-4} molL^{-1} were prepared with pure water. From these solutions, several standard working solutions were prepared.

Floatation-spectrophotometric procedure

A 1 mL portion of the standard solution containing the tin (II) at concentration level of 10 flask μg/mL was placed into a 100 mL volumetric. 8 mL of 1×10^{-4} mol L^{-1} kalmagyte,5 mL of buffer with pH=8, 6 mL of 1 M NaCl and 3 mL of 1×10^{-4} $molL^{-1}$ CTAB are added to this solution. This mixture was diluted to the mark with freshwater. After 6 min, the flask contents were completely transferred into a 100 mL separating funnel containing 9 mL of *n*-hexane. The funnel is sealed and vigorously shacked for 75s and, then, it was allowed to stand for 6 min. After this time, the aqueous phase was extracted and 2.5 mL of methanol was added to the organic phase. The complex was dissolved in methanol and the absorbance was read in 637 nm against a reagent blank.

Results and discussion

The aim of this work was to evaluate the experimental conditions providing the highest recovery of tin (II), from different aqueous matrix. In the present research, the optimization process was carried out using one variable at a time; this method can be used for simplifying the optimization procedure. In order to achieve good sensitivity, precision and recovery for the extraction and determination of tin (II) from the water samples, the effects of different parameters such as reagent concentration, pH, surfactant, standing time and interfering ions on the extraction efficiency were evaluated and optimized.

Effect of pH and volume of buffer

Among the chemical variables in flotation method, the pH of sample solution plays an important role in metal–chelate formation. The effect of pH and volume of buffer (5mL) upon the complex formation of the analyte was studied in the range of 1–10. Figure 1 shows the effect of pH on the extraction of tin (II) complex. According to our obtained results, the maximum signal was obtained at pH= 8. At lower pHs, a competition occurred between protons and the tin (II) ions for occupying the ligand active sites, while at higher pHs, the effective charge of CTAB decreased. The result clarified that an optimum volume of buffer with pH= 8 has obtained 5 mL.
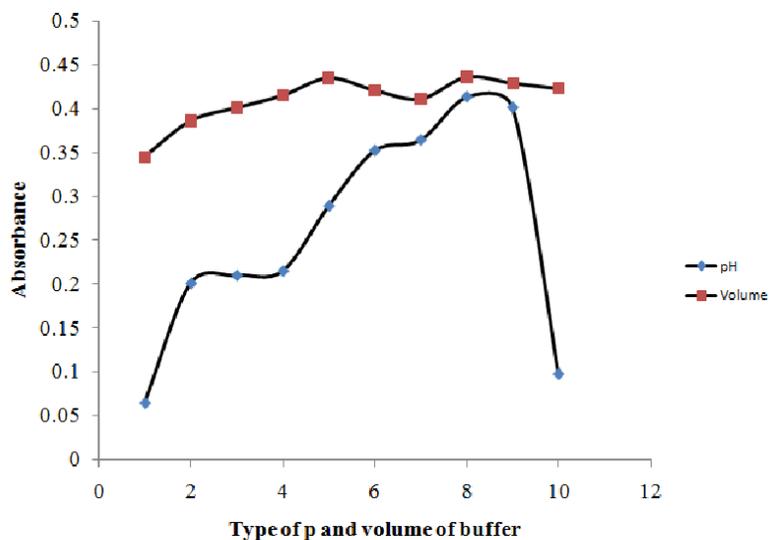
Figure 1. Effect of pH and volume of buffer. Experimental condition: kalmagyte concentration=$8×10^{-6}$ molL^{-1}, concentration of surfactant=$3 ×10^{-6}$ mol L^{-1}, volume of n-hexane=9mL, volume of methanol =2.5mL, standing time=6 min.

Effect of kalmagyte concentration

The effect of kalmagyte concentration used for the floatation of tin (II) was evaluated in the range from $4×10^{-6}$ molL^{-1} to $1.4×10^{-5}$ molL^{-1}.The result, as shown in Figure 2, demonstrates that the maximum absorbance occurs to kalmagyte concentration above $7×10^{-6}$ molL^{-1}. Therefore, a concentration value of $8×10^{-6}$ molL^{-1} was chosen for further investigation.
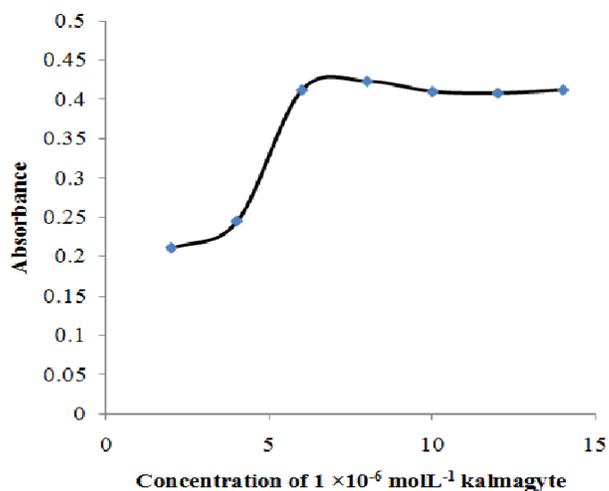
Figure 2. Effect of kalmagyte concentration. Experimental condition: pH=8, volume of buffer=5mL, concentration of surfactant=$3 ×10^{-6}$ mol L^{-1}, volume of *n*-hexane=9mL, volume of methanol =2.5mL, standing time=6 min.

Effect of surfactants concentration

The effect of surfactant concentration is shown in Figure 3. In this figure, the volume of surfactants (SDS, CTAB and CPC) with the concentration 1×10^{-4} mol L^{-1} was investigated in the range of 0.5 to 8 mL. The differences observed in the signals at various surfactant concentrations are shown in Figure 3. At lower concentrations of surfactant, the efficiency is low probably due to the inadequacy of the assemblies to entrap the complex quantitatively. Accordingly, all further experiments were carried out at the optimum volume of 3 mL of CTAB.
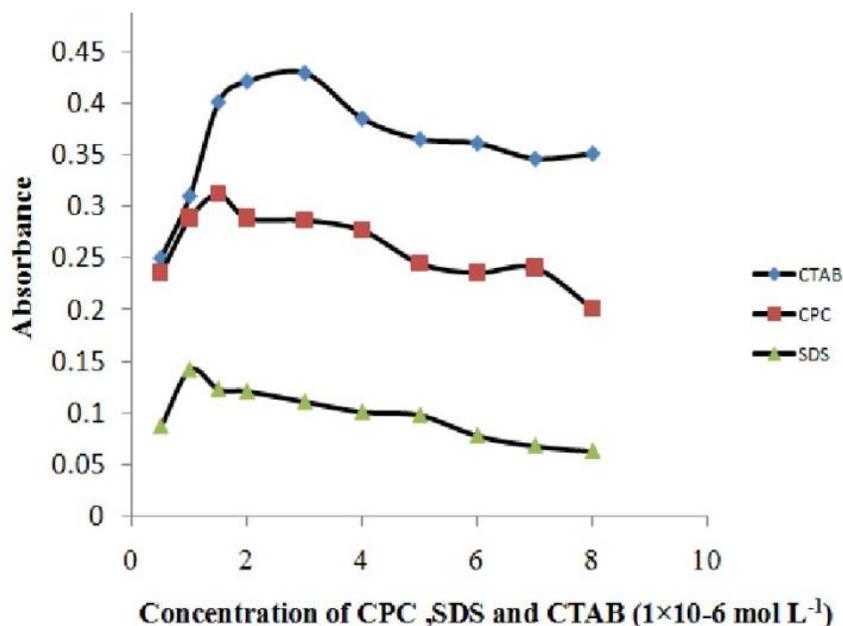
Figure 3. Effect of surfactants concentration. Experimental condition: kalmagyte concentration=8×10^{-6} molL^{-1}, pH=8, volume of buffer=5mL, volume of *n*-hexane=9mL, volume of methanol =2.5mL, standing time=6 min.

Effect of volume of the *n*-hexane

The effect of the volume of the *n*-hexane on the flotation process was examined in the range of 4-11 mL. The results of Figure 4 show that by increasing the n-hexane volume, the absorbance of extracted content increases up to 8 mL. For tin, a similar pattern is observed in the volume range between 8-11 mL. Therefore, 9 mL of *n*-hexane was selected for subsequent experiments.

Effect of volume of methanol and acetonitril

In flotation-spectrophotometric method, after removing the aqueous phase from organic phase, the floated particles should be dissolved in suitable organic solvents such as methanol and acetonitril which are immiscible in n-

hexane phase. Therefore, the effect of volume of methanol and acetonitril on absorbance was studied. In Figure 5, as can be seen, 2.5 mL of methanol provided better results than other volumes.
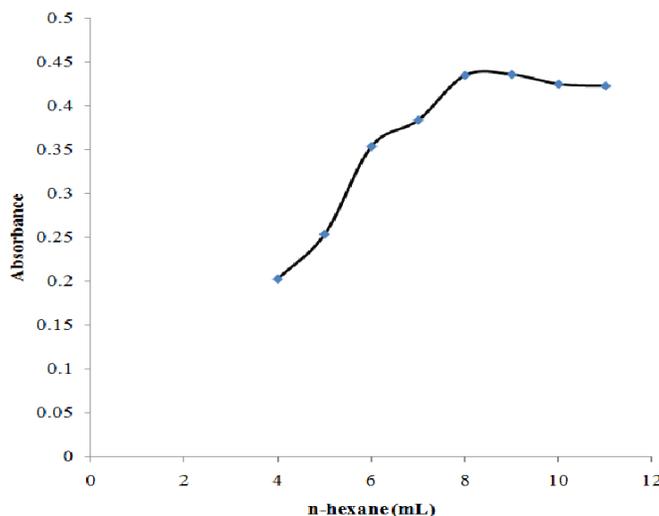
Figure 4. Effect of volume of the *n*-hexane: Kalmagytecon centration=8×10^{-6} molL^{-1}, pH=8, volume of buffer=5 mL, concentration of surfactant=1.5×10^{-6} mol L^{-1}, volume of methanol =2.5mL, standing time=6 min
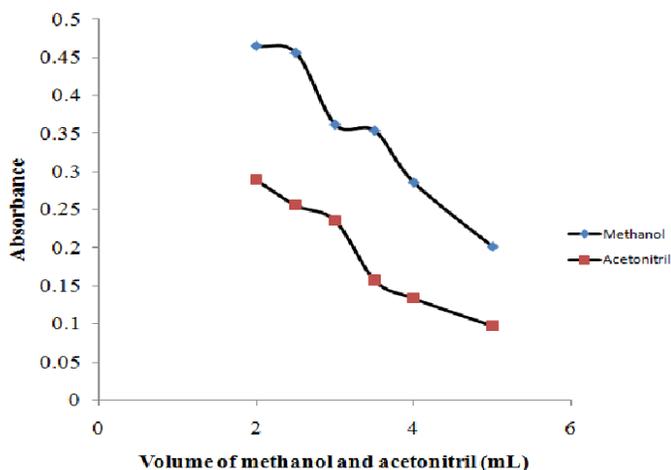
Figure 5. Effect of type and volume of organic solvent. Experimental condition: kalmagyte concentration=8×10^{-5} molL^{-1}, pH=8, volume of buffer=5mL, concentration of surfactant=3×10^{-6} mol L^{-1}, volume of n-hexane=9 mL, standing time=6 min.

Standing time

Figure 6, obviously, indicates that adequate time must be allowed for the system to reach equilibrium in the partitioning of analyte between the aqueous phase and organic phase. The effect of standing time on the extraction

efficiency was examined in the range of 2–12 min. The extraction signals were greatly increased in extraction time from 6 to 12 min and remained constant at this time. So, the standing time was chosen as 6 min.
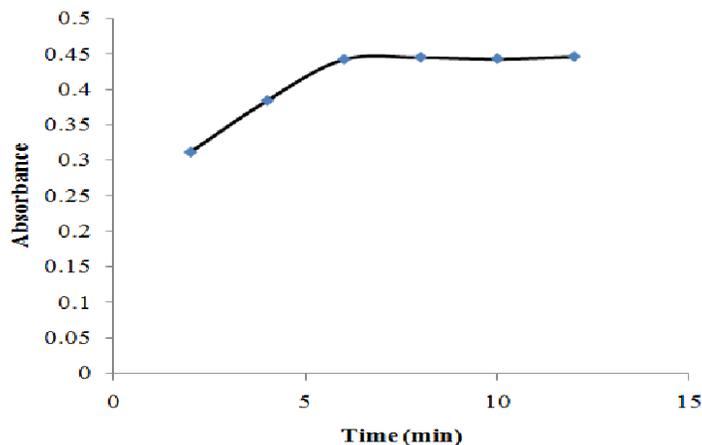
Figure 6. Standing time. Experimental condition: Kalmagyte con centration=8×10^{-6} molL^{-1}, pH=8, volume of buffer=5 mL, concentration of surfactant=3×10^{-6} mol L^{-1}, volume of *n*-hexane=9mL, volume of methanol =2.5mL.

Conformity with Beers law and figure of merit

Under the above optimized conditions, linearity, precision, and limit of detection (LOD) were used to test the validation of the method. The calibration curve was constructed from tin (II) over the concentration range 4–350 ng/mL. The equation for the line is $\Delta A = 2\times10^{-3}C+ 0.165$ with regression coefficient (r^2) of 0.9991 (n = 7) where A is the absorbance and C is the concentration of Tin (II) in ng/mL showing the plot was linear for target compound. In order to determine the precision of the analytical procedure, 10 consecutive analyses were performed at about 100 ng/mL level. The precision for tin (II) was satisfactory with a relative standard deviation value less than 3.66%.

The limit of detection for tin is defined as the concentration of analyte which gives a signal 3σ above the mean blank signal (where σ is the standard deviation of the blank signal). The limit of detection was found 1.7 ng/L for tin (II).

Table 1. Determination of tin (II) in water samples

Test no.	Volume of drinking water	Standard volume added of 2 μg/mL Sn (II)	Measured (ng/mL) This method (n=5, SD^a)	Final Concentration ng/mL	Recovery (%)
1	60	0.0	0.00(±0.13)	0	0.0
2	60	2.0	37.06(±0.18)	40	92.6
3	60	3	57.13(±0.42)	60	95.2
4	60	5.0	100.19(±0.38)	100	100.19

Effect of foreign ions

The influences of some cations and anions on the determination of tin have been thoroughly investigated and a relative error not greater than ±5% of the recovery at a concentration of 20 ng mL^{-1} tin was reported. The tolerance limits of a foreign species are as follows: 1500-fold excess of Na^+ ,K^+, NH^{4+}, SCN^-, SO_4^{2-} and NO_3^-; 550-fold excess of Mn^{2+}, MoO_4^{2+} ,ClO_4^- and HPO_4^{2-} , WO_4^{2-} ,CO_3^{2-}; 200-fold excess of Ba^{2+}, $Hg^{2+}$and Sr^{2+}; 150- fold excess of Fe^{3+} ,Cr^{3+} and Cd^{2+}, F^-; and 70- fold excess of Al^{3+}, Pb^{2+} and Th^{4+}, and do not interfere with the determination of tin in this method.

Application of real samples

In order to investigate the recovery of the proposed method, several water samples were collected, spiked with standard solution of tin (II) at three concentration levels (40, 60, and 100 ng

L^{-1}) and then extracted. The results are summarized in Table 1. The recoveries of the samples ranged from 92.6-100.19% and relative standard deviations (RSDs) were less than 4.21%. The preceding results demonstrated that the proposed method was feasible for quantitative determination of tin (II) in real samples.

Conclusion

In this study, a fast, simple, sensitive and selective method was proposed for the determination of tin in several water samples in the range of 4–350 ng/mL. Based on the results, this method provides an efficient, and inexpensive extraction procedure for the determination of trace amounts of tin in real samples. Since the proposed method is highly accurate, selective and precise, it can be used for a routine quality control analysis and quantitative determination of tin (II) in water

samples. The method is also fast and requires approximately 15 minutes for analysis.

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