Original Research Article

Selective Separation and Preconcentration of trace Amounts of Gallium in Water and Rice Samples using Cloud Point Extraction and Determination by Inductively Coupled Plasma-Atomic Emission Spectrometry

Asadollah Beiraghi[*] and Mina Roshdi

Faculty of Chemistry, Kharazmi University, Mofatteh Avenue, No. 49, P.O. Box 15614, Tehran, Iran

*Corresponding author Fax number: Tel.:+98 2186072706

*E-mail: beiraghi@khu.ac.ir

ABSTRACT

In the present study a cloud-point extraction process using non-ionic surfactant Triton X-114 for selective extraction of gallium from aqueous solutions was developed. The method is based on the complex formation of Ga (III) with N, N′ -bis (salycilidene)-1, 2-phenylenediamine (salophen) as a chelating agent in buffer media of pH 5. After phase separation and dilution of the surfactant-rich phase with 0.2 mL of a (80-20) propanol-water mixture containing 0.02 mL HNO_3, the enriched analyte was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The variables affecting the complexation and extraction steps were optimized. Under the optimum conditions (i.e. 7.5×10^{-5} mol L^{-1} salophen, 0.5% (v/v) Triton X-114, 45°C equilibrium temperature, incubation time 15 min) the calibration graph was linear in the range of 20–120 ng mL^{-1} with detection limit of 1.5 ng mL^{-1}. The precision (R.S.D. %) for

five replicate determinations at 60 ng mL^{-1} of Ga (III) was better than 4%. In this manner, the preconcentration factor was 22.2. Under the presence of foreign ions, no significant interference was observed. Finally, the proposed method was utilized successfully for the determination of gallium in water and rice samples.

Keywords: Cloud point extraction; Gallium; Inductively coupled plasma atomic emission

spectrometry; Salophen; Rice

Introduction

Although, some of the inorganic cations (such as calcium) act as vital micronutrients in the body and their deficiency can lead to various sicknesses [1] there are cations that not only have no nutritional value for human but also are highly toxic and dangerous. Because of their un-degradability and accumulation in the human body, they can eventuate too many diseases, such as cancer, kidney and liver damage, hair loss, hearing loss and very severe toxic effects [2]. Gallium is ideal example for this type of cations. The supply and demand of gallium products has gradually increased during the past decade. Gallium salts are used in medicine as tumor-scanning [3] and antitumoral agents [4]. Important application of Ga is in the semiconductor industry [5-7]. In recent years, it has been employed in many applications, such as microwave transceivers, laser diodes in compact discs and other electronics [8]. From an environmental point of view, the increasing importance and use of compounds such as gallium arsenide in the semiconductor industry, has posed the question of its toxicity and potential hazard when it is suspended in the industrial atmosphere [6, 9-12]. These are reasons for developing sensitive analytical methods for the determination of gallium. In recent years, several techniques have been reported for the determination of gallium in different types of matrices including, spectrophotometry [13], derivative spectrophotometry [14], AAS [15,16], ICP-AES [17,18], ICP-MS [19], X-ray fluorescence spectrometry [20], electro analytical techniques such as voltammetry [21,22], polarography [23], chronopotentiometry [24,25], ion-selective electrode [26], coulometric [27] and PVC-membrane bulk optode [28]. In almost all these methods,

especially in spectrometry methods, a prior separation and preconcentration of the analyte is necessary for trace gallium determination, in order to improve the precision, accuracy and to overcome matrix and reagent interferences. Solvent extraction is one of the widespread methods, which was used for recovering gallium from dilute sources [19-34]. Also other extraction and preconcentration techniques such as solid phase extraction [35,36], extraction by micro emulsions [37], ion exchange [38,39], supercritical fluid extraction (SFE) [8,9] and membrane [40] have been used for gallium ions.

In the last decade, an increasing interest is shown all over the world in developing surfactant-based methods in all fields of analytical chemistry. One of these methods is called cloud point extraction (CPE) which is based on the clouding phenomenon of surfactant solutions above a certain temperature and obtaining a concentrate phase of hydrophobic solutes [41,42].

Salophen, which is one of the most popular symmetrical tetra dentate ligands, forms complexes with various metal ions [43]. The structure of salophen is depicted in Figure 1. In literature, there is no report on the complex formation of this reagent with Ga^{3+} ion. Thus in order to obtain information about the stoichiometry and stability of this complex, some experiments were carried out.
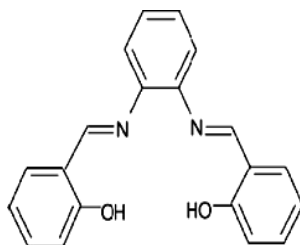

Fig 1. Salophen's structure.

In this work after preliminary spectrophotometric studies on the complex formation of salophen with Ga (III), we report a highly selective, sensitive and accurate method based on cloud point extraction coupled with ICP-AES for selective determination of gallium at $\mu g\ L^{-1}$ levels, using salophen as a chelating agent, in water and rice samples. It is important to say neither

Spectrophotometric studies on the complex formation of salophen with Ga^{3+} ion nor the cloud point methodologies have been reported in the literature as being used for gallium determination, in fact both are reported for the first time.

Experimental

Materials

All the chemicals and reagents were of the highest purity available and used as received. The nonionic surfactant Triton X-114 was from Sigma (St. Louis, MO, USA). Standard gallium solutions were prepared by serial dilution of a 1000 mg L^{-1} standard (Fluka, Gallium Standard for AAS) with water. The pH was adjusted with the buffer solutions CH_3COONa/HCl, for pH 3–6 and $KH_2PO_4/NaOH$, for pH 7–8. A stock solution of salophen (1×10^{-3} mol L^{-1}) was prepared by dissolving an appropriate amount of this ligand in methanol.

Synthesis of N, N′ -bis (salycilidene)-1, 2-phenylenediamine

An ethanol solution (10 mL) containing 1,2-phenylenediamine (approx 3 g) was transferred into a 150 mL quick fit round-bottomed flask, fitted with a quick fit condenser and then salycilaldehyde (approx 5 mL) was added drop wise. The mixture was refluxed for 10 h, filtered and recrystalized twice in ethanol [43].

Apparatus

A Perkin-Elmer model lambda 25 double beam UV–Vis spectrophotometer with a 1 cm quartz cells was used for recording all spectra and absorbance measurements. Simultaneous inductively coupled plasma optical emission spectrometer (ICP-AES, Varian Vista-PRO, Mulgrave, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD) detector was used for measurement of Ga in the surfactant-rich phase. A Metrohm 827 pH meter equipped with a Metrohm glass electrode was used for pH measurements. A Julabo model F12

water bath (Germany) with $\pm0.1°C$ temperature control was used for cloud point extraction experiments and a centrifuge with 10 mL calibrated centrifuge tubes (Superior, Germany) was utilized to accelerate the phase separation process.

Procedure

An aliquot of Ga (III) standard solution was transferred to a 10 mL centrifuge tube; 0.75 mL of 1×10^{-4} mol L^{-1} salophen solution and 1mL of a buffer solution (0.1 mol L^{-1}, pH 5) were added. The mixture was left for 15 min to complete complex formation before the addition of 0.5 mL of 5% (v/v) of Triton X-114 solution. Then the solution was up to the mark (10 mL) with doubly distilled water. Subsequently, the sample was shaken and left to stand in a thermostatted water bath for 15 min at 45°C. Separation of the aqueous and surfactant-rich phase was accelerated by centrifugation for 7 min at 3500 rpm. After cooling in a salt-ice bath, the surfactant-rich phase became viscous. Then the aqueous phase was carefully removed with a pipette and 0.2 mL of a 80:20 methanol-water mixture containing 0.02 mL HNO3 was added to the surfactant-rich phase to reduce its viscosity and increase the sample volume for the ICP-AES measurement. Finally, the samples were introduced into the plasma with a peristaltic pump. The intensity was measured at 294.363 nm as the selected emission wavelength for gallium and the concentration was determined using the regression equation given in Table 3.

Analysis of Water and Rice Samples

Tap and seawater samples were collected from Tehran and the Caspian Sea (Zibakenar) in Iran, respectively. Each sample was filtered using a 0.45μm PTFE filter, and adjusted to approximately pH 5 by adding NaOH\HNO3. An aliquot of sample (7 mL) first directly and then spiked with appropriate amount of Ga^{3+} was subjected to the cloud-point extraction methodology as described above.

Pretreatment of rice sample was carried out according to the literature [44]. The rice sample was first dried at 110 °C and then grounded using an agate mortar. Then 0.5 g of the sample was

weighed and transferred into a beaker. 9 mL of concentrated HNO_3 was added and the mixture was kept overnight. Then the contents of the beaker were evaporated near to dryness (at about 130°C) on a hot plate. After cooling to room temperature, 3 mL of concentrated HNO_3 and 2 mL of concentrated $HClO_4$ were added into the beaker and again it was evaporated near to dryness, diluted to volume with distilled water in a volumetric flask (25.0mL). 7mL of this solution subjected to the cloud point extraction as described about water samples.

Results and discussion

3.1. Preliminary Complexation Studies

In order to obtain some information about the stoichiometry and stability of the Ga (III)-salophen complex, in preliminary experiments, the complexation of salophen with this cation was investigated spectrophotometrically in methanol solvent. In this manner, a solution containing a constant concentration of salophen (7.0×10^{-5} mol L^{-1}) was titrated with a methanol solution of Ga (III). The resulted spectrum is given in Figure 2. As it is obvious, an increase in the absorption band at 393 nm and a decrease in the absorption band at 263 nm were apparent as the concentration of complex is increased and the concentration of free ligand is decreased. The absorption data at 393 nm was used for stoichiometry study of complex (Figure 3). As can be seen from this figure, the absorbance-mole ratio plot reveals distinct inflection at metal to ligand ratio of 1:1, indicating that the resulted complex has 1:1 (metal-to-ligand) stoichiometry. The formation constant (Log K) of the resulting complex was evaluated as 5.4, by computer fitting of the absorbance-mole ratio data using KINFIT program [45] at the same wavelength.
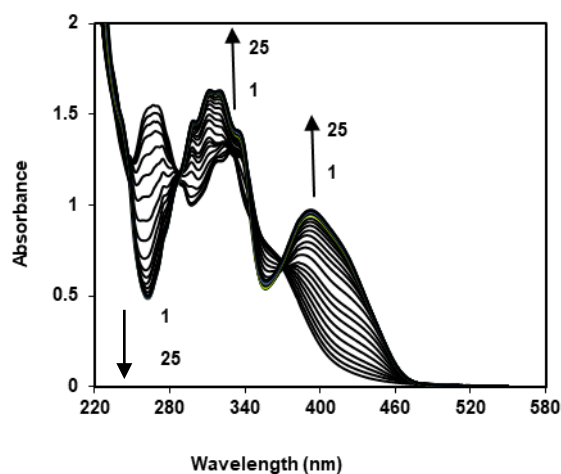
Fig 2. Absorption spectra of salophen (7.0×10^{-5} M) in methanol solution at 25◦C in the presence of varying concentration of Ga(III) ion (mol L^{-1}): (1) 0.0×10^{-5}, (2) 0.53×10^{-6}, (3) 1.06×10^{-5}, (4) 1.60×10^{-5}, (5) 2.14×10^{-5}, (6) 2.67×10^{-5}, (7) 3.21×10^{-5}, (8) 3.74×10^{-5}, (9) 4.28×10^{-5}, (10) 4.81×10^{-5}, (11) 5.34×10^{-5}, (12) 5.88×10^{-5}, (13) 6.41×10^{-5}, (14) 6.95×10^{-5}, (15) 7.49×10^{-5}, (16) 8.02×10^{-5}, (17) 8.56×10^{-5}, (18) 9.09×10^{-5}, (19) 9.63×10^{-5}, (20) 1.02×10^{-4}, (21) 1.07×10^{-4}, (22) 1.12×10^{-4}, (23) 1.18×10^{-4}, (24) 1.28×10^{-4} and (25) 1.82×10^{-4}.
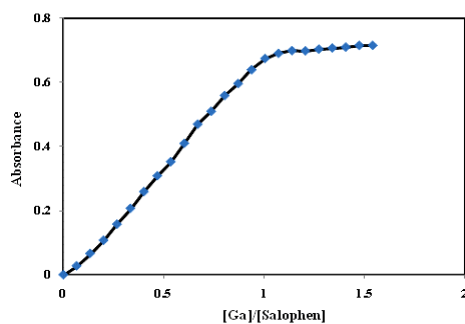

Fig 3. Mole ratio plot of complexation of salophen with Ga (III) in methanol solution at 393 nm.

3.2. Method Development

At first and before analysis of standards and real samples, different variables, which affect the intensity of atomic emission signal of extracted gallium in ICP-AES, were optimized using a standard solution of this element. The instrumental parameters (i.e. generator power, generator frequency, plasma gas flow rate, and auxiliary flow rate, nebulizer pressure, viewing height, stability time and wavelength) are given in Table 1.

Table 1. Operation parameters of ICP-AES

Parameter	Value
RF generator power (W)	1400
Frequency of RF generator (MHz)	40
Plasma gas flow rate (L min^{-1})	14
Auxiliary gas (L min^{-1})	1.5
Nebulizer pressure (kPa)	200
Viewing height (mm)	8
Stability time (s)	38
Wavelength (nm)	294.363

3.3. Optimization of the System

Effect of pH: The separation of metal ions by cloud point method involves prior formation of a complex with sufficient hydrophobicity which then can be extracted by the small volume of surfactant-rich phase; thus obtaining the desired preconcentration. pH plays a unique role on metal-chelate formation and subsequent extraction. Figure 4 shows the influence of pH on the

emission intensity of the gallium at 294.363nm. As can be seen, at pH 5 maximum extraction efficiency was obtained. Hence, this pH was chosen for the subsequent experiments.
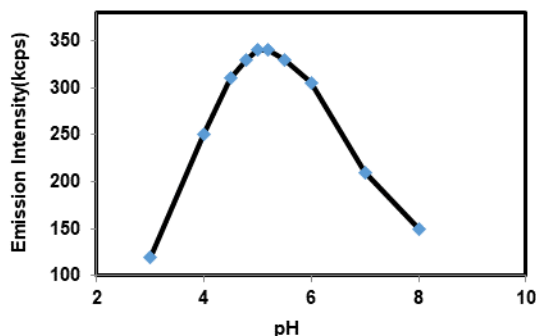

Fig 4. Effect of pH on the emission intensity of gallium after extraction. Extraction Condition: Ga (III) 60 ng mL^{-1}; salophen $7.5{\times}10^{-6}$ mol L^{-1}; Triton X-114 0.5% (v/v); equilibrium temperature 45°C for 15 min extraction time; centrifugation time 7 min in 3500 rpm.

Effect of salophen concentration: The extraction efficiency as a function of the salophen concentration is shown in Figure 5. For this study, 10 mL of a solution containing 600 ng Ga (III) with various amounts of salophen ($(0.25-1.4) {\times}10^{-5}$ mol L^{-1}) was subjected to the CPE method. The results revealed that the extraction recovery increases by increasing salophen concentration up to $7.5{\times}10^{-6}$ mol L^{-1} and remained nearly constant at higher concentrations. Therefore, this concentration was selected as optimum value.
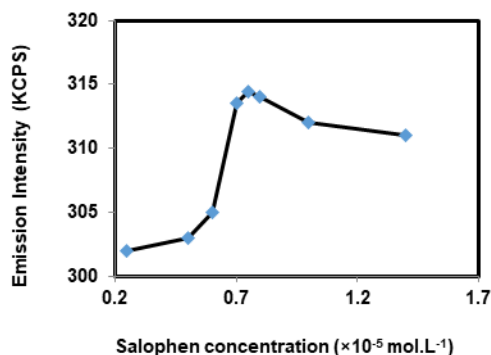

Fig 5. Effect of reagent concentration on the emission intensity of gallium after extraction. Ga (III) 60 ng mL^{-1}; Triton X-114 0.5% (v/v); extraction condition as described in text.

Effect of Triton X-114 concentration: The amount of nonionic surfactant Triton X-114 is critical because it affects the quantitative extraction of analyte and therefore method sensitivity [41]. In addition, the high density of the surfactant-rich phase facilitates phase separation by centrifugation [46]. The effect of Triton X-114 concentration on the emission intensity of the extracted phase was investigated in the range of 0.1-1% (v/v). As seen in Figure 6 the concentration of 0.5% (v/v) was chosen as optimum for the quantitative recovery of complex. At lower concentrations, the extraction efficiency of complex is low, probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively.
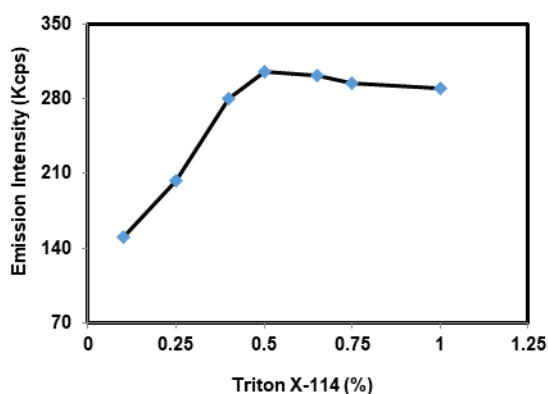

Fig 6. Effect of Triton X-114 on the emission intensity of gallium after extraction. Ga (III) 60 ng mL^{-1}; salophen 7.5×10^{-6} mol L^{-1}; extraction condition as described in the text.

Effects of the equilibration temperature and time: The equilibration temperature above the critical point temperature (CPT) of Triton X-114 and the incubation time were the parameters optimized next. It is desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which compromise with the completion of the reaction and the efficient separation of phases. The dependence of emission intensity upon equilibration and incubation times was studied within the range of 5-30 min. Time of 15 min was chosen as optimal time for completion of the clouding process and analyte extraction. It was also observed that a temperature of 45ºC is sufficient for the maximum recovery of the analyte.

Effect of centrifugation time: Centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same sense as in conventional separation of a precipitate from its original aqueous environment [40]. A centrifuge time of 7 min was selected as optimum, as

complete separation occurred within this time and no appreciable improvements were observed for longer periods.

Effects of added electrolyte: The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency [46]. It was observed that the addition of inorganic salts including NaCl, KNO_3 and Na_2SO_4 in the range of 0–2 mol L^{-1} had no significant effect on the cloud point extraction efficiency.

3.4. Selectivity Studies

In view of the high selectivity provided by inductively coupled plasma spectrometry, the only interferences studied were those related to the preconcentration step, and thus affecting extraction efficiency. After selecting the optimum conditions, to carry out this study, a series of solutions (10 mL) containing 60 ng mL^{-1} of Ga^{3+} and different concentrations of interfering ions were subjected to the complete procedure. The results revealed that the Ga^{3+} recovery was almost quantitative in the presence of other ions with tolerance limits shown in Table 2. The tolerance limit was defined as the concentration of added ion causing less than ±5٪ relative error. As can be seen, a number of bivalent and some trivalent cations can interfere with the determination of Ga^{3+} at different ratio. It is important to note that interferences by foreign cations only affect the salophen concentration because the detection step is highly selective; therefore, any ligand loss can be avoided by increasing its concentration. Most of the Interfering cations can also be eliminated by the appropriate dilution of sample, or the addition of KSCN, KI and trisodium citrate, as removing and masking agents. It is evident that among the interfering ions which were tested; alkali, alkaline earth elements and anions (such as nitrate, sulfate and others) do not have any significant effects on the extraction efficiency.

Table 2. Tolerance limits of interfering ions in the determination of Ga (60 ng mL^{-1})

Ions	Interferents-to-analyte ratio
Li$^+$, Na$^+$, K$^+$, Mg^{2+}, Ba^{2+}, SO$_4^{2-}$, NO$_3^-$, CH$_3$COO$^-$, PO$_4^{3-}$, ClO$_4^-$	1000:1
Al^{3+}, Ca^{2+} , Pb^{2+}	500.1
Fe^{3+} , Sn^{2+}	100:1
Ni^{2+}, Co^{2+}, Mn^{2+}, Hg^{2+}, Cu^{2+}	20:1

3.5. Analytical Characteristics

Table 3 summarizes the analytical characteristics of the optimized method, including regression equation, linear range, and limit of detection (LOD), reproducibility and preconcentration factor. The limit of detection which was defined as $CL = 3s_B/m$ (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 1.5 ng mL^{-1}. Because the amount of gallium in 10 mL of sample solution is measured after preconcentration by CPE in a final volume of 0.45 mL (0.25 mL surfactant-rich phase + 0.2 mL diluents), the solution is concentrated by a factor of 22.2. The relative standard deviation (R.S.D.) for five replicate measurements of 60 ng mL^{-1} of gallium was 4.0%.

Table 3. Analytical characteristics of the proposed method

Parameter	Value
Linear range (ng mL^{-1})	20–120
Regression equation (n = 7) (C, ng mL^{-1})	Y = 14.07C- 67.50
Correlation coefficient (R^2)	0.9997
Reproducibility (R.S.D., %) (n = 5)	4
Limit of detection (ng mL^{-1}) (n=5)	1.5
Preconcentration factor	22.2

3.6 Validation and Application

In order to validate the proposed method, it was applied to the determination of gallium in tap water and seawater samples. The results are shown in Table 4. The mean recoveries for the addition of different concentration of gallium to water samples were in the range of 97.5-108%. The results showed that the proposed method could be successfully applied to the determination of trace amounts of gallium in water samples. To assess the applicability of the method to other real samples, it was applied to the determination of gallium in rice. In this case, 7 mL of rice sample was first preconcentrated and then its gallium was determined using standard addition method. An average content of Ga (III) in rice was determined to be162 ng/g with average recovery of 95%.

Table 4. Determination of Ga^{3+} in real-spiked samples

Ga $(ng\ mL^{-1})$			
Samples	Added	Found	Recovery (%)
Tap water	0.0	0.1 ± 0.20^a	-
	60	62 ± 0.48	103
	80	78 ± 0.42	97.5
	100	101 ± 0.23	101
Seawater	0	1.5 ± 0.38	-
	60	65 ± 0.82	108
	80	81 ± 0.63	101
	100	98 ± 0.46	98

a.   Mean $\pm$ RSD%

4. Conclusion

Spectrophotometric studies on salophen indicated that it forms a complex with Ga (III) having a stoichiometry of 1:1. Based on this complex formation, a cloud point extraction method coupled with ICP-AES was developed for the selective separation, preconcentration and determination of this cation at $\mu g\ L^{-1}$ levels. The proposed method provides a good reproducibility and gives a precise, highly sensitive and selective procedure for the determination of gallium that is applicable to the water and rice samples containing trace amounts of this element. It is important to say neither Spectrophotometric studies on the complex formation of salophen with Ga^{3+} ion nor the cloud point methodologies have been reported in the literature as being used for gallium determination, in fact both are reported for the first time.

Acknowledgments

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