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Utility of solid phase extraction for UV-visible spectrophotometric determination of gallium in environmental and biological samples

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A sensitive, selective and rapid method for the determination of gallium based on the sensitive reaction of Ga(III) with 1-(2-benzothiazolylazo)-2-hydroxy-3-naphthoic acid (BTAHN) and the solid phase extraction of the BTAHN – Ga(III) complex on a column of Amberlite XAD-4 resin was developed. In the presence of 2.0 mol L^{-1} of nitric acid solution and cetylpyridinium chloride (CPC) medium, BTAHN reacts with gallium(III) to form a deep red complex with a molar ratio 2:1 {BTAHN to Ga(III)}. The complex was enriched by solid phase extraction with an Amberlite XAD-4 resin. An enrichment factor of 500 was obtained by elution of the complex from the column with the minimal amount of dimethylformamide (DMF). The molar absorptivity of the complex in DMF medium was 5.57×10^7 L mol^{-1} cm^{-1} at 599 nm. Beer's law was obeyed in the range of 0.01 – 0.70 µg mL^{-1}. The relative standard deviation for eleven replicate samples at the 0.50 µg mL^{-1} level was 0.95 %. The attained detection and quantification limits amounted to 3.1 and 10.2 ng mL^{-1}, respectively. This method was applied to the determination of gallium in environmental water and biological samples with good results.

Keywords: Solid phase extraction; Gallium determination; Thiazolylazo dyes; Spectrophotometry; Environmental and biological analysis.

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Introduction

Gallium does not occur in nature, but the gallium(III) salt exists in trace amounts in bauxite and zinc ores. Gallium(III) has the major application in semiconductor devices as gallium arsenide and gallium nitride which in turn is used in light emitting diodes (LEDs).[1] The concentration of Ga in natural water is very low, typically less than 5 ng L^{-1}. Again, the average gallium concentrations in subsoil and topsoil are 13.8 mg kg^{-1} and 13.5 mg kg^{-1}, respectively.[2] Ga(III) is known to be highly toxic and cause carcinogenesis in animals and humans. Symptoms of acute poisoning (including gastrointestinal discomfort, vomiting, coma, and sometimes death) usually occur within 30 min of ingestion of gallium arsenide (GaAs), whereas the consequences of chronic poisoning (including anemia, leucopenia, skin cancer, and other internal cancers) are much more insidious. A single dose of 100 mg kg^{-1} of GaAs results in acute pulmonary inflammation and pneumocyte hyperplasia after 14 days of ingestion.[3] Chronic exposure (2-year observation period) to as low as < 1.0 mg L^{-1} dose of GaAs produced systemic toxicity and definite pulmonary lesions. In addition, testicular toxicity was observed, and tumor occurrence increased significantly in mice when GaAs were injected intraperitoneally.[4] There was also evidence of renal toxicity. Therefore its determination is very crucial for health and economic purposes.

Several techniques have been reported for the determination of gallium, spectrophotometric,[5–7] chromatography,[8–10] ET–AAS,[11–13] AAS,[14,15] ICP–AES,[16,17] X-ray fluorescence spectrometry,[18–20] GF–AAS,[21,22] calorimetry,[23] fluorimetry,[24] voltammetry,[25–27] chronopotentiometry,[28] electrochemical reduction,[29] and polarography.[30] A solid phase extraction method combined with ICP-AES for determination of trace gallium in different real samples has been reported.[31,32] Up till

now, no solid phase extraction combined with UV-Vis spectrophotometric measurements for gallium determination was found in the literature.

Aside from the more sensitive and relatively interference-free atomic absorption and emission spectrometric methods of gallium quantification,[33] the cheaper and more common spectrophotometric methods require the use of colour-forming reagents such as rhodamine B,[34] 4-(2-pyridylazo)- resorcinol (PAR),[35] 1-(2-pyridylazo)-2-naphthol (PAN),[36] xylenol orange,[37] eriochrome black T,[38] 2,6,7-trihydroxy-9-phenyl-3H-xanthen-3-one (phenyl fluorone),[39] salicylaldehyde-4-aminobenzoylhydrazone,[40] and 2-[2-(3,5-dibromopyridyl)-azo]-5-diethylamino-benzoic acid.[41] Unfortunately, most of these chromogenic reagents require preliminary operations in the form of Ga extraction into organic solvents.[39] Generally, colorimetric ligands having O- and N donor atoms, like PAR, PAN, 8-hydroxyquinoline and xylenol orange, are non-selective and subject to interference caused by hard Lewis acid cations, especially Fe(III) and Al(III), in the determination of Ga. Thus suitable masking agents can hardly be developed for differentiating the corresponding Ga complex from that of A1 and other hard acids which have similar stabilities.[42]

Solid phase extraction is the one of the sensitive, fast, and economic preconcentration method for the traces analyte ions in the various materials including natural waters, ores, biological samples etc. Various solid phase extract ants including Amberlite XAD resins, Ambersorb resins, naphthalene, Diaion HP-20, Chromosorb resins, silica gel activated carbon[43–56] have been used for the separation and preconcentration of traces of heavy metal ions.

This article describes the investigation of separation and preconcentration of gallium as a BTAHN complex on a column of Amberlite XAD-4 resin. XAD-4 was used as retaining material in the column. Gallium retained was eluted with the

minimal amount of DMF. The presented method was extended to determine gallium in environmental water and biological samples.

Experimental

Apparatus

A PerkinElmer Lambda 12 UV-Visible spectrophotometer with a 10 mm quartz cell was used for all spectral measurements. The extraction was performed on a Waters Solid Phase Extraction (SPE) device (that can prepare 20 samples simultaneously). A PerkinElmer atomic absorption spectrometry model *AAnalyst* 300 was used for all GFAAS measurements.

Reagents

All chemicals used were of analytical grade unless otherwise stated. All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Amberlite XAD-4 resin (polystyrene divinyl benzene type, 20–60 mesh and surface area of 725 m^2 g^{-1}) was obtained from Aldrich. Cetylpyridinium chloride (CPC) solution (3.0 % w/v) was prepared by dissolving CPC in 20 % ethanol. Dimethylformamide (DMF) (Aldrich) was used.

A standard stock solution of gallium(III), 1000 μg mL^{-1}, was prepared by dissolving 1.0 g of gallium (Aldrich) in aqua regia (3.0 mL HCl : 1.0 mL HNO_3) and the mixture was diluted to 1.0 L of bidistilled water. They were standardized by titration with EDTA (Aldrich). Working solutions were prepared by appropriate dilutions. BTAHN used in the present investigation was prepared according to the procedure described previously.[57] A stock 2×10^{-3} mol L^{-1} solution of BTAHN was prepared by dissolving an appropriate weight of the reagent in a minimum amount of pure ethanol and brought to 100 mL in a calibrated flask with ethanol.

General procedure

To a standard of a sample solution containing no more than 0.70 μg of Ga(III) in a 500 mL volumetric flask, 10 mL of 2.0 mol L^{-1} nitric acid, 5.0 mL of 2×10^{-3} mol L^{-1} BTAHN solution and 2.5 mL of 3.0 % CPC solution were added. The mixture was diluted to the mark and mixed well. After 5.0 min, the solution was passed through a column of Amberlite XAD-4 resin at a flow rate of 50 mL min^{-1}. After the enrichment had finished, the retained complex was eluted from the column with 1.0 mL of DMF at a flow rate of 5.0 mL min^{-1}. The absorbance of the eluant was measured in a 10 mm cell at 599 nm against a reagent blank prepared in a similar way without gallium.

Analysis of the real samples

A 500 mL of tap water, wastewater, well water and seawater samples were filtered through 0.45 μm membrane filter, acidified with HNO_3 and subjected to the recommended procedure for the preconcentration and determination of Ga(III) ions.

Determination of gallium in human serum

Mineralization of 2.0 mL of the samples was carried out for 1.0 h at 100 ^{o}C with the addition of 4.0 mL of concentrated nitric acid.[58] Then samples were analyzed directly after dilution with water to a suitable volume applying the standard addition techniques.

Determination of gallium in urine samples

Gallium may enter human body through contamination in water or food etc. Thus, its quantification in biological fluid is anticipated. A known amount of gallium(III) was added to 30 mL of healthy human urine that was previously tested negative for gallium, which was taken in a 100 mL micro-Kjeldahl flask, a glass bead and 5.0 mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was removed

and cooled. Then 1.0 mL of concentrated sulphuric acid was added carefully followed by the addition of 1.0 mL of 70% perchloric acid and heating was continued to dense white fumes, repeating nitric acid addition if necessary. Further, heating was carried out for at least 30 min, followed by cooling. The contents of the flask were filtered and diluted up to the mark with distilled water in 500 mL calibrated flask. A suitable aliquot of urine sample was taken and analyzed by using the procedure outlined earlier using the standard addition techniques.

Results and discussion

Absorption spectra

The absorption spectra of BTAHN and its Ga(III) complex are shown in Fig. 1. The absorption bands of BTAHN and its complex are located at 524 nm and 599 nm. When extracted into DMF medium, the absorption bands of BTAHN and its complex do not change. Therefore, 599 nm was selected for the absorbance measurements.

Effect of acidity

The results showed that the optimal condition for the reaction of Ga(III) with BTAHN is in acid medium. Therefore, the effect of hydrochloric, nitric, sulfuric, perchloric, phosphoric acids, *etc.*, on the color reaction of BTAHN with Ga(III) was studied. The results showed that nitric acid has the best effect, and a concentration of nitric acid within 2.0 mol L^{-1} was found to give the maximum and constant absorbance. Moreover the volume of 10 mL of 2.0 mol L^{-1} HNO_3 solution was examined to achieve maximum color intensity (Fig. 2) which included that, 10 mL of 2.0 mol L^{-1} HNO_3 is recommended for all further studies.

Effect of surfactants

The effect of surfactants on the BTAHN–Ga(III) complex was studied. The results indicated that in the presence of nonionic, or cationic surfactants, the absorption of the chromogenic system increased markedly. Cationic surfactant gave highly and constant absorbance, in addition to consuming time. The results indicated that CPC is the best additive of the examined cationic ones. The use of 2.0 – 3.0 mL of 3.0 % CPC solution give a constant and maximum absorbance (Fig. 3). Accordingly, the use of 2.5 mL of 3.0 % CPC solution is recommended, since the results is highly concordant at this concentration.

Effect of the BTAHN concentration

For up to 0.70 µg of Ga(III), the use of about 4.5 – 5.5 mL of 2×10^{-3} mol L^{-1} BTAHN solution (Fig. 4) was found to be sufficient for complete reaction. Accordingly, 5.0 mL of 2×10^{-3} mol L^{-1} BTAHN solution was added in all further measurements.

Solid phase extraction

Both the enrichment and the elution were carried out using a Waters SPE device (which can prepare 20 samples simultaneously). The flow rate was set to 50 mL min^{-1} for the enrichment and 5.0 mL min^{-1} for the elution. The column was washed with 5.0 mL of ethanol and then washed with 10 mL of water before the enrichment. Some experiments were carried out in order to investigate the retention of BTAHN and its Ga(III) complex on the column. It was found that both BTAHN and its Ga(III) complex were quantitatively retained on the column when the medium was nitric acid. The capacity of the column was determined as 23 mg for the BTAHN–Ga(III) complex in 500 mL of solution. In the present experiment, the maximum amount of gallium was only 0.70 µg. Therefore, the column has adequate capacity to enrich the BTAHN–Ga(III) complex.

In order to chose a proper eluant for the retained BTAHN and its Ga(III) complex, various organic solvents were studied. The volume of solvent required to elute the BTAHN – Ga(III) complex from the column was 0.8 mL DMF, 1.8 mL for isopentyl alcohol, 1.6 mL for acetone, 2.7 mL for acetonitrile, 3.5 mL for ethanol, 3.8 mL for methanol. The maximal enrichment was achieved when DMF was selected as eluant. Hence, DMF was selected as the eluant. It was experimentally shown that it was easier to elute the retained BTAHN and its Ga(III) complex in the reverse direction than in the forward direction, hence it was necessary to upturn the column for the elution. 1.0 mL of DMF was sufficient to elute BTAHN and its Ga(III) complex from the cartridge at a flow rate of 5.0 mL min^{-1}.

Composition of the complex

The nature of the complex was established at the optimum conditions described above using the continuous variation and molar ratio methods. The plot of absorbance versus the mole fraction of Ga(III), showed inflection 0.34, indicating presence of two BTAHN molecules in the formed complex. Moreover, the molar ratio method showed a ratio of BTAHN to Ga(III) = 2.0. Consequently, the results indicated that the stoichiometric ratio was (2:1) {BTAHN : Ga(III)}. The conditional formation constant, calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 6.55, whereas the true constant was 6.50.

For ion associate complexes of Ga–BTAHN–CPC, the stoichiometric ratio as obtained from molar ratio indicated the formation of 1:1 for $[Ga(BTAHN)_2]$: CPC; so we conjectured that an ion association complex $[Ga(BTAHN)_2]^-$ $[CPC]^+$ is formed in the system. The structure of which is probably as follows:

$$Ga(III) + 2\ BTAHN \rightleftharpoons [Ga{-}(BTAHN)_2]^-$$

$$[Ga–(BTAHN)_2]^- + [CPC]^+ \rightleftharpoons \{[Ga(BTAHN)_2]^- [CPC]^+\}$$

Stability of the chromogenic system

After mixing the components, the absorbance reaches its maximum within 5.0 min at room temperature and remains stable for 6.0 h in aqueous solution. After extracted into DMF, the complex was stable for at least 15 h.

Effect of diverse ions.

In order to assess the possible analytical applications of the recommended procedure, the effect of foreign ions on the separation and preconcentration of Ga(III) ions was studied. A fixed amount of analytes was taken with different amounts of foreign ions and the recommended procedure was followed. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding ± 5.0 % in the determination of investigated analyte ions by the combination of the column solid phase extraction and spectrophotometric determination methods. The results are summarized in Table 1. As it is seen, most of ions used have no considerable effect on the determination of Ga(III) ions.

Calibration curve and sensitivity

The calibration curve show that Beer law is obeyed in the concentration range of 0.01 – 0.70 µg Ga(II) per mL in the measured solution. For more accurate analyses, Ringbom optimum concentration range was investigated to be 0.05 – 0.67 µg mL^{-1}. The linear regression equation obtained was: A = 0.8 C (µg mL^{-1}) – 0.0061, (r = 0.9994).

The molar absorptivity, was calculated to be 5.57×10^7 L mol^{-1} cm^{-1}, whereas Sandell sensitivity was found to be 0.0013 ng cm^{-2} at 599 nm. The detection and quantification limits, based on 3 and 10 times the relative standard deviation of the blank,[59] were 3.1 and 10.2 ng mL^{-1}. The relative standard deviation at a concentration

level of 0.5 μg mL^{-1} (11 repeat determinations) was 0.95 %. The comparative data for the figure of the merits of some previous reports[60 −64] on solid-phase extraction of gallium ions using various sorbents and those for the proposed method are summarized in Table 2. As is obvious from Table 2, the preconcentration factor of 500 reported in this work for the Amberlite XAD-4 impregnated with BTAHN for Ga(III) ions is improved over most of the methods given in Table 2. The detection technique applied in this work is more available and easier to use in comparison with that used in other methods. The elution was easily performed with 1.0 mL of DMF. The low matrix effects, as is evident from the analyses of sea and well water samples and blood serum, good tolerance towards most foreign ions and low values of relative standard deviations are the additional advantages of the present method.

Applications

The procedure was checked by applying it to several real samples, namely water, and biological samples. The very low concentrations involved make it difficult to check the reliability of the results. Because the amount of Ga(III) ions in the initial sample solution is measured after DLLME in a final volume of 1.0 mL, the solution is concentrated by an enrichment factor of 20. The detection limit, defined as DL = 3SB/m (where DL, SB, and m are the detection limit, standard deviation of the blank, and slope of the calibration graph, respectively) is sufficiently low and lies around 3.1 μg L^{-1}.

The accuracy of the proposed method was tested by separation and determination of Ga(III) ions in river, waste, tap, well, sea waters, urine and human blood serum samples. In order to validate the method, analytes were determined in spiked real samples. The obtained results are recorded in Tables 3. As is evident, the Ga(III) ions added were quantitatively recovered from the biological and water matrices. Also this method was applied to the determination of gallium in

wastewater sample (electronic industry). As seen, there is good agreement between the results obtained by proposed and GFAAS methods.

The performance of the proposed method was assessed by calculation of the t-value (for accuracy) and F- test (for precision) compared with GFAAS method. The mean values were obtained in a Student's t- and F- tests at 95% confidence limits for five degrees of freedom.[65] The results showed that the calculated values (Table 3) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consuming, shows the advantage of the proposed method over other method

Conclusion

The proposed method has the following characteristics:

(1) BTAHN is one of the most sensitive and selective spectrophotometric reagents for gallium. The molar absorptivity of the complex was 5.57×10^7 L mol^{-1} cm^{-1} in the measured solution. Most foreign ions do not interfere with the determination of gallium.

(2) By solid phase extraction with a column of Amberlite XAD-4 resin, the BTAHN – Ga(III) complex in 500 mL solution could be concentrated to 1.0 mL, an enrichment factor of 500 was achieved. By high enrichment factors, the sensitivity of the method was greatly improved compared to that of the other techniques using solid phase extraction method.

(3) The detection and quantification limits were 3.1, and 10.2 ng mL^{-1}, respectively, in the original sample, and

(4) A successful application of the proposed method in low level of gallium in environmental water and biological samples were determined with good results.

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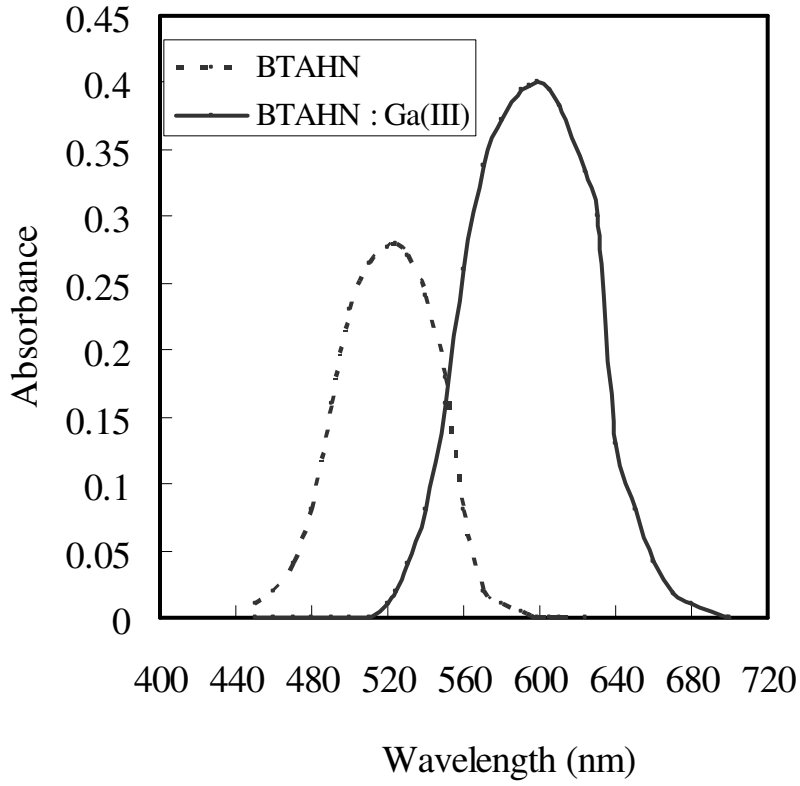


Fig. 1. Absorption spectra of 2 x 10^{-5} mol L^{-1} BTAHN and its complex with 0.5 µg mL^{-1} Ga(III) at the optimum reaction conditions after SPE.

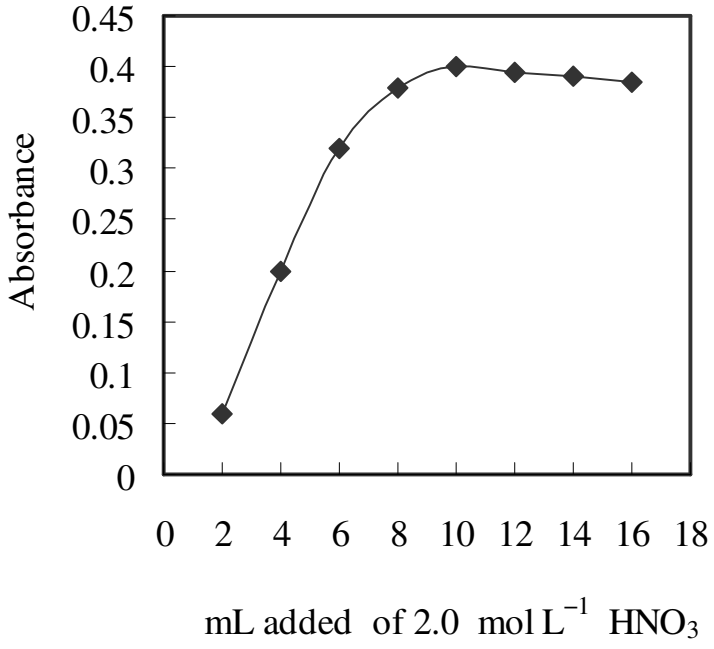


Fig. 2. Effect of volume of 2.0 mol L^{-1} nitric acid on the complexation of 0.5 µg mL^{-1} Ga(III) at optimum conditions.

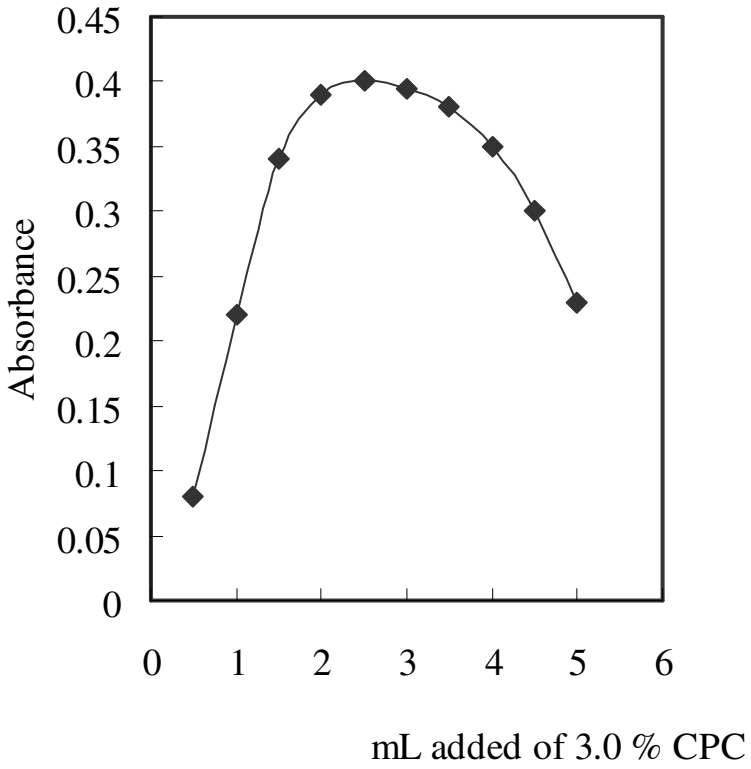


Fig. 3. Effect of 3.0% CPC volume on the complexation of 0.5 μg mL^{-1} Ga(III) at the optimum conditions

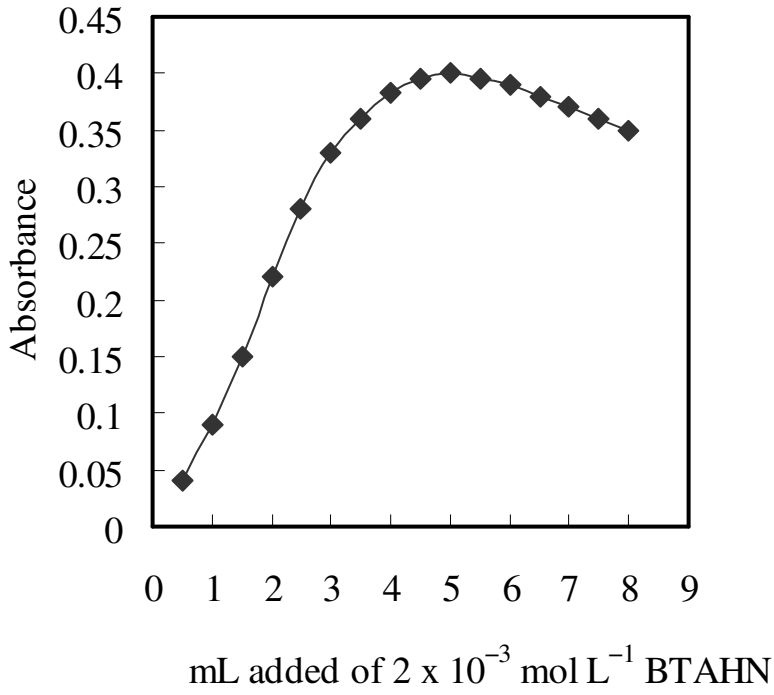


Fig. 4. Effect of 2 x 10^{-3} mol L^{-1} BTAHN volume on complexation of 0.5 µg mL^{-1} Ga(III)

Table 1 Separation of Ga(III) from binary mixtures in the presence of different diverse ions.

Ion	Added as	Concentration (μg mL^{-1})	Recovery (%) Ga(III)
Na^{+}	NaCl	20000	99.4
K^{+}	KCl	15000	99.5
Mg^{2+}	$MgCl_2$	12000	98.0
Ca^{2+}	$CaCl_2$	10000	98.9
Ba^{2+}	$BaCO_3$	8000	97.7
Mn^{2+}	$Mn(NO_3)_2$	5000	97.3
Co^{2+}	$Co(NO_3)_2$	3500	97.7
Ni^{2+}	$Ni(NO_3)_2$	2500	98.3
Cu^{2+}	$Cu(NO_3)_2$	1500	96.9
Cd^{2+}	$Cd(NO_3)_2$	1250	97.8
Zn^{2+}	$Zn(NO_3)_2$	1000	98.7
Hg^{2+}	$HgCl_2$	750	99.0
Pb^{2+}	$Pb(NO_3)_2$	600	98.5
Tl^{+}	$Tl_2(SO_4)$	500	98.6
Ag^{+}	$AgNO_3$	400	99.5
Pd^{2+}	$Pd(NO_3)_2$	300	98.3
Fe^{3+}	$Fe(NO_3)_3$	250	97.2
Al^{3+}	$Al(NO_3)_3$	125	96.2

Conditions: sample volume, 500 mL; 10 mL 2.0 mol L^{-1} HNO_3, 5.0 mL 2 x 10^{-3} mol L^{-1} BTAHN; 2.5 mL 3.0 % CPC, 0.5 μg mL^{-1} of Ga(III), flow rate, 5.0 mL min^{-1}.

Table 2 Comparative data from some studies on solid-phase extraction of gallium using different spectroscopic techniques

System	Detection technique	Eluent	E.F.	D.L. μg L^{-1}	RSD (%)	Ref.
Amberlite XAD-4/5-phenylazo-8-quinolinol	XRF	–	–	81.0	< 5.0	60
poly(acryl-phenylamidrazone phenylhydrazide)	ICP-AES	4.0 mol L^{-1} HCl	50	–	< 2.7	61
Polyurethane foam	FAAS	MIBK	40	6.00	< 3.3	62
Poly(Acrylphenylamidrazone-phenyl- Hydrazide-acylphenyl hydrazine)	CP-AES	4.0 mol L^{-1} HCl	85	–	< 2.5	42
Activated carbon/ 8-quinolinol	GFAAS	–	100	1.00	< 3.2	63
Amberlite XAD-2/1-(2-pyridylazo)-2-naphthol	GFAAS	0.1 mol L^{-1} HCl / 2.0 mol L^{-1} HNO_3	200	2.1	< 4.6	47
Amberlite XAD-4/HMPN	FAAS	0.5 mol L^{-1} HNO_3	200	3.42, 0.92	< 3.0	64
Amberlite XAD-4/ BTAHN	UV-visible	1.0 mL DMF	500	3.1	<0.95	This work

E.F.: Enrichment factor
D.L: Detection limit
RSD: Relative standard deviation

Table 3 Determination of Ga(III) in spiked different water and biological samples.

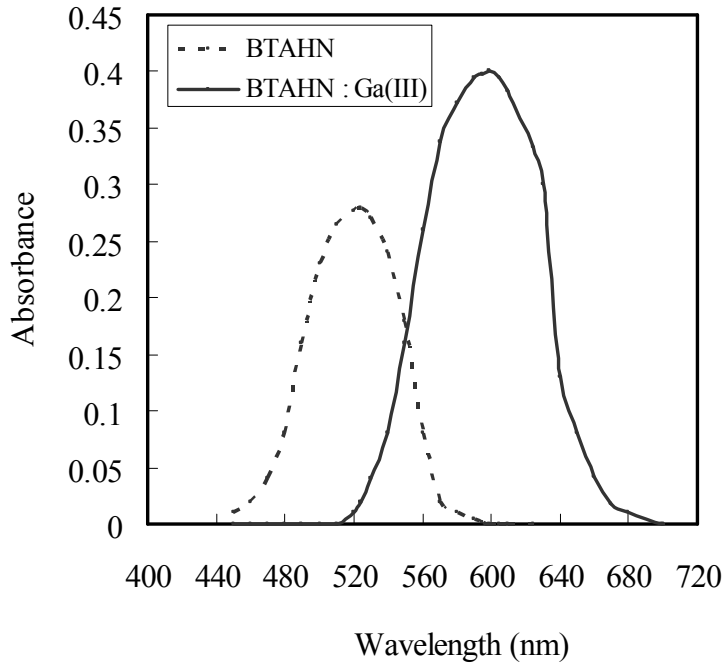
Sample	Ga added	Proposed method		GFAAS method		t-test[b]	F-test[c]
	µg mL^{-1}	Ga Found [a]	Recovery %	Ga Found [a]	Recovery %		
River water [d]	0.00	BDL	--	BDL	---		
	0.20	0.198 ± 0.33	99.00	0.201 ± 1.66	100.50	0.87	2.18
	0.40	0.398 ± 0.65	99.50	0.401 ± 0.67	100.25	0.78	2.09
	0.60	0.602 ± 0.41	100.33	0.602 ± 0.52	100.33	0.84	2.14
waste Water [d]	0.00	BDL	---	BDL	---		
	0.15	0.149 ± 0.31	99.33	0.152 ± 1.67	101.33	1.12	2.85
	0.30	0.299 ± 0.65	99.67	0.296 ± 0.45	98.67	0.75	2.01
	0.45	0.446 ± 0.38	99.11	0.451 ± 0.29	100.22	1.27	3.07
Tap water [d]	0.00	BDL	---	BDL	---		
	0.25	0.251 ± 0.31	100.40	0.247 ± 1.97	98.80	1.06	2.66
	0.50	0.503 ± 0.57	100.60	0.492 ±1.42	98.80	0.82	2.11
	0.70	0.700 ± 0.40	100.00	0.695 ± 1.48	99.29	0.72	1.98
Sea water [d]	0.00	BDL	---	BDL	---		
	0.22	0.219 ± 0.36	99.55	0.222 ± 1.84	100.91	0.87	2.22
	0.44	0.441 ± 0.42	100.23	0.438 ± 1.43	99.55	0.76	2.11
	0.66	0.661 ± 0.21	100.16	0.658 ± 1.29	99.70	0.95	2.33
Well water [d]	0.00	BDL	---	BDL	---		
	0.25	0.249 ± 0.57	99.60	0.252 ± 1.66	100.80	0.85	2.16
	0.45	0.451 ± 0.31	100.22	0.448 ± 1.48	99.56	0.96	2.29
	0.65	0.649 ± 0.38	99.85	0.653 ± 1.74	100.46	0.81	2.13
Serum [d]	0.00	BDL	---	BDL	---		
	0.18	0.179 ± 0.57	99.44	0.181 ± 1.57	100.56	0.95	2.36
	0.36	0.361 ± 0.33	100.28	0.358 ± 1.73	99.44	1.03	2.56
	0.54	0.541 ± 0.46	100.19	0.542 ± 1.48	100.37	1.11	2.79
Urine [d]	0.00	BDL	---	BDL	---		
	0.23	0.231 ± 0.46	100.43	0.229 ± 1.36	99.57	1.08	2.67
	0.46	0.461 ± 0.63	100.22	0.462 ± 1.58	100.43	1.19	2.98
	0.69	0.689 ± 0.55	99.86	0.692 ± 1.64	100.29	0.96	2.41

[a] Mean ± Relative Standard Deviation (n = 5);

[b] Tabulated t-value for five degrees of freedom at P (0.95) is 2.57;

[c] Tabulated F-value at P (0.95) is 5.05;

[d] Gave no test for gallium. BDL: Below the detection limit.



Absorption spectra for 2 x 10^{-5} M BTAHN complexed with 0.5 µg mL^{-1} Ga(III) at the optimum conditions.