



Micellar Flow Injection Spectrophotometric Determination of Indium and its Application to the Environmental Samples

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Abstract

A selective and fairly sensitive automatic spectrophotometric method for the determination of indium by flow injection analysis (FIA) has been developed. Anionic micellar medium of sodium dodecyl sulfate has been used for the system Indium reacts with 1,5-diphenylthiocarbazone (dithizone) at pH 7.00 in micellar medium, to give red-violet chelate, which absorb at 530 nm. The molar absorptivity and Sandell's sensitivity were found to be $6.7 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 20 ng cm^2 of indium, respectively. Linear calibration graph was obtained for 0.25 to $6.0 \mu\text{g ml}^{-1}$ of indium. The reaction is instantaneous and absorbance remain stable for 45 h. Various analytical parameters, such as effect of pH, flow rate, sample volume, dispersion coefficient, time and reagent concentration were studied. The interference of over 40 anions, cations and complexing agents has been studied at $1 \mu\text{g ml}^{-1}$. Method has been applied to determine indium in synthetic mixture and water samples.

Key words: Flow-injection analysis, Spectrophotometry, indium determination, environmental samples

Introduction

Since the rapid expansion of III-V semiconductor and liquid crystal display production, the consumption of indium has been increasing. From the mid-1990's, animal experiments have shown that the inhalation or intratracheal instillation of indium compounds causes severe lung inflammation and mild adverse reproductive effects. Recently Koichi et al [1] has reported the comparative study of indium exposed and non-exposed workers for their urine, blood and serum samples.

¹¹¹Indium- and technetium have been used for the development of monoclonal radio labeled antibodies of high affinity and selectivity for tumor antigens for diagnostic localization and target delivery [2]. It is also used in alloys, solders, and as a hardening agent for bearings.

Due to diverse and increasing use of indium in industry and medicine, it is important from an analytical point of view to develop simple, selective and economical methods for its trace determination in various complex matrices. Indium contents can be determined photometrically using suitable chromogenic reagents such as Rhodamine B, Eriochrome cyanine R, pyrocatechol violet, 1-(2-pyridylazo)-2-naphthol and 4-(2-pyridylazo)-resorcinol. Indium in environmental and water samples has been determined by AAS, XRF, NAA, ICP-AES and ICP-MS, but these techniques are expensive and not suitable for routine analysis [3].

Indium also has been determined fluorometrically using 5-bromo salicylaldehyde salicyl hydrazone [4].

The aim of this study is to develop a simpler direct flow injection spectrophotometric method for the determination of indium. Dithizone

has been used for the determination of zinc, lead and other metal ions spectrophotometrically using solvent extraction in chloroform or in carbon tetrachloride [5]. Solvents used to extract the complex are classified as toxic and environmental pollutants and have been listed as carcinogens by EPA [6,7].

Organized molecular assemblies can be used to advantage in analytical chemistry, because their ability to solubilize hydrophobic material in aqueous media or vice versa [8]. The altered environment provided by a new reaction medium in which reaction rates, equilibrium constant, products formed, spectral parameters and some times stereochemistry could be altered. As a result, the introduction of a given reagent into altered environment can afford many beneficial changes that could eventually be advantageous to enhance the performance of the analytical method [9].

Due to unique properties offered by micellar assemblies, they have found wide applications in many analytical techniques, both in determination of trace elements and in separations [8-11].

In present study, an automatic spectrophotometric analytical method for the determination of indium by FIA using dithizone and anionic micellar medium of sodium dodecyl sulfate has been developed.

Experimental

Apparatus

A four channel peristaltic pump (Gilson Minipuls 3) was used to propel the carrier stream, equipped with PVC pump tubes with i.d 0.5 mm (anachem). Samples were injected via rotary PTFE valve (Rheodyne 5020). PTFE 0.5mm i.d. tubing was used throughout the remainder system. The detector was Spectronic 20 at λ 530 nm equipped with 100- μ L flow thorough cell. Yew strip chart recorder was used to record the signal. Shimadzu UV-365 spectrophotometer was used to record the spectra of indium-dithizone system. A Perkin-Elmer (Lamda-2, Germany) double beam spectrophotometer was used for the comparison of the results. A digital pH meter (WTW, Inolab pH

level 1, Germany) was used to measure the pH of the solution.

Reagents

All chemicals used were of analytical reagent grade or highest purity available. Double distilled de-ionized water was used throughout.

Dithizone solution (3.89×10^{-3} M)

Prepared by dissolving the 0.1 g of dithizone (Merck, Darmstadt, Germany) in minimum volume of propanol (Merck) in 100 ml volumetric flask and diluted to mark with it. More dilute solutions were prepared as required.

Indium(III) standard solution

A 100 ml stock solution (1 mg ml^{-1}) of indium was prepared by dissolving 0.261g of indium nitrate (Fluka, Switzerland) in double distilled de-ionized water containing 1ml of 1+1 nitric acid. More diluted solutions were prepared from this stock solution freshly when requires in double distilled de-ionized water.

Sodium dodecyl sulfate stock solution

A 500 ml stock solution of SDS (Merck) was prepared by dissolving 86.4 g of pure salt of sodium dodecyl sulfate in 250-300 ml of water and sonicated for 15 minutes and was diluted to mark with double distilled de-ionized water when become transparent.

Other solutions

Solutions of the large number of anions, cations and complexing agents were prepared from their analaR grade or equivalent grade water-soluble salts. All glassware was kept in nitric acid (1+1) for at least a day and then washed with de-ionized water. Stock solutions and environmental water sample were kept in polypropylene bottles containing 1 ml concentrated nitric acid.

Procedure

Preparation of reagent for FIA

A single channel FIA manifold was used through out (Fig.1). Reagent 'R' was prepared by

taking 4.0 ml of SDS (0.6M) and 1.0 ml of buffer (NH_3/NH_4 acetate buffer, $\text{pH}=7.00$ and $I=1$) was mixed and 1 ml 3.89×10^{-3} M of dithizone was added and mixed well, then diluted to 25.0 ml with de-ionized water. The reagent was pumped at the flow rate at 2.3 ml min^{-1} .

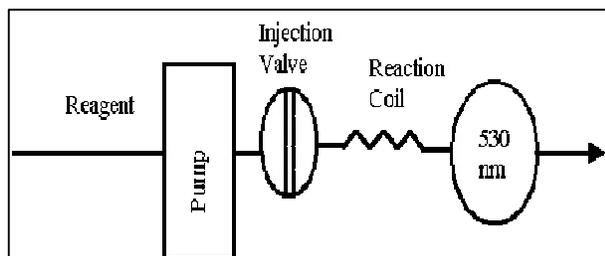


Fig. 1 FIA manifold

Preparation of indium standard solution

To 0.25 to 6.0 ml of acidic solution containing 2.5 to 60 μg of indium and 0.4 ml of buffer was added diluted to 10.0 ml with de-ionized water. A 50 μL of each standard solution was injected into the reagent stream and monitored at 530 nm. The indium content in unknown samples was determined by using concurrently prepared calibration graph. Standard error in determination of unknown samples was calculated by using Zar formula [12].

Results and Discussion

Various chemical and FIA parameters were studied to get optimum signal, studied range and selected parameters are shown in Table 1.

Table – 1. Selected chemical and FIA parameters obtained with the optimization experiments

Parameter	Studied range	Selected value
Size of sample loop (μL)	50-150	50
Reagent flow rate (ml min^{-1})	1.0-4.2	2.3
Length of reaction coil (cm)	50-300	250
pH	2-10	7.0
Concentration of reagent (M)	1.95×10^{-5} - 1.55×10^{-4}	1.55×10^{-4}
SDS (M)	0.04-0.16	0.1
$\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ (M)	0.01-0.1	0.1

Factors affecting absorbance

Absorption Spectra

The absorption spectra of indium-dithizone in 0.1 M SDS at pH 7.00 was recorded using Shimadzu UV-365 spectrophotometer, Japan. The absorption spectrum of indium-dithizone shows the maximum absorbance at 530 nm and average molar absorption of $6.2 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. In all instances measurements were made at 530 nm against reagent blank.

Effect of Surfactant

The different type of surfactants; anionic (sodium dodecyl sulfate), cationic (cetyl trimethyl ammonium bromide) and nonionic (Brij-35[®]) were studied; SDS was found to be best surfactant for the system. In 0.1 M SDS medium, however, maximum absorbance was observed; hence 0.1 M SDS was used in the determination procedure (Fig.2).

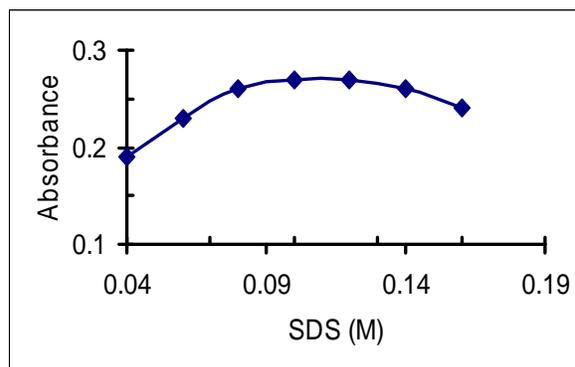


Fig. 2 Effect of surfactant concentration on the absorbance of Indithizone system

Effect of pH

Effect of pH was observed by varying pH of reagent from 2.0-10.0 using NH_3/NH_4 acetate buffer system at room temperature. The absorbance was maximum at pH 7.0, using final concentration of buffer 0.1 M at room temperature 25 ± 5 $^{\circ}\text{C}$. Outside this range, the absorbance decreased (Fig.3). For all subsequent measurements 0.1M buffer at pH 7.0 was used.

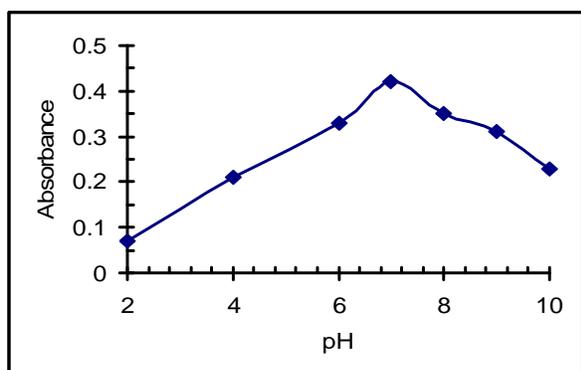


Fig. 3 Effect of pH on the absorbance of indium-dithizone system

Effect of reagent concentration

Different volumes of stock 3.89×10^{-3} M solution were added to prepare reagent 'R' for FIA and fixed concentration of metal ion was injected (50 μ L). It was observed that on increasing concentration signal increases but reagent concentration above 0.004% (final concentration) cannot be made zero due to absorption of reagent itself (Fig.4). Reagent concentration 1.55×10^{-5} M was used for further studies.

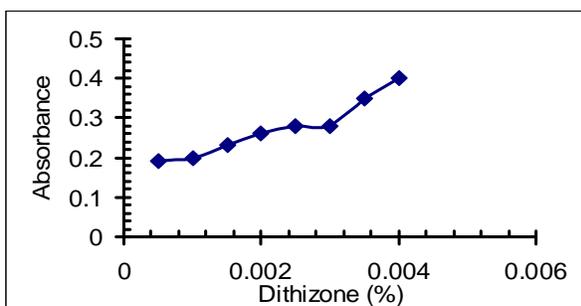


Fig. 4 Effect of reagent concentration

Effect of FIA parameters

Flow parameters like pump speed, reaction coil length and sample volume were studied by varying pump speed, home made reaction coils from Teflon tubes and loops of different volumes respectively. The effect of various parameters on the signal is shown in Fig.5. There is nearly no effect on the signal on increasing sample volume and pump speed and little increase in absorbance

on increasing reaction coil length. So, reaction coil length of 250 cm was used and pump speed 10 rpm (corresponds to 2.3 ml min^{-1}) was used. The system have dispersion of $D=4.4$.

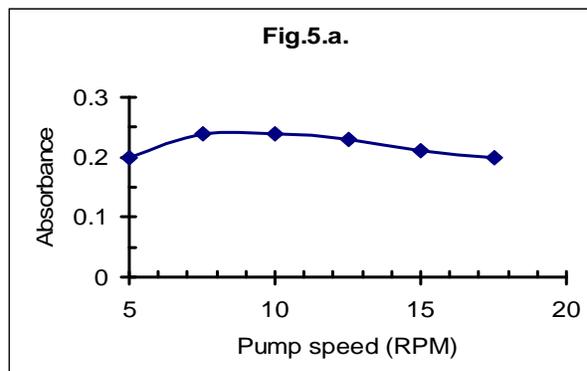


Fig. 5(a) Effect of flow parameters; Effect of pump speed,

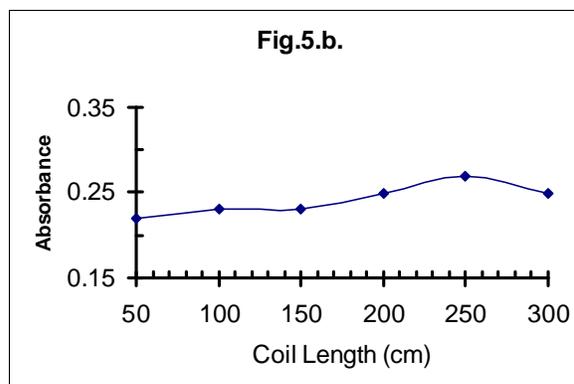


Fig. 5(b) Effect of coil length

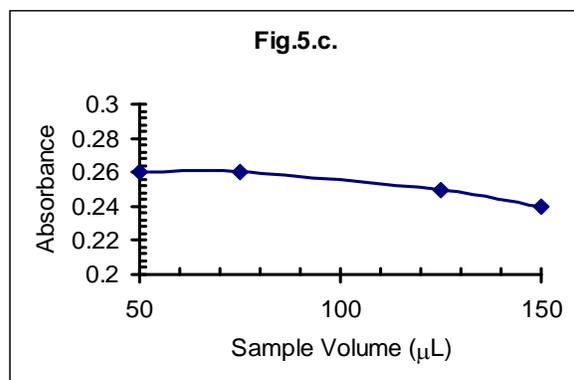


Fig. 5(c) Effect of sample volume

Analytical figures of merit

The absorbance was linear from 0.25 to 6.0 $\mu\text{g ml}^{-1}$ of indium at 530 nm, with $R^2 = 0.9948$ and equation of straight-line $y = 0.0538x + 0.0272$ (Fig.6). The molar absorption coefficient and Sandell's sensitivity were $6.7 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 20 ng cm^{-2} respectively.

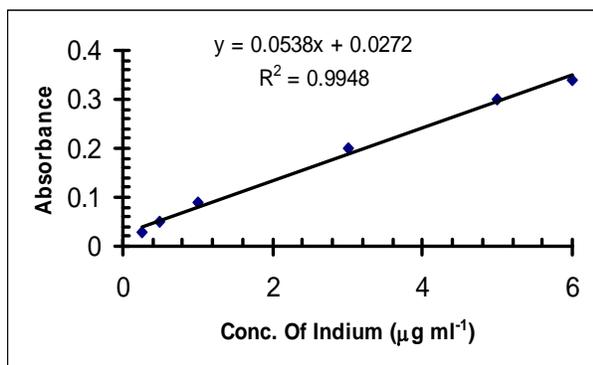


Fig. 6 Calibration graph, 0.25-6.0 $\mu\text{g ml}^{-1}$ of indium

The sample throughput of the method is 100 samples per hour and reagent 'R' consumption of 1.8 ml per sample. The RSD (n=5) is 0.01 – 0.0% for 0.25 – 6.0 $\mu\text{g ml}^{-1}$ indium, indicating that the method highly precise and reproducible. Salient features of proposed method are summarized in Table 2.

Table-2. Analytical features of proposed method

Parameter	Optimized value
pH	7.0
Reagent molar excess	1:3
Linear Range ($\mu\text{g ml}^{-1}$)	0.25-6.0
Detection limit ($\mu\text{g ml}^{-1}$)	0.17
Dispersion Co-efficient	4.4
Reproducibility (%)	0.0-0.1
Sample throughput (Samples h^{-1})	100

Effect of foreign ions

The effect of over 40 cations, anions and complexing agents were studied on the determination of only 1 $\mu\text{g ml}^{-1}$ of indium. The

criterion for interference was an absorbance value varying for more than 5% for the expected value of indium alone [13]. There was no interference from following; 1000-fold amount of sulfate, sulfite, nitrate, bromide, chloride, iodide, thiocyanate, Na, K, Ca, NH_4^+ , tartarate, citrate and azide. 50-fold amount of Fe^{2+} , Cd^{2+} , Ni^{2+} , Cr^{3+} , Mo^{VI} , Ce^{IV} , Sb^{3+} , Cr^{VI} , Co^{2+} , Cu^{2+} , Fe^{3+} , Ag^+ , As^{3+} , Pd^{2+} , Tl^+ , Mn^{2+} , Pd^{2+} , V^{V} , Be^{2+} , Sn^{2+} , Bi^{2+} , Hg^+ , and Hg^{2+} . A 10-fold excess of zinc was masked by using thiocyanate.

During the interference study, if a precipitation formed, it was removed by centrifugation.

Applications

Determination of indium in synthetic mixtures

Several synthetic mixtures of varying compositions containing indium and diverse ions of known concentration were determined by the present method. The results are shown in Table 3.

Table – 3. Determination of indium in some synthetic mixtures

Sample	Composition of mixture	Indium $\mu\text{g ml}^{-1}$		
		Added	Found %	Recovery \pm
A	Indium	2.00	2.00	100 \pm 0.00
B	As in A + Fe^{2+} (25) + Cr^{3+} (25) + Ce^{IV} (25)	2.00	2.1	105 \pm 0.1+
C	As in B + Mo^{VI} (25) + Cu^{2+} (25)	2.00	1.86	93 \pm 0.2
D	As in C + As^{3+} (25) + Ag^+ (25) + NO_3^- (25) + tartarate (50)	2.00	2.0	100 \pm 0.0
E	As in D + Mn^{2+} (25) + V^{V} (25) + Cl^- (25)	2.0	2.1	105 \pm 0.00

Determination of indium in environmental water samples

The 1 ml solution containing 100 μg of indium was added to each environmental water sample (100 ml). Samples were filtered and evaporated nearly to dryness with a mixture of 1 ml concentrated sulfuric acid and 5 ml concentrated nitric acid in a fume cupboard and

was then heated with 10 ml de-ionized water in order to dissolve the salts. The solution was then cooled and neutralized with NH_4OH solution in the presence of 1-2 ml of KSCN (1% w/v). The resulting solution was then quantitatively transferred into 25 ml volumetric flask and diluted to mark with de-ionized water. The indium content was determined as described under procedure. The results are shown in Table 4.

Table – 4. Determination of indium in some environmental water samples

Sample	Indium, $\mu\text{g ml}^{-1}$			
	Added	Found	Recovery % \pm s	RSD%
Tap water	0.0	1.0	± 0.01	1.01
	1.0	2.0	100 ± 0.1	5.1
Drinking water	0.0	0.0	100 ± 0.12	6.0
	1.0	2.0	100 ± 0.12	6.0
Industrial water	0.0	1.8	± 0.04	2
	1.0	2.75	95 ± 0.03	0.93
Ground water	0.0	1.55	± 0.05	3.6
	1.0	2.55	100 ± 0.04	1.45

^a Average of three determinations

Validation of method

Some of the spiked and unspiked environmental samples were determined for their indium content by conventional extraction procedure [5]. The results are shown in Table 5. Data were subjected to statistical analysis using Microsoft Excel, the 't test' value shows that two methods provides same results at 95% confidence level with Pearson's correlation coefficient 0.9998.

Table – 5. Comparison of data

Sample	Extraction method ($\mu\text{g ml}^{-1}$)	Proposed method ($\mu\text{g ml}^{-1}$)
Drinking water (unspiked)	0.07	0.00
Tap water (unspiked)	0.93	1.0
Tap water (spiked)	1.93	2.0

Conclusion

A fairly sensitive, simple, rapid and selective method for the determination of indium using dithizone in anionic micellar medium has been developed. Use of anionic micelles eliminates the toxic organic solvents, otherwise necessary. Using homogenous environment of organized assemblies, the system was coupled with FIA, which increases sample throughput and minimizes sample consumption. The method was successfully applied for the determination of indium in environmental water and complex synthetic mixtures.

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