

Abstract

Determination of low levels of ZN metal by different Spectroscopic methods in water samples.

1- Pre-concentration and determination of Zn (II) across a ligand assisted pseudo stirbar hollow fiber solid/liquid phase microextraction method in water samples has been investigated. All detections were carried out by differential pulse anodic stripping voltammetry (DPASV). The method involves microextraction and apre-concentration of Zn (II) on the pseudo stir bar hollow fiber. Then desorption has been done using suitable solvent containing suitable ligand as complexing agent. The optimized conditions were obtained. The relationship between the peak current and concentration was linear over the range of 0.05–500 ng / mL1. The limit of detection was 0.015 ng / mL1. Under the optimized conditions, the pre-concentration factor is 5140. The applicability of the developed technique was evaluated by application to spiked, environmental water samples.

2- 3-Hydroxybenzylaminobenzoic acid synthesized in the laboratory as a reagent for the determination of zinc in various water samples. Zinc(II) reacts with 3-hydroxybenzylaminobenzoic acid and forms a light yellow colored complex at pH 5.0. The complex has a maximum absorbance at 460 nm. The complex is stable for more than twelve hours. Hence, a detailed study of the extraction of zinc(II) with 3-hydroxybenzylaminobenzoic acid has been studied. Other parameters like effect of pH, choice of solvent, interference of electrolytes has also been investigated

Introduction

Water is one of the most essential constituents of the human environment the water resources generate development in socio-economic issues crucial to the Society in general And more specifically for industries, agricultural activities and for the public use although it is agreed that water is an economic good, it is also a social good, finite, non-substitutable and vital to all forms of life. the last three elements make water not just like any other commodity but a good that should be conserved and treasured water is vulnerable to contamination at all points in the hydrologic cycle ,and all pathways that transport water can also carry pollutants .land use activities and waste water discharges can degrade water quality Some heavy metals are considered to be essential trace elements for the human body because act as catalysts in enzymatic reactions and are deeply in evolved in the metabolism of glucose and lipids. In contrast, other heavy metals have higher toxicity and carcinogenicity. Therefore, it is important to determine. The heavy metal content of environmental samples, Instrumental sensitivity is not always sufficient for the determination for heavy metals in water because their concentrations are generally at Sub - pp bevels ,There for it is necessary to combine a per – concentration technique with an instrumental analysis method , such as atomic absorption spectrometry (AAS) inductively coupled plasma atomic emission spectrometry(ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) , for the determination of heavy metals in water.

Zinc imparts an undesirable astringent taste to water tests indicate that 5% of a population could distinguish between zinc – free water and water containing zinc at a level of 4 mg / liter (as zinc sulfate) . The detection levels for other zinc salts were somewhat higher.

Water containing zinc at concentrations in the range 3-5 mg / liter also tends to appear opalescent and develops a greasy film when boiled in natural surface waters, the concentration of zinc is usually below 10mg / liter, and in ground water, 10-40mg /liter In tap water, the zinc concentration can be much higher due to the leaching of zinc from piping and fitting The most corrosive waters are those of low pH , high carbon dioxide content , and low mineral salts content , in a Finnish survey of 67% of public water supplies , the median zinc content in water samples taken upstream and downstream of the water works was below 20 mg /liter . Much higher concentrations were Found in tap water, the highest being 1.1 mg /liter . Even higher zinc concentrations (up to 24 mg / liter) were reported in a Finnish survey of water from almost 6000 wells

EFFECTS OF ZN METAL ON HUMAN

Acut toxicity arises from the ingestion of excessive amounts of zinc salts, either accidentally or deliberately as an emetic or dietary supplement. Vomiting usually occurs after the consumption of more than 500 mg of the zinc sulfate.

mass poisoning has been reported following the drinking of acidic beverages kept in galvanized containers , fever , nausea , vomiting , stomach cramps , and diarrhea occurred 2-3 h after ingestion .

ANALYTICAL METHODS

Atomic absorption Spector photometry is the most widely used method for the determination of zinc , the detection limit of the direct air - acetylene flame method is 50 mg / litter Low concentrations can be measured by chelating zinc with ammonium pyrimidine dithiocarbamate and extracting it with methyl iso butyl ketone

(detection limit 0 - 5 – 1 mg / litter)

1-1 Atomic Absorption spectroscopy (AAS)

Atomic absorption spectrophotometer analytical instrument is based on the principle of atomic absorption spectroscopy and is very useful to detect the metal ion concentration present in drinking water samples.

when a sample solution is a pirated into a flame then sample element is changed into atomic vapor of that element , flame contains atoms of element furthermore some atoms are thermally excited by flame whereas most of them remain in ground state . The ground state atoms then absorb the radiation of specific wavelength produced by source i.e hallow cathode lamp of that specific metal.Now the wave length of radiation given off by the source or lamp is similar as that absorbed by atoms in the flame.Table 1 – A comparison of USEPA, WHO and BIS guideline values (mg / L) Of metal ions for drinking water

Metal Name	USEPA (maximum ontaminant level)	WHO (Guideline value)	BIS : 10500 (permissible limit)
Arsenic	0.01	0.01	0.05
Aluminum	0.05-0.2	NM	0.2
Boron	--	2.4	1.0
Cadmium	0.005	0.003	0.003
Chromium	0.1	0.05	0.05
Copper	1.3	2.0	1.5
Iron	0.3	NM	0.3
Lead	0.015	0.01	0.01
Mercury	0.002	0.006	0.001
Manganese	0.05	NM	0.3
Nickel	--	0.07	0.02
Selenium	0.05	0.04	0.01
Zinc	5.0	NM	15.0

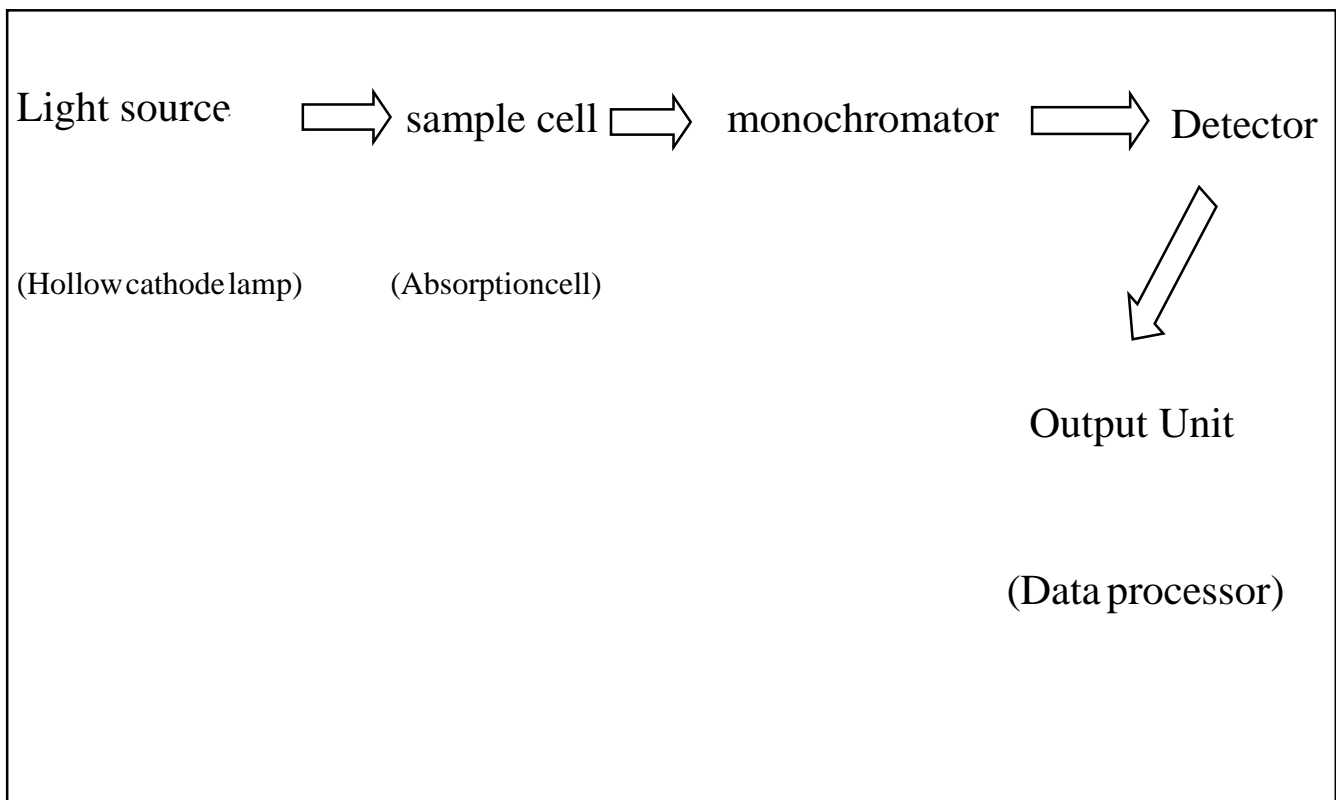
NM : Not mentioned

AAS method follows the Beers law, which states that absorbance is directly proportional to concentration .Each atomic absorption spectrometer possesses a light source i.e. Lamp.

Sample cell mono chromate, detector and Output device.

The schematic diagram of an atomic absorption spectrophotometer is given as figure.

The most common type of burner is a premix which introduces the spray into a



condensing chamber for removal of lager depletes.

Figure 1. Schematic diagram of an atomic absorption spectrophotometer

Important sections of an ASS instrument are described as:

A. Light source (lamps)

Use either a hollow – cathode lamps or electrode less discharge lamp (EDL) for a particular element being measured. Moreover multi- element hollow – cathode lamps generally provide lower sensitivity than single element lamps whereas EDLs take a longer time to warm up and stabilize.

B. Output Unit (Readout)

Most of the instruments are equipped with either a digital or null meter readout mechanism, generally, the modern instruments are with a micro process or capable of integrating absorption signals over at high concentrations.

C. Pressure Controlling Valve

Generally , a separate reducing valve should be used for each gas.

Suitable reducing valves maintain the supplies of fuel and oxidant at pressure somewhat higher than the controlled operating pressure of the instrument .

D. Exhaust (vent)

Fix a vent about 6 – 12 inches above the burner to remove the fumes and vapors from the flame . this practice protects laboratory personnel from vapours , protects the instrument from corrosive vapours , and prevents flame stability from being affected by room drafts . besides, in laboratory sites with heavy particulate air pollution , prefer the clean laboratory facilities AAS analysis for various metal ion needs a suitable flame – gas combination which is given in the table 2 .table 2 , flame – gas combination for metal ion analysis by ASS

Metal name	Flame – gas combination	Metal Name	Flame – gas combination
Arsenic	Air – Act	Mercury	Air – Act
Aluminum	N - Act	manganese	Air – Act
Boron	N - Act	Magnesium	Air – Act
Cadmium	Air – Act	Nickel	Air – Act
Calcium	N - Act	Lead	Air – Act
Chromium	Air – Act	Selenium	Air – Act
Copper	Air – Act	Zinc	Air – Act
Iron	Air – Act		

Air – Act = air – acetylene ; N – Act = nitrous – oxide-acetylene

1-2 SPECTROPHOTOMETRIC

Spectrophotometric measurements were made in a Varian Cary 1E UV-visible spectrophotometer with 1.00 cm glass cells. The pH measurements were carried out with an ANALYSER 300 pH meter. Infrared spectra were recorded on a Jasco Valor III spectrometer. ¹³C and ¹H-NMR spectra were obtained with a Gemini 300 (Varian). An Applied Research Laboratories model 3410 minitorch sequential inductively coupled plasma spectrometer was used for the atomic emission spectroscopy measurements.

2- Experimental Section

2-1 Reagents and instruments

Purified water by Millipore Milli-Q system was used in all experiments and the reagents used were of analytical grade or better.

Standard solutions of Zn(II) and Pb(II) were prepared from 1,000 µg/mL SRM

(standard reference material) solutions of NIST (National Institute of Standard and Testing, U.S.A.) by diluting with deionized water to the proper concentrations. A 0.1 M 1-naphthoic acid (Aldrich Co.) in ethanol was used for the ligand, 0.03 M solution of tetrabutylammonium bromide (Aldrich Co.) for a counter ion, and 0.2%(w/v) of sodium lauryl sulfate (Aldrich Co.) for a surfactant. A pH meter (Model PHM-2000 from Tokyo Rikakikai Co. and In gold combined electrode) was used after it was corrected with buffer solutions. Zn(II) and Pb(II) in MIBK were determined with a Perkin-Elmer model

2380 atomic absorption spectrophotometer (AAS) equipped with HGA400 graphite furnace system (GF) Instrumental conditions.

EXPERIMENTAL

Atomic absorption spectrophotometry (AAS) is an analytical technique used to measure a wide range of elements in materials such as metals, pottery and glass. Although it is a destructive technique (unlike ED-XRF), the sample size needed is very small (typically about 10 milligrams – i.e. one hundredth of a gram) and its removal causes little damage. The sample is accurately weighed and then dissolved, often using strong acids. The resulting solution is sprayed into the flame of the instrument and atomized. Light of a suitable wavelength for a particular element is shone through the flame, and some of this light is absorbed by the atoms of the sample

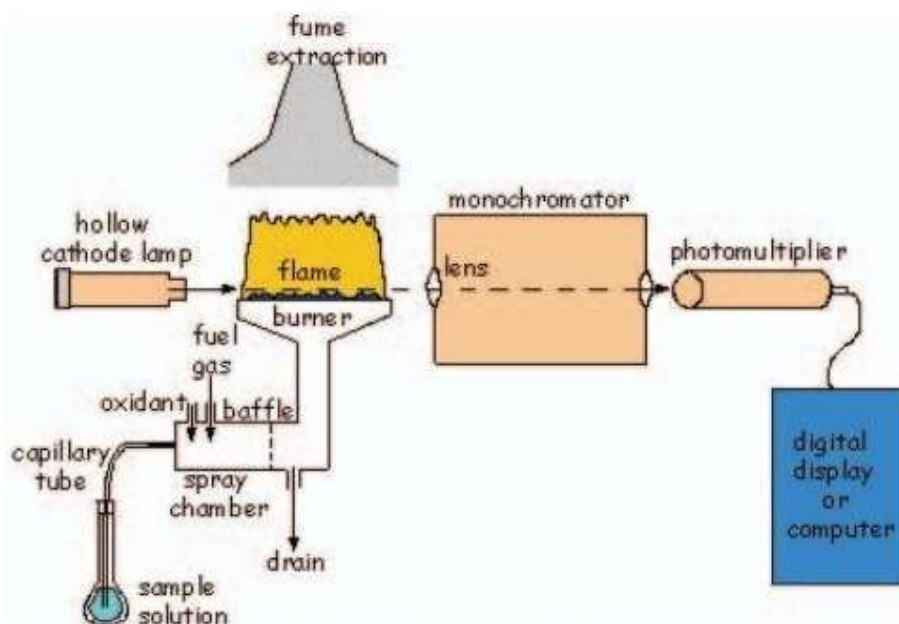


Fig. 1. – The experimental set-up.

2-2-1 Experimental procedure

After the water sample was filtered to remove floating materials, 1.00 L of the sample was accurately taken in an Erlenmeyer flask. An 8.0 mL sample of 0.1 M 1-naphthoic acid (HNPh) solution was added and the pH was adjusted to 5.0 with dilute HNO₃. The solution was stirred for 4 minutes by a magnetic stirrer to form Zn(II)- and Pb(II)-naphthoate

(NPh₃ -) complexes completely. Ion pairs were created by adding 10 mL of 0.03 M tetra-n-butyl ammonium bromide for a counter ion. A 2.0 mL sample of 0.2%(w/v) sodium laurylsulfate solution was added and the experimental solution was additionally stirred for 4 minutes. It was then transferred to a flotation cell, and nitrogen gas was bubbled at the flow rate of 30 mL/min for 5 minutes to float and extract the ion-pairs of analytes into 20.00 mL MIBK on the solution surface.

The absorbances of the elements were directly measured in MIBK solution by GFAAS.

2-2-2

All reagents were purchased from local market. The stock and standard solutions were prepared freshly throughout the experiment. Under recommended conditions, Zn(II) metal was determined in various water samples following UV-VIS Spectrophotometer. An Elico pH meter was used for the pH adjustments.

General procedure for the preparation of ligand

1.0 g of 3-Hydroxybenzaldehyde was dissolved in 25 mL of double distilled water and mixed in a flask with 1.0 g of 4-aminobenzoic acid and refluxed for 3 h. A pale yellow colored crystal product was formed. After filtering the product, it was dried at room temperature. Finally the product was recrystallized by using ethanol. The resulting product has melting point of 165 oC and the yield was 80-90%. The above reaction is shown in Figure 1.

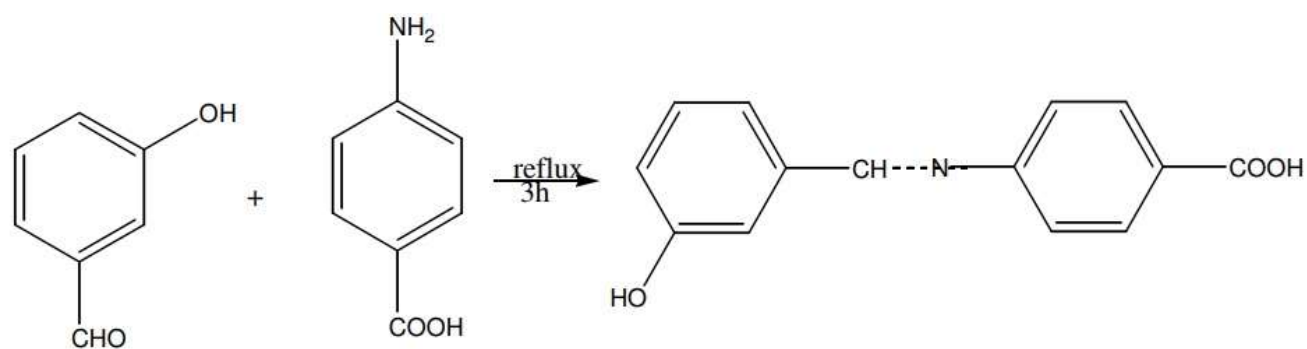
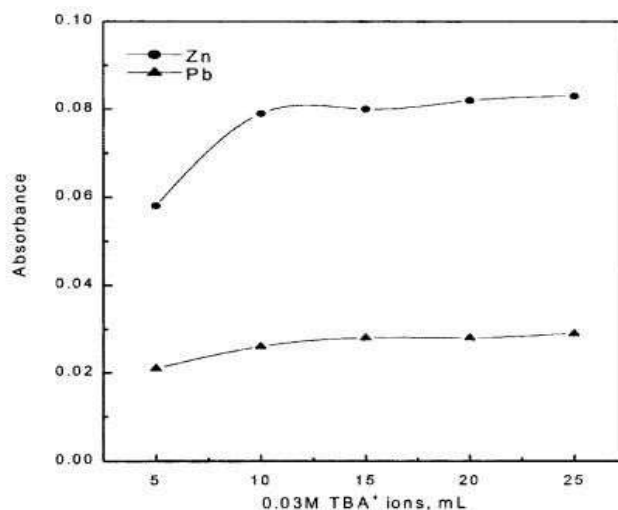
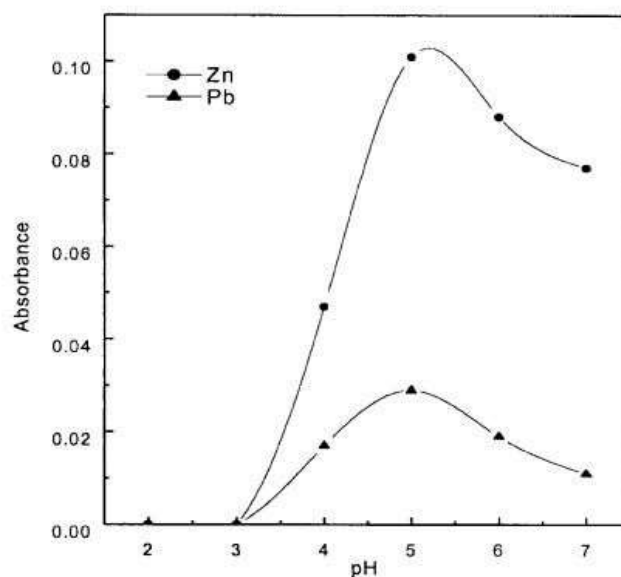
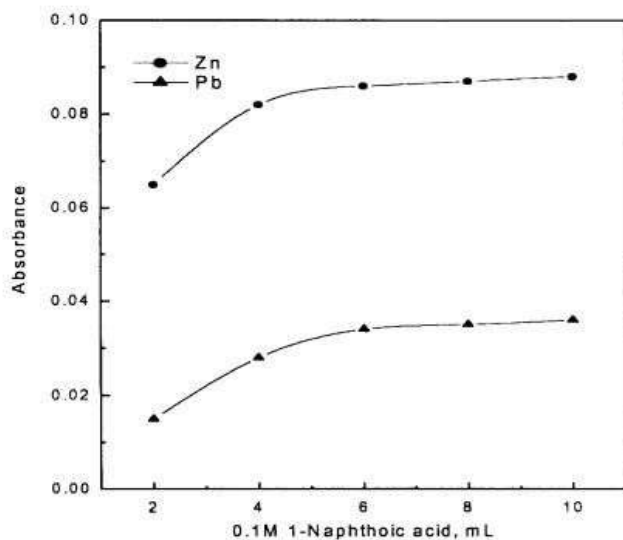


Figure 3. Schematic diagram of 3-hydroxybenzylaminobenzoic acid

3- Results and Discussion

A series of standard solutions (up to 12 ng/mL for both elements) was prepared from NIST-SRM solutions and the solutions were treated with the same procedure as that for samples. Calibration curves were plotted and metal ions were determined by application of the curves. Ligand, metal-complexes and ion pairs. 1-Naphthoic acid as a ligand has the following structure, and its carboxylic acid group is ionized in an aqueous solution. The carboxylate anion coordinates with metallic ions to



form neutral complexes in the equivalent concentrations of both di-valent ions.

3-2

Zinc(II) reacts with 3-hydroxybenzylaminobenzoic acid and forms a light yellow colored complex at pH 5.0. The complex has a maximum absorbance at 460 nm. The complex is stable for more than twelve hours. Hence, a detailed study of the extraction of zinc(II) with 3-hydroxy benzyl amino benzoic acid has been studied.

Absorption spectrum of the reagent complex

1.0 mL of zinc(II) solution was transferred into a 25 mL standard flask and to it, 3.0 mL of buffer (pH 5.0), 2.0 mL of 3-hydroxybenzylaminobenzoic acid solutions were added and the volume of the aqueous phase was brought upto 10.0 mL with double distilled water. The absorption spectrum of the complex was recorded. The absorption spectrum of the reagent was also recorded, using the solvent as a blank. The absorption spectrum of the reagent complex is depicted in Figure 2. The reagent metal complex gave maximum absorbance at 460 nm.

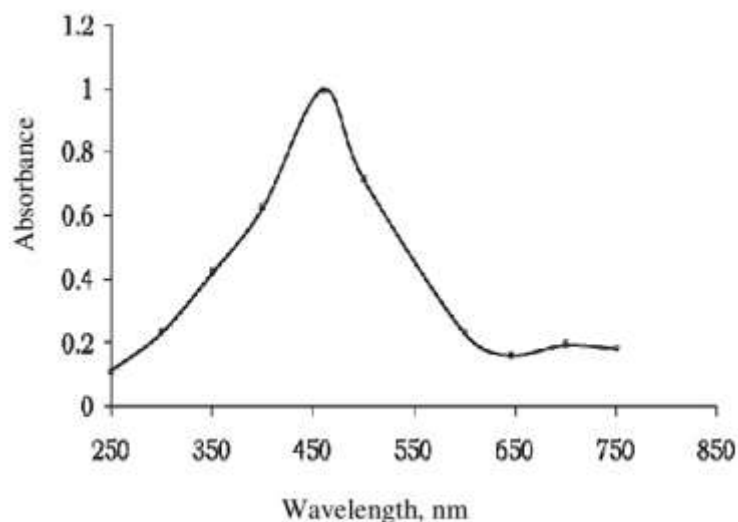


Figure 4. Absorption spectrum of 3-hydroxy benzyl amino benzoic acid-zinc complex

3-3 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectrophotometer analytical instrument is based on the principle of atomic absorption spectroscopy and is very useful to detect the metal ion concentration present in drinking water samples. When a sample solution is aspirated into a flame then sample element is changed into atomic vapour of that element. Flame contains atoms of element. Furthermore, some atoms are thermally excited by flame whereas most of them remain in ground state. The ground state atoms then absorb the radiation of specific wavelength produced by source i.e. hollow cathode lamp of that specific metal. Now, the wavelength of radiation given off by the source or lamp is similar as that of absorbed by the atoms in the flame.

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Zinc	5.0	NM	15.0

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Discussion

1. Experimental optimization of extraction conditions To achieve the best extraction performance, several parameters were optimized. These parameters included effect of pH, organic solvent, ligand as stripping agent, functionalized

2 . Effect of pH

The pH of aqueous feed-phase plays an important role in the extraction process. The difference in acidity between the donor phase and sorbent can promote the extraction of analytes from the donor phase to the acceptor phase As results display, when the pH value of the working solution was 5, the pre-concentration factor of Zn (II) on adsorbent is at the highest value. Extraction efficiency decreases at the higher and lower pH values. Therefore pH 5.0 was selected for further experiments. The peak current fluctuations observed in pH values less than 5.0 were attributed to the partial protonation of the ionizable species

3. Effect of organic solvent type used for sol dispersion

It is important to choose a suitable extracting organic solvent for an efficient extraction of target analyte from aqueous solution to pores of the hollow fiber. This organic solvent should be able to make homogeneous composite from synthesized sol as described in Section 2.3. In addition, the organic solvent should have a low solubility in water and low volatility and vapor pressure to prevent the solvent loss during the extraction and should withstand high stirring speed without leakage. Especially when faster stirring rates and long extraction time are used (Shrivastava and Patel, 2011) and most important of all, those

selected solvents should ensure high enrichment for tested analyte. Several dispersion solvents were investigated. According to the results, 1-octanol was found to possess higher extraction efficiency.

4. Effect of reagent concentration

The effect of reagent concentration has been studied by keeping 1.0 mL of zinc(II) solution and 3.0 mL of pH 5.0 buffer constant. The concentration of 3-hydroxybenzylaminobenzoic acid was varied between 1.0×10^{-3} M and 11.0×10^{-3} M to obtain maximum color formation. The total volume of aqueous phases was brought to 10.0 mL with double distilled water. The aqueous phases were shaken with 10.0 mL of n-butanol in each case; the organic phases collected in 25 mL standard flasks and made upto 25 mL with n-butanol. The absorbance of these phases was measured at 460 nm, against their corresponding reagent blanks. The experiment revealed that six folds of reagent to that of metal ion are sufficient for maximum color development of the complex. Hence, a six-fold molar excess of the reagent is maintained for all further studies.

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