PRECONCENTRATION OF LEAD USING MERCAPTOSEPHADEX AND ITS DETERMINATION WITH NEW REAGENT BY SPECTROPHOTOMETRY

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Abstract

A highly sensitive and selective spectrophotometric method for the determination of traces of Lead in water after pre-concentration using Mercapto sephadex (MS-50) has been developed. The method is based on the color reaction of lead (II) with dichlorohydroxyl phenyl porphyrin. Under the optimum condition, Pb(II) reacts with reagent to from 1:2 yellow complex in presence of Triton X-100, which has a maximum absorption peak at 482 nm. The color reaction can be completed rapidly and remain stable for more than 24 h at room temperature. The molar absorption co-efficient of the lead complex, the limit of quantification, the limit of detection and relative standard deviations were found to be 2.45 H 10^5 L Mol^{-1} cm-1, 4.4, 1.45 ng ml^{-1} and 1% respectively. The absorbance of the lead complex at 482 nm is linear up to 0.46 µg ml^{-1} of lead(II). The effect of various co-existing ions in water were examined seriously. No interfere was observed. Moreover, a simple pre-concentration method for trace of lead in water was also studied using MS-50. It was found that traces in lead in water can be absorbed.

Introduction:

Human activity may result in increasing level of contamination in the environment. Lead pollution in water system has influenced on the quality of life seriously especially in developing countries. Lead is accumulated in tissues and may bring serious health problems for human and animals such as cacerization and hypogenesis. Therefore, lead analysis in water has received attention strongly. At present, the method for the determination of trace lead mainly were atomic absorption spectrophotometry[1-3] and the spectrophotometry based on various reagents such as Dibromo-p-methyl carboxy sulfonazo[4], 1-(2-thizoylazo-2-)-naphthol[5], Diathiazone[6], Arsenazo-TB[7], 4-(2-pyridialzo)-resorcinol[8], Malachite green[9], Monothiothenyl trifluoroacetone[10], Xelenol Orange[11], pyridine-2-acetaldehyde salicyloy hydrazone[12], Butylrhodamine B[13], Arsenazo III[14], Diethyl dithiocarbamate[15], 2-(2-thiazolylazo)-p-

cresol[16], Diphenyl carbazone[17]. Among these methods, the spectrophotometry is most convenient for use of its simplicity and low cost. In literature, many reagents have been reported as reagents for spectrophotometric determination of lead. Although each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity, these reagents are not fit for determine very low lead (1.0 μ gl^{-1} or even lower) in water due to low sensitivity or selectivity.

Dichlorohydroxyl phenyl porphyrin is excellent chromogenic reagent (Fig.1), Dichlorohydroxyl phenyl porphyrin, has been applied spectrophoto-metric determination of Zinc[17]. In this work, we studied the reaction of the reagent with lead(II), the results indicate that the reagent also can react with lead sensitively, its molar absorption coefficient of lead complex is 2.45 H 10^5 l mol^{-1} cm^{-1}, most of metal ions can be tolerated in considerable amounts. But Dichlorohydroxyl phenyl porphyrin is not sensitive enough to determine trace lead in water samples directly. Therefore, a simple preconcentration method for lead is necessary and valuable very much.

Main pre-concentration methods for metal ions have organic solvents soluble membrane (OSSM) and extraction method with various organic solvents mainly. However, these methods exist serious drawbacks. OSSM required dissolving the membrane with some special organic solvents this may result in reducing sensitivity of the method remarkably[18], and the extraction method may bring secondary pollution. In order to overcome the above problem, Mercaptosephadex (MS-50) was studied as a sorbent for concentration trace lead in water.

Fig.1. The structure of the reagent
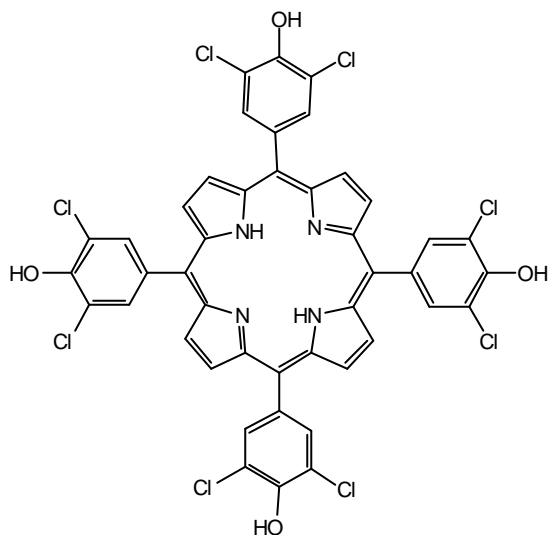
Experiments shows that MS-50 has excellent adsorbent characteristics for lead. In different concentration of HCl, lead can be absorbed and dissociated quantitatively. Because trace lead is concentrated in water largely, the detection limit for lead in water samples was in creased to 0.25 ng ml^{-1}. The proposed method has been used to the determination of lead in water samples successfully.

Experimental

Apparatus : All absorption spectra and absorbance at 482 nm were measured on a HITACHI U 2001 spectrophotometer using 1 cm quartz cell. All pH values measured on a pHs - 29 A model pH meter.

Materials : The order to avoid lead contamination, unless otherwise stated, all reagents used were of analytical grade and all solution were prepared with ultra pure water (the purity of water is spec pure). All solutions including samples and standards were stored in polythelene bottles. All glass calibrated flask, the beaker and the fitters were of high grade and immersed in 2.0 mol l^1 HNO_3 for 12h at least, then washed with water.

A stock standard lead (II) solution (1.0 mg ml^{-1}) was prepared by sissolving lead oxide (spec pure) in 2.0 Mol 1^{-1} HNO_3, then the solution was evaporated to remove the excess acid, and diluted with (1 + 100) nitric acid, to a given volume. The working standard solution (1.0 Fg ml^{-1}) was prepared by diluting the standard lead solution with water. Dichlorohydroxylphenyl prophyrin (0.04%) was prepared by dissolving 100 mg of the solid reagent in 10 ml of water, 0.5 ml of 2.0 mol l^1 sodium hydroxide solution was added to make the reagent dissolved completely, the solution was diluted to 250 ml with water. Dichloro hydroxylporphyrine was synthesized and purified in the laboratory as a similar method[19]; Triton X - 100 solution (2%) was prepared by dissolving 2 ml of Triton X -100 in 100ml of water.

Synthesis of MS-50[20]

10 ml of mercaptoacetic acid and 10 ml of tetrahydrofuran were transferred into a 250 ml of conical flask. After mixing well, 10g of sephadex C-50 was added, then the conical flask sealed up was warmed in a 40"2? C waterbath for 2 days. MS-50 was filtrated and washed to pH 7.0 with water. After washed with 5.0 ml of 95% alcohol last, MS-50 was cut up and dried in a vaccum drying oven under 35?C. In order to determine the content of mercapto content in MS-50, 0.1g of MS-50 was transferred in to 150 ml of a conical flask 50 ml of water and 2 ml of concentrated nitric acid were added. After the mixtur was deposited 1 h, excess $AgNO_3$ was added to the conical flask and stirred well, then the superfluous $AgNO_3$ was determined by titration with potassium thiocyanate standard solution in which Fe (III) was selected as indicator. A 0.97 mmol g^{-1} of the content of mercapto content in MS-50 was obtained. Other types of MS were synthesized by using a similar method.

General Procedure :

An aliquot containing not more than 12 μ g of lead (II) was transferred into a 25 ml calibrated flask and 1.0 ml of 0.04% dichlorohydroxylphemylporphyrin solution. After depositing 10.0 min under room temperature, 2.0 ml of 2% Triton X-100 was added, then the flask was diluted to volume with water. The absorbance was measured at 482 nm on the spectropholometer in a 1 cm cell. A reagert blank was prepared in a similar manner but with out lead. All measurements were carried out at room temperature.
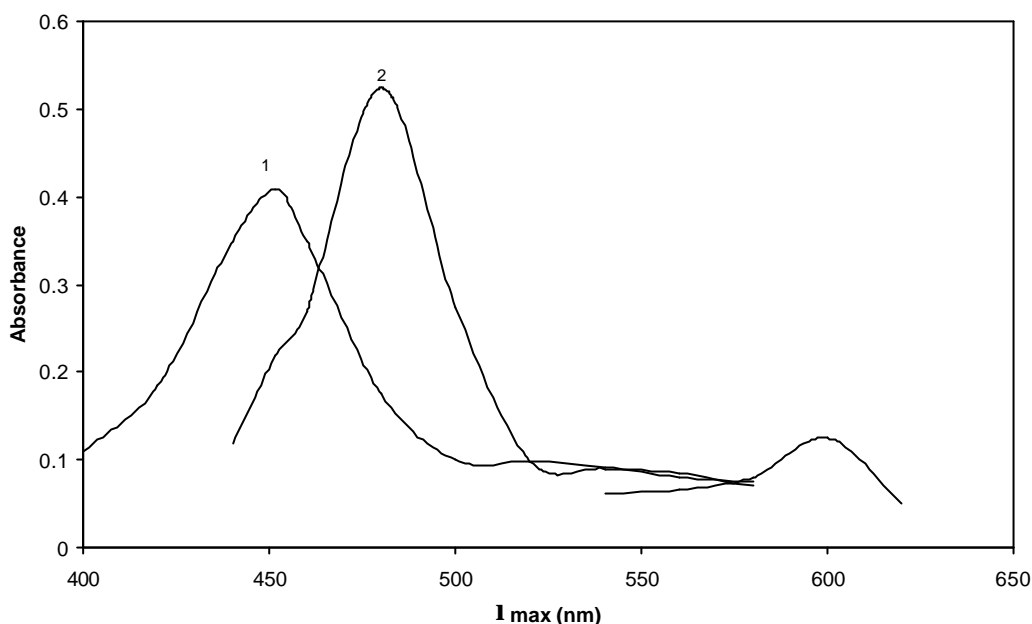
Results and Discussion :

Absorption Spectra :

The absorption Speetra (Fig. 2) of the complex and reagent blank were shown in Fig. 2.   From the figure it can be seen that the absorption speectra of the complex has two peaks at 482 and 682 nm, respectively, and absorbance at 482 nm is higher than that of 600 nm, and dichlorohydroxylphenylporphyrine blank solution give maximum absorption peak at 451 nm and its adsorbance at 482 nm is very low. In order to obtain higher sensitivity, all measurements in following experiments were carried out at 482 nm.

Effect of Acidity :

The effect of acidity on the reaction of dichloro hydroxylphenylporphyrin with lead (II) was studied. Experiment indicated the complex can form in alkaline media. With increasing pH value of solution, the absorbance of the complex at 482 nm increased with increasing with pH value up to 9.0 rapidly, and then remained almost constant from the range borad buffer of pH 9.0 to 0.16 mol l^{-1} NaOH.   When NaOH concentration is more than 0.16 mol l^{-1}, the absorbance decreased A 0.08 mol l^{-1} NaOH solution was selected for subsequent studies.

Effect of the Reagent Concentration :

The concentration of dichlorohydroxylphenylporphyrin has a large effect on the absorbance of the lead complex. With other concentration fixed, for a lead concentration of 0.45 µg ml l^{-1} , the absorbance of the complex increased rapidly with increasing in dichlorohydrpxylphenylporphyrin concentration then the leveled off with a maximum in the range 0.8-2.0 ml 0.04% dichlorohydroxyl-phenylporphyrin, followed by a slight decrease with further increase in dichlorohydroxyl phenyl porphyrin concentration. In subsequent experiments the volume of 0.04% dichlorohydroxyl phenylporphyrin was fixed at 1.5 ml.

Effect of Surfactants :

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Both dichlorohydroxyl phenylporphyrin and its complex have good water solubility in alkaline media, but the sensitive of its complex with out surfactants is very low. In order to improve the sensitive, the effect of various surfactancts on the reaction were examined in detail.

It was found that different types of surfactants exhibited different effects on the absorbance from the system [See Fig. 3] the results indicated that the anionic surfactants such as sodium dodecanesulphonate do not influence on the absorbance in considerable amounts of surfactants; nonionic surfactants, such as Tween-80, AEO-9 and Triton X-100, and catonic surfactauts such as CTMAB increased the absorbance of the complex ostensibly. Owing to CTMAB give smaller absorbance increment than nonionic surfactants, and Triton X-100 gave highest sensitivity and low background signals, so Triton X-100 was choosen. It has been suggested that the effect of nonionic surfactants in the similar compexes is due to form an ternary compound between lead (II) - dichlorohydroxyl phenylporphyrin and the surfactant and it may be that, under there acidic conditions, the cationic surfactants work in a similar manner[16]. The effect of the concentration of Triton X-100 on the molar coefficient of the complex was tested. When the concentration of Triton X-100 is less than 0.2 mg ml^{-1}. The absorbance increases sharply with increasing in Triton X-100 concentration, and then tends to remain constants, reach a maximum in the Triton X-100 concentration range 0.2-8 mg ml^{-1}. Therefore, an addition of 2 ml of 2% Triton X-100 was recommended in subsequent experiments.

Fig, 3: The effect of different types of surfactants on the reaction
a. The absorption spectra of the reagent in the presence of CTMAB
b. The absorption spectra of the reagent in the presence of Triton X-100
c. The absorption spectra of the complex in the presence of Triton X-100
d. The absorption spectra of the complex in the presence of CTMAB
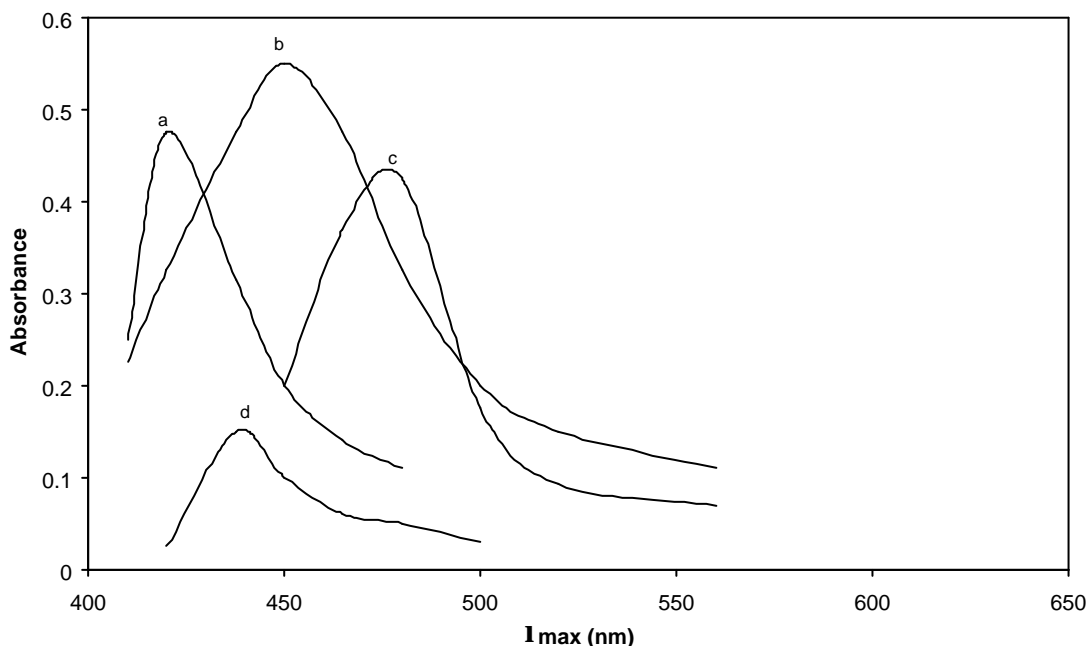
Effect of Reaction Time and Stability of the Color System :

The effect of reaction temperature on the formation of complex was tested closely. It was found that temperature influenced the rate of the reaction slightly. When room temperature is higher than 10? C, the color reaction of lead with reagent can complete within 5 min. Thus, a 10 min reaction time was selected in following work. The reaction completed, the absorbance of the complex remains stable for 36 h under the room temperature, its accumulated stability constant of the complex is 1.22 H 10^5 at 25?C.

Calibration, Precision and Sensitivity :

A calibration graph, obtained by the proposed procedure under the optimum conditions, was found to be linear up to 0.46 µg ml^{-1} of lead (II). The equation (n=12, r=0.9996) of relative absorbance at 482 nm (A) against concentrations (C µ g^{-1} per 25 ml^{-1}) was A=0.093 C+0.0012. The molar absorption coefficient of the comple was calculated from the scope of the calibration graph to be 2.32 H 10^5 l mol^1 cm^{-1}. The limit of quantification and limit of detection[21-23] were found to be 4.4 and 1.41 µ g ml^{-1}. Ten replicate analyses of a test solution containing 5 µg of lead by the procedure gave a relative standard deviation of 1.02%. According to the procedure, another calibration graph, constructed on a various lead concentration plus 100 ml of water with MS-50 for pre-concentration as following procedure and determination, were almost the same as that discussed, this shows that the pre-concentration has not effect on the results. However, pre-concentration steps can increase the ditection limit of method 0.2 µ g ml^1 of lead (0.2 ppb) in water sample can be determined well and truly.

Composition of the Complexes :

The compositions of the complexes were studied by the continous variation and molar ratio methods. Both showed a molar ratio of lead (II) ; dichlorohydroxyphenylporphyrin; Triton X-100 = 1:2:2.

Effect of Foreign ions :

The effect of potential interfering ions on the determination of lead (II) were investigated by addition known concentrations of each ion in a solution containing 0.46 µg ml^{-1} lead (II). The tolerated amounts of each ion were the concentration values tested that caused less than 6% the absorbance alteration. The results obtained are summarized in Table - 2. In water samples, main metal are Ca (II) and Mg (II), other metal ion content are very low, as dichlohydroxylphenylporphyrin has good selectivity, and most of Ca(II) and Mg(II) has been seperated by prior to pre-concentration step with MS-50. Thus, all ions in water do not interfere with the determination of trace lead.

Table-2 : Effect of foreign ions on the reaction

Foreign ion	Tolerated limit (μg)	Tolerated limit after adsorbed with MS-50 (μg)	Foreign ion	Tolerated limit (μg)	Tolerated limit after adsorbed with MS-50 (μg)
Cl^-	10,000	200,000	Bi^{3+}	800	1500
I^-	10,000	30,000	Sn^{4+}	300	200
CO_3^{2-}	2,60,000	50,000	Ti^{4+}	150	300
SO_4^{2-}	10,000	30,000	Fe^{3+}	400	1000
PO_4^{3-}	60,000	25,000	Co^{3+}	450	2000
$C_2O_4^{2-}$	25,000	28,000	Ni^{2+}	1000	2000
Na^+	10,000	10,25,000	Cu^{2+}	600	1500
K^+	15,000	50,000	Zn^{2+}	2500	3000
Mg^{2+}	2,000	15,000	Ag^+	450	1000
Ca^{2+}	1000	10,000	Hg^{2+}	200	500
Ba^{2+}	600	2,000	Cd^{2+}	1000	1300
Sr^{2+}	500	1,000	V^{5+}	200	300
Al^{3+}	10000	30,000	Mn^{2+}	100	1500
Sb^{3+}	500	5,000	La^{3+}	350	450

Adsorbent Characteristics of MS-50 for lead (II) :

Adsorbent characteristics of MS-50 for metal ions were examined seriously. It was found tht MS-50 for heavy metal ions such as Ag^+, Se^{+4}, Hg^{2+}, Cu^{2+}, Sb^{3+}, Sn^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} has strong sorption. However, number of metal ions adsorbed decreases with increasing in acidity of the solution ostensibly. When adsorbent acidity was adjusted to 1.0 mol l^{-1} HCl, only Ag^+ Hg^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Se^{+4} can combine with MS-50 adsorbing above metal ions was immersed in 4.0 mol l^{-1} HCl solution. Zn^{2+} and Pb^{2+} were transferred into a the solution, other metal ions were yet fixed on MS-50. Thus, adsorbent acitivity and dissociation acidity were fixed at 1.0 mol l^{-1} HCl and 4.0 mol l^{-1} HCl in subsequent work, respectively, in order to obtaine good selectivity.

To check the accuracy of the proposed method, a study was carried out on a various amounts of lead for adsorb with MS-50 and determination. The relative difference between the absorbance obtained with and without preconcentration with MS-50 did not exceed "0.25% and the absorbent recovery ranged from 99.75 to 99.98%.

Analysis of Water Samples :

Water sample was transferred into the beaker, the acidity of solution was adjusted to 1.0 Mol 1^{-1} HCl with concentration HCl, 1.5 g of MS-50 (prior to swelling with water) was added. After mixed round on the magnetic stirrer for 5.0 min, the solution was filltered, the MS-50 was transferred into the beaker, abore procedure was repeated time after time. Lastly, MS-50 was immersed in 4.0 mol 1^{-1} HCl and stirred for 2 min, then the solution was filterated, the filtrate was evaporated to drive out HCl, then the solution was transferred into 25 ml of calibrated flask. The concentration of lead (II) were determined as procedure method, the results are shown in Table. 3, it can be seen that the results are good agreement with those for lead found by electrothermal atomic absorption spectroscopy (EAAS).

Table 3 :   Determination of Lead(II) in Sample (n=5)

Sample	Lead found by proposed method $(\mu g l^{-1})^{a}$	Lead found by EAAS method $(\mu g l^{-1})^{a}$
The mineral water	5.42 " 0.12 f=1.34 t=0.162	5.40 " 0.14
The river water	9.75 " 0.14 f=1.39 t=0.47	9.78 " 0.19
Lake	11.28 " 0.15 f=1.51 t=0.46	11.32 " 0.12
Tap water	1.74 " 0.06 f=1.53 t=0.49	1.71 " 0.19
Ground water-1	144.36 " 0.19 f=2.09 t=0.81	144.24 " 0.32
Ground water-2	14.69 " 0.15 f=2.37 t=0.87	14.71 " 0.17

a results expressed as $\dfrac{\bar{x} \pm st}{\sqrt{n}\ (n\ =\ 5)}$. The f and t values refer to comparison of the proposed method

with EAAS method. Theoretical values at 95% confidence level t=2.78.

Conclusion :

The molecular structure of the reagent influence on the stability of color system ostensibly. As bromide atom has strong withdrawing electron and p-p conjugate effect, the dichlorophydroxylphenylporphyrin reagent and its lead complex both are very stable

the reaction of dichlorohydroxylphenyl prophyrin with lead can complete in a wide acidity range from buffer solution of pH 9.0 to 0.16 mol l^{-1} NaOH media, this is more simple than other reagent published, it is benificial to obtain good accuracy and precision in the routine lead analysis. In comparion with other prophyrin reagents in literature, dichlorohydroxyl-phenylporphyrin has high selectivity, most of the metal ions can be tolarated in considerable amounts, this is mainly due to big steric hidrance brought by two chloride atoms in dichlorohydroxylphenylporphyrin molecule structure.

The proposed method more sensitive than the flame atomic absorption spectrometry and similar in sensitivity to EASS. compared with the other reagents for spectrophotometric determination of lead (see table 1), dichlorohydroxylphenylporphyrin is one of the most sensitive reagents. Thus, proposed method can be used to determine lead in low levels.

MS-50 is an excellent a dsorbent characteristics to lead (II). compared with other pre-concentration method such as extraction method and organic solvent - soluble membrane (OSSM). MS-50 has stronger sorption for lead (II), which do not result in decreasing sensitivity of determination method.

Unlike OSSM and using toxic organic compound. More over, MS-50 is easy to systhesize and pre-concentration procedure is simple and rapid compared with other high polymeric mercaptosephadex, MS-50 has better mechanic as strength, this is benificial to repeated use.

Table - 1 :   Comparision of analytical parameters for the spectrophotometric determination of lead.

Reagent	Phase	?max nm	E	Comments	Reference
Dibromo-p-methyl sulfonazo	H_3PO4	642	$1.05H10^5$	KI-methyl isobutyl ketone extaction, Ca, Ba and RE seriously interfered	4
1-(2-thiazoylazo-2-)-naphthol	Aqueous	575		Light sensitive, Mn, Se, Co, Zn, EDTA interfere seriously	5
Diathiazone	CCl_4	520	$2.5H10^4$	Light sensitive Hg, Zn, Cu and Fe interfere	
Arsenazo-TB	Aqueous	620		Light sensitive, Th and Ti interfere	6
4-(2-pyridialzo)-resorcinol	Aqueous pH (9.0 - 10.4)	525	$7.2H10^4$	-	7
Malachite green	Toluence	642		Ca, Hg, Sb, Bi, Co, Sn and Ti interfere.	8
Monothiothenyl trifluoroacetone	Benzene	384		Equilibration time 3 min Ni, Ca, Co, Cu, Zn and Pd interfere seriously	9
Xylenol Organe	Aqueous (pH4.5-5.5)	580	$1.94H10^4$	Light sensitive, Al, Bi, Hg, Ni, RE and Zn interfere seriously	10
Pyridine-z-acetaldelyde salicyloyhydrazone	$CHCl_3$	380		Salting out agent used	11
Butylrhodamine B	C_6H_6	570		Hg, Bi, Ti and Ag interfere	12
Argenazo III	Aqueous pH2.5-4.5	660	$3.0H10^4$	Fe, Al, Cu, Th, Ti and U interfere	13
Diethyldithiocarbamate	CCl_4	435	$1.3H10^4$		14
2-(2-thiazolylazo)-p-cresol	Aqueous pH (9-10)	650	$20.07H10^4$	Cu, Ni, Co, Zn, Fe and Cd interfere	15
Diphenyl Carbazone	Aqueous pH (9-10.4)	585	$7.2H10^4$		16
Dichlorohydroxyl phenylporphyrin	NaOH	482	$2.45 H 10^5$	High Sensitive and selective	Present work

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