Adaptation Optimization of Solvent Extraction Spectrophotometric Method for Mercury(II) based on Ion Association with Thiacrown Ether and Bromocresol Green to FIA

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Abstract

A simple, fast, economical and safe method has been reported. The method is based on the previously reported on line solvent extraction of mercury(II) complexed with thiacrown ether as a cationic complex associate with Bromocresol Green as an anionic pairing ion using chloroform as the extracting solvent. The absorbance of the extracted ion–associate is spectrophotometrically measured at the λ_{max} 420 nm. Full chemometrical optimization treatment was employed for determining the proper optimum operating conditions for both system and chemical variables. The experimental design approach was employed and a 2^f factorial design was run for studying the interaction effects of four factors namely, a Bromocresol Green concentration, a buffer concentration, a Thiacrown ether concentration and a flow rate. The super modified simplex algorithm was utilised for optimising the two highly interacting factors which were, the Bromocresol Green and the buffer concentration. The proper operating conditions obtained were 8.18×10^{-4} mol L^{-1} BCG, 4.70 pH , 1.11×10^{-2} mol L^{-1} TCE and 3.9 mL/min flow rate for 200 μL mercury. The method was found to be accurate as the recovery percent indicates with a high precesion as the relative standard deviation is no more than 2.5% with the determination range of 2.49×10^{-4} mol L^{-1} to 3.4897×10^{-3} mol L^{-1} The interference study carried out indicates that the proposed method is suitable for the determination of mercury in the environment.

Keywords Mercury extraction, FIA, chemometrics and optimization

1. Introduction

Mercury is considered one of the major elements causing hazardous effects to our environment; there for enormous efforts by analysts have been exerted towards establishing reliable and convenient method for its determination in different media. Mercury and other compounds have been determined by solvent extraction procedure using different techniques for detections including spectrophotometry, fluorimetry, neutron activation, optical and electrochemical methods which, have been recently reviewed[1-2]. Stockwell and co-workers have recently developed a fully automated system for mercury determination based on atomic emission flourescence (AEF) technique which proved to be suitable for ultra low level detection and better than the continuous emission monitors recently published by French et al[3].

Crown ethers are macrocyclic polyethers, and the one used for mercury is chemically known as 1,4,7,10,13,16-hexathia-cyclooctadecane. A comprehensive introduction of the chemistry and use of crown ethers in solvent extractions has been reviewed[4]. Crown ethers have been characterized as macrocyclic compounds by Christense et al[5].

The stability of the resulting complex depend to a large extent on the relative sizes of the diameter of the cavity in the crown and the diameter of the cation, and is also influenced by the charge and "hardness" of the cation, as well as the kind of donor atoms present, which determine "hardness" and basicity. Generally, O-containing macrocycles form stable complexes with the alkali, alkaline earth, lanthanides and actinides; N-containing macrocycles with the transition metals; and the S-containing macrocycles with the heavy metals. The complexes formed are normally of the 1:1 type. However other stoichiometries are also possible. They have been extensively investigated as ligands in solvent extraction because of their selectivities towards particular metal ions. A metal, a neutral crown ether and a chromogenic pairing anion or binary complexes of a metal ion and an anionic chromogenic crown ether can form ion-pair extraction systems based on a ternary complex

formation and they are useful for the spectrophotometric determination of metal ions[1,2]

The utilization of a flow injection analysis FIA technique in solvent extraction systems with different types of separators, designed for different possible extractions using varieties of solvents has been investigated by Karlberg and co-workers[6-10]. Only a few publications on extraction separation by FIA have been reported so far, as the on-line separation on line is challenging and difficult to be designed or constructed. Therefor some workers have devoted an exerted amount of effort mainly in the design and construction of different and suitable separators for quantitative extraction. In the extraction process carried out by FIA it is necessary to keep the dispersion of an injected and extracted sample as minimum as possible, as well as obtaining complete separation.

In this work, a considerable effort and quite a number of experimentation and trials have been made to construct an adequate FIA manifold and design reasonable membrane suitable for metal extraction. Crown ether is used to extract mercury ion on line, selectively using bromocresol green as an anionic pairing ion for the metal-thiacrown complex. The resulting neutrally charged ion-paired complex is then partitioned into an organic phase and detected spectrophotometrically[1] at the wavelength of maximum absorbance at 420 nm.

2. Experimental

2.1. Reagents and chemicals

Double-distilled deionised water was used throughout the preparation of stock and working solutions. Otherwise chloroform stabilised with ethanol purity, at least 99.9% supplied by Fluka was used for preparing the thiacrown ether solution.
All inorganic chemicals used were of analytical reagent grade. Sulfates of chromium(III), copper(II), manganese(II), iron(II), zinc(II) and cadmium(II), nitrates of nickel(II), lead(II) and silver(I) and chloride of cobalt(II) were used for interference study.

2.2. Stock solutions

Mercury(II) (0.01 mol L^{-1}) standard solution is provided by E. MERCK AG Darmstadt, Germany as mercury(II) nitrate $Hg(NO_3)_2$. Working solutions were prepared by dilutions with water.
Bromocresol green (BCG) (6.95 x 10^{-3} mol L^{-1}) stock solution was prepared by dissolving 0.5005 g of the sodium salt (MM 720.0), purchased from Allied Chemical Corporation, in water and diluting

to 100 ml with water. Working solution of 8.18 x 10^{-4} mol L^{-1} was prepared by diluting the stock solution with water.

Thiacrown ether (TCE) (8.3 x 10^{-3} mol L^{-1}) stock solution was prepared daily by dissolving 0.3 g of 1,4,7,10,13,16-Hexathia-cyclooctadecane, MM 360.71, in chloroform and diluting to 100 mL. This compound was supplied by Aldrich Chem. Co.. Macrocyclic sulfur ligands are highly toxic and should be handled with care.

Buffer solutions of a pH range of 3.0 – 5.5 were prepared by dissolving 100.0 g of ammonium acetate (BDH Chemicals Ltd. Pole England), in water and adjusting the pH with 7 mol L^{-1} hydrochloric acid, followed by dilution to 200 ml with water.

Hydrochloric acid (7.0 mol L^{-3}) Prepared by diluting concentrated acid (Fisher Scientific Co.), and other working solutions were prepared by further dilution.
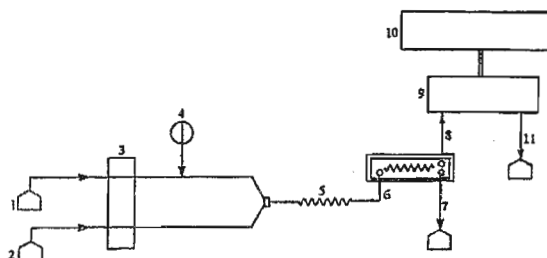
2.3. Apparatus

Fig. 1 FIALab apparatus

A FIALab apparatus (Fig. 1) was obtained from Alitea (Medina, Washington DC, USA). The apparatus consists of the following units: A peristaltic pump used was the one with cassette drive and variable speed; two direction; 4 channels. A Rheodyne Model 5041 four-way Teflon rotary valve mounted on an angle bracket in the injector position of FIA lab was used. Pump tubing of 1.40 mm I.D AcidFlex type supplied by Global FIA, Houston, USA, were used. Other connecting and a reactor module tubing of 0.5 mm I.D Microline tubing supplied by Thermoplastic Scientifics, Inc., (New Jersey) were used. A spectrophotometer is the Spectronic Mini 20 Spectrophotometer used as a detector with a 20 µL was a flow-through cell having a path length of 1.0 mm and connected to a Cole-Palmer (Chicago, IL, USA) Model 0555 single-channel strip-chart recorder with the speed adjusted at 1 cm min^{-1}. A Lambda 5 UV-visible spectrophotometer (Perkin-Elmer) together with 10 mm cells was used for measuring absorbance of samples prepared for analysis by the

spectrophotometric original method for comparative study.

2.4. Extraction cell Design

An extraction unit was assembled as in Fig. 1. The unit consists of two blocks (top and bottom) with flow channels cut at the surface of a microporous PTFE membrane sheet of 1 µm pore size. These two blocks were fixed with screws. If the top and bottom blocks are mated in one orientation, there is a total overlap of the channels. The unit is made of stainless steel (2 cm thick; 3 cm wide and 11 cm long) with a zigzag channel (9 cm long). Fig. 1 shows how the unit is assembled and ports are connected Three holes were drilled, two on the donor side, one hole (port 6) was drilled for the inlet of the mixture coming from the reaction coil; the other one (port 7) was drilled on the same side with the inlet and functions as an outlet for the aqueous waste solution. The third (port 8) on the opposite side and used for the outlet of the organic layer carrying the mercury associated complex and connected directly to the spectrophotometer. This assembly was regularly tested to ensure the efficiency of separation of the two layers and check for any leakage. A mixture of water and chloroform was introduced through the donor flow; and observing smooth exiting of the aqueous waste through one outlet and the chloroform through the other opposite outlet.

2.5. FIA Manifold and Procedure

The above described extraction unit was used for mercury extraction. Fig. 1 shows a two line FIA manifold used during this work. A TCE solution was pumped (3) through line (1) and a solution of the BCG with the buffer (5 mL each was made up to 25 mL with water) , were pumped through line (2). Metal ion (mercury) was injected (4) onto line (1), where it mixed with the crown ether and an ion associate with BCG at the confluence point before the extraction coil. They all mix in the reaction coil (5) and flew to the PTFE extraction unit through line (6). The aqueous solution exits to waste through line (7) while the extracted metal ion (mercury) passes through the PTFE membrane in a form of ion associate through line (8) to the spectrophotometer (9), where a signal for its absorbance is recorded (10) at the wavelength at 420 nm. Waste of the ion associated form of mercury exits through line (11).

2.6. Software Packages

Sigmaplot, version 1.02 (Jandel Scientific, Erkrath, Germany) was employed for data handling and statistical calculations and constructing graphs.

The COPS i.e. "Chemometric Optimization by Simplex" program was obtained from Elsevier Scientific Co., The Netherlands, and utilized for the optimization of variables using a compatible IBM personal computer.

3. Results and Discussion

On line extraction is carried out by FIA technique based on our recent publication in this topic[1] which was primarily based on the manual extraction of the ion-associate formed by mercury(II) thiacrown ether cationic complex with bromocresol green as the anionic pairing using chloroform as the extracting solvent. It is previously reported that mercury forms a 1: 1 complex with thiacrown. Based on this the extracted species is believed to be a 1:1:2 complex with BCG in the form $Hg(TCE)(BCG)_2$.

The previous[1] investigation on the conditions affecting the formation, extraction and sensitivity of the ion-associate complex reveals that the complex formation was extremely dependent on the BCG concentration, the buffer pH, TCE concentration and flow rate. During this micro technique infinite quantities of the analyte and reagents were used for careful adjustment of all variable parameters, therefore a full chemometrical optimization for these operating parameters was found to be necessary. An experimental design approach[11-14] was employed and a 2^k factorial design was run where 2 stands for variable levels considering the upper and lower values; and k is the number of factors studied. The four factors described above have been considered for chemometrical optimization. The upper and lower values were determined and assigned +1 and – 1 coded levels respectively and both are introduced in Table 1. For BCG, the higher concentration was 1.67×10^{-3} and the lower was 5.56×10^{-4} mol L^{-1}; for pH, the higher was 4.7 and the lower was 3.0. For the TCE concentration, the higher was 1.11×10^{-2} and the lower was 2.77×10^{-3} mol L^{-1} and for the flow rate, higher was 6.5 mL/min and the lower was 3.4 mL/min. Sixteen experiments were conducted and the equivalent response function taken as peak height in mm was recorded. Peaks were very narrow at base and for this reason peak width was not considered.

The results obtained were treated by the Sigmaplot Software and every two factors were considered for a 3D response surface plots. Fig. 2 shows the response surface as a function of pH and BCG levels. This plot reveals that the response increases as the BCG concentration increases and decreases as the pH increases.

Among the four factors, crown ether effect was found to be highly and significantly affecting the response and to a certain concentration level beyond
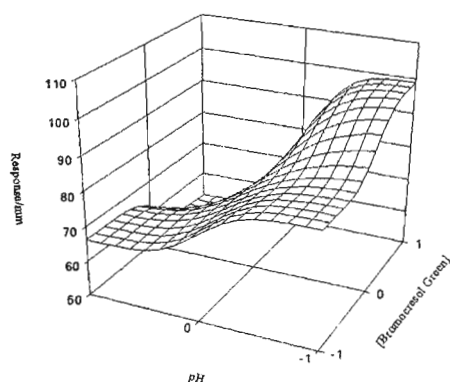
Fig.2 Surface plot of the response in mm versus pH and bromocresol green levels.

Table 1 Full treatment combinations in both their original and coded levels along with the responses obtained by injecting 200 μL of 1.5 10^{-3} mol L^{-1} mercury(II)

Experiment No.	[BCG] x 10^{-4} mol L^{-1}	[Buffer]/pH	[TCE] x 10^{-3} mol L^{-1}	Flow rate/ mL min^{-1}	Response /mm
1	5.5556	3.00	2.7723	20	67
2	16.667	3.00	2.7723	20	105
3	5.5556	4.60	2.7723	20	47
4	16.667	4.60	2.7723	20	60
5	5.5556	3.00	11.089	20	92
6	16.667	3.00	11.089	20	115
7	5.5556	4.60	11.089	20	68
8	16.667	4.60	11.089	20	55
9	5.5556	3.00	2.7723	50	76
10	16.667	3.00	2.7723	50	76
11	5.5556	4.60	2.7723	50	75
12	16.667	4.60	2.7723	50	40
13	5.5556	3.00	11.089	50	97
14	16.667	3.00	11.089	50	100
15	5.5556	4.60	11.089	50	75
16	16.667	4.60	11.089	50	55
1	-1	-1	-1	-1	67
2	+1	-1	-1	-1	105
3	-1	+1	-1	-1	47
4	+1	+1	-1	-1	60
5	-1	-1	+1	-1	92
6	+1	-1	+1	-1	115
7	-1	+1	+1	-1	68
8	+1	+1	+1	-1	55
9	-1	-1	-1	+1	76
10	+1	-1	-1	+1	76
11	-1	+1	-1	+1	75
12	+1	+1	-1	+1	40
13	-1	-1	+1	+1	97
14	+1	-1	+1	+1	100
15	-1	+1	+1	+1	75
16	+1	+1	+1	+1	55

which it maintains a constant response value.
Multiple linear regression statistical analysis was employed to make use of the data in Table 1 and the results of the analysis of variance (ANOVA) is introduced in Table 2. Four variables, namely, the BCG concentration, the buffer pH, the TCE concentration and the flow rate were considered to

Table 2 Analysis of variance

Source of variation	d.f. (degree of freedom)	SS (sum of squares)	MS (mean square)	Variance ratio
Regression	4	4789.8	1197.4	
Residual	11	2256.7	205.2	5.8
Total	15	7046.4	469.8	
Main effect BCG Buffer TCE Flow rate	= 1.125 = 31.625 = 13.875 = -1.875			
Interactive effects BCG*Buffer BCG*TCE Buffer*TCE BCG*Buffer *TCE	= 14.875 = -2.875 = -6.125 = 0.125			

generate the results therein. The sum of squares (SS) due to the regression as a percentage of the total sum of squares is found to be 68%, showing that a reasonably large proportion of the variance is explained by the regression equation. The variance ratio of the regression mean square (MS) to the residual mean square gives a value of 5.8, indicating that the regression equation accounts for a reasonable proportion of the variance in the responses at a probability level of P equals 0.001.

Table 2 shows that the main effect of the buffer is found to be the highest and the interactive effect of it with the BCG is highly significant compared with the other interactions. The results obtained, justifies ignoring the variation of the TCE and the flow rate and not including them in the optimization procedure. As the result of the above treatment, the TCE concentration of 1.11×10^{-2} mol L^{-1} and the flow rate of 3.9 mL/min were fixed for further chemometrical treatments and all experimental analysis. The super modified simplex algorithm[11-14] was performed to obtain exact optimum experimental conditions for the pH and BCG concentration. The simplex experiment was performed at fixed concentration of 1.11×10^{-2} mol L^{-1} crown ether, 3.9 mL/min flow rate and injecting 200 μL mercury. The step values for pH were 3.0 to 5.5 and for BCG green concentrations were 1.5×10^{-4} to 1.5×10^{-3} mol L^{-1}. The simplex was started by feeding the program with the initial simplex chosen on the light of experimental trials on the system. Twelve experiments were found to be enough to judge on the suitable conditions for maximum extraction concentration of mercury.
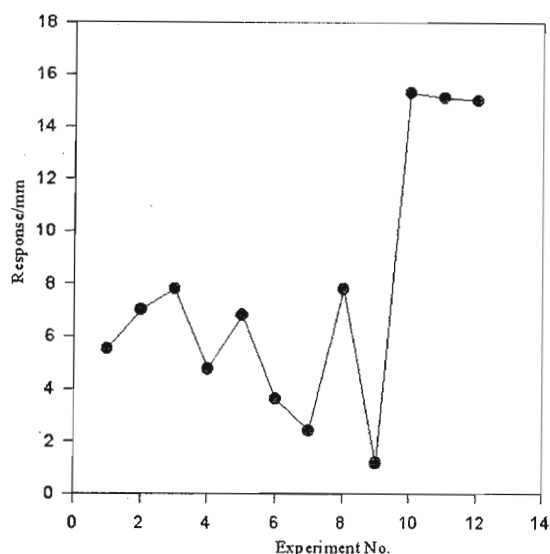
Fig. 3 shows the response versus experiment

Fig.3 Response function progress of the simplex.

number demonstrating the progress of the simplex gradually towards the maximum. Experiment 10 gave the highest response and considered for the optimum experimental conditions for quantitative analysis of mercury. To conclude the optimum operating conditions were, 8.18×10^{-4} mol L^{-1} BCG, 4.70 of pH , 1.11×10^{-2} mol L^{-1} of TCE and 3.9 μL/min of flow rate for 200 μL mercury.

3.1. Analytical Appraisals

Analytical appraisals were carried out under the optimum conditions. Absorbance versus mercury concentration was computed and the following calibration equation was obtained:

$A = -0.00673 + 63.73\ C$

where C is the concentration of mercury in mol L^{-1}.
The above calibration equation was found to be linear over the concentration range 2.49×10^{-4} mol L^{-1} to 3.49×10^{-3} mol L^{-1} with a correlation coefficient of 0.997 and a relative standard deviation of 0.52 % for 3 injections.The method was found to be very sensitive to the determination of mercury with the detection limit of as low as 7.5×10^{-6} mol L^{-1}.

3.2. Interferences

The proposed method was applied to the determination of mercury in synthetic samples containing sulfates of chromium(III), copper(II), manganese(II), iron(II), zinc(II), and cadmium(II), nitrates of nickel(II), lead(II), and silver(I) and chloride of cobalt(II). The interference of alkalies and alkaline earth metal ions were also investigated (Table 3). The results obtained showed no

Table 3 The effect of added metal ions to the result of analysis of 1.2463 mol L^{-1} mercury by the FIA extraction method

Metal ion added	Metal ion/molL^{-1}	% Recovery	σ for 3 runs
Li^{1+}	0.0075	99.2	1.2
Na^{1+}	0.0075	99.7	0.98
K^{1+}	0.0075	100.8	2.1
Mg^{2+}	0.0075	99.2	1.1
Ca^{2+}	0.0075	101.3	2.5
Co^{2+}	0.0075	100.7	1.7
Cr^{3+}	0.0075	98.9	2.0
Fe^{2+}	0.0075	99.2	2.8
Zn^{2+}	0.0075	99.5	1.8
Pb^{2+}	0.0075	98.8	1.0
Mn^{2+}	0.0075	99.6	2.3
Ni^{2+}	0.0012	100.4	2.1
Cu^{2+}	0.0012	102.2	2.7
Cd^{2+}	0.0012	103.1	1.9
Ag^{1+}	0.0012	211.5	2.2

interferences of anions or the cations added except for the silver ions. This is probably due to the fact that silver has high affinity to form a stable complex with the thiacrown ether the cavity of which is expected to accommodate silver and mercury of the ionic diameters of 2.52 and 2.2 Angstrons respectively[2,14-17]. Copper and cadmium seems to cause lesser degree of interference than that caused by silver especially at higher than the mercury concentration. Although the ionic size of these metal ions are 1.44 and 1.94 Angstron respectively[18] that of the silver, yet they cause less interference effect and this could be attributed to the nature of the extracting solvent and its interaction with the metal ion. The present method is faster and more selective than the earlier reported fluorometric[19] and spectrophotometric[20] methods. The results of the above interference study indicates that the present FIA method is suitable for the determination of mercury in the environmental samples such as oil sludge, waste water and sewage

water. For many environmental samples, food and feed samples, the analytical range is seldom attained.

4. Conclusion

On-line solvent extraction of mercury by FIA technique is considered a great advantage over the traditional manual extraction procedure with better sensitivity, lower cost, faster and higher throughput and the method is simple, fast, and safe. Extraction by an expensive reagent such as thiacrown ether is not suitable for traditional extarction flasks[1], and by this FI micro technique it is economical and highly recommendable.
The employment of a thorough comprehensive chemometrical optimization of the affecting extraction parameters made this challenging procedure possible to carry out efficient extraction with the highest recovery.

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