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Flow injection spectrophotometric determination of lead using 1,5-diphenylthiocarbazone in aqueous micellar

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ABSTRACT

A simple flow injection colorimetric procedure for determining lead was established. It is based on the reaction of lead in sulfuric acid with 1,5-diphenylthiocarbazone and sodium dodecyl sulfate, resulting in an intense red–blue complex with a suitable absorption at 500 nm. A standard or sample solution was injected into the sulfuric acid stream (flow rate of 2.0 ml min^{-1}), which was then merged with sodium dodecyl sulfate stream (flow rate of 2.0 ml min^{-1}) and 1,5-diphenylthiocarbazone stream (flow rate of 1.5 ml min^{-1}). Optimum conditions for determining lead were investigated by univariate method. Under the optimum conditions, a linear calibration graph was obtained over the range 1.0–12.0 μg ml^{-1} and the detection limit was 0.027 μg ml^{-1} ($s/n = 3$). The relative standard deviation of the proposed method calculated from 12 replicate injections of 4.0 and 8.0 μg ml^{-1} of lead was 0.42% and 0.38%, respectively. The sample throughput was 80 h^{-1}. The proposed method has been satisfactorily applied to the determination of lead in water samples.

1. Introduction

Lead (Pb) poisoning of a person has been described as the most consequential environmental health problem in the country [1]. Of most concern is lead's adverse effect on the nervous system of the developing fetus and small child; thus exposure of pregnant women prompts concern [2]. Although very low doses cause no obvious adverse health effects on the fetus or small child, low doses are associated with a lowered intelligency quotient [3].

A simple and accurate analytical method is required for the quantitation of lead, which are present in the water samples. Several methods have been reported for the determination of lead, including spectrophotometric [4–8], electrochemical method [9–11], atomic absorption spectrophotometry [12–14], chromatography [15–17] and capillary electrophoresis [18,19]. These previous methods are time consuming, imprecise and require multiple steps of extraction and purification for sample preparation procedures. Therefore, it is necessary to develop a simple method for quantitation of lead.

Lead has been determined by using flow injection analysis through complexation with 2-(5-bromo-2-pyridylazo)-5-dimethylaminophenol [20,21], 4-(2-pyridylazo)resorcinol [22], arsenazo [23], malachite green and iodide [24] and meso-tetra(4-trimethylammonium phenyl) porphyrin [25]. However, flow injection method for the determination of lead in water samples using 1,5-diphenylthiocarbazone with sodium dodecyl sulfate as complexing agent and sensitizer, respectively, is not yet available in the literature. This proposed method does not require a solvent-extraction step; hence, the use of organic solvent is avoided.

This paper studies a rapid, sensitive and cost-effective flow injection method for the determination of lead based on the spectrophotometric detection of the intense red–blue complex formed by the reaction of lead standard in sulfuric acid, 1,5-diphenylthiocarbazone and using sodium dodecyl sulfate as a sensitizer. Measurements were made at 500 nm.

2. Experimental

2.1. Apparatus

The flow injection manifold consisted of a peristaltic pump (Eyela® MP3A, Tokyo Rikakikai Co. Ltd., Japan), and the standard or sample solution was injected via a four-way PTFE rotary valve with a 150 μl sample loop (Upchurch Scientific® model V450, Oak Harbor, WA). PVC tubing (Elkay®, Galway, Ireland) with 0.8 mm i.d. was used as a flow line for sulfuric acid, sodium dodecyl sulfate and 1,5-diphenylthiocarbazone, and Y-shaped connectors were used for merging the reagent streams. Two mixing coils used were

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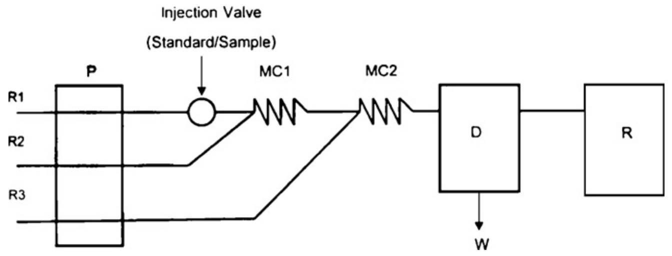

Fig. 1. Proposed FI manifolds: R1, sulfuric acid; R2, sodium dodecyl sulfate; R3, 1,5-diphenylthiocarbazone; P, pump; MC 1, mixing coil No. 1; MC 2, mixing coil No. 2; D, detector; R, recorder; W, waste.

made from PTFE tubing with appropriate length for the recommended configuration. The FI peaks were acquired by using an UV–visible detector (Thermo Separation Product®, TSP UV-2000, USA), equipped with a chart recorder (Kipp & Zonen® BD50, The Netherlands).

2.2. Reagents and solutions

All chemicals were of analytical reagent grade and were used without further purifications. Lead nitrate standard (1000 μg ml^{-1}) was purchased from BDH Spectrosol (England). Solutions of the desired concentrations were obtained by diluting the stock solution to volume with distilled deionized water.

The solution of sodium dodecyl sulfate (1.0 mol l^{-1}) was obtained by dissolving 144 g of sodium dodecyl sulfate (Ajax Finechem, Australia) in distilled deionized water and diluting to 500 ml. Solution (0.1%, w/v) of 1,5-diphenylthiocarbazone (Panreac, Spain) was prepared by dissolving 0.1 g in 75% of ethanol and diluting to 100 ml. Sulfuric acid solution (1.0 mol l^{-1}) was prepared by measuring 56.5 ml of concentrated sulfuric acid and diluting to 1000 ml with distilled deionized water. All laboratory glasswares were cleaned by soaking in a detergent solution and acidified solution, followed by washing with concentrated nitric acid and rinsing several times with distilled deionized water.

2.3. Recommended procedure

Using the three channel manifold as shown in Fig. 1, a 150 μl sample or standard solution containing lead was injected into the reagent stream consisting of 0.75 mol l^{-1} of sulfuric acid and 0.4 mol l^{-1} of sodium dodecyl sulfate at the same optimum flow rate of 2.0 ml min^{-1}, which were then merged with 0.0025% 1,5-diphenylthiocarbazone with an optimum flow rate of 1.5 ml min^{-1}. Subsequently, the sample zone flowed through the mixing coils No. 1 and No. 2 with 100 and 150 cm in reaction coil length, respectively, where the complexation occurred and flowed through the detection unit. The signal was monitored by the spectrophotometric detector at 500 nm and the FI signal was recorded on a chart recorder.

2.4. Sample preparation

The water samples were collected in 1000 ml polyethylene bottles from natural pond within Khon Kaen University, Khon Kaen Province without treatment with concentrated nitric acid, and analyzed immediately after sample digestion. The water samples were filtered through No. 41 Whatman filter paper, then 100 ml of each filtered water sample was accurately transferred into a 250 ml round bottom flask, and 10.00 ml of a nitric acid was added. These samples were digested by heating under reflux for 1.5 h. The cooled samples were neutralized with dilute ammonium hydroxide solution and transferred into each of 25 ml volumetric flask and made up to the mark with distilled deionized water, mixed, subsequently analyzed by the proposed FI method and FAAS.

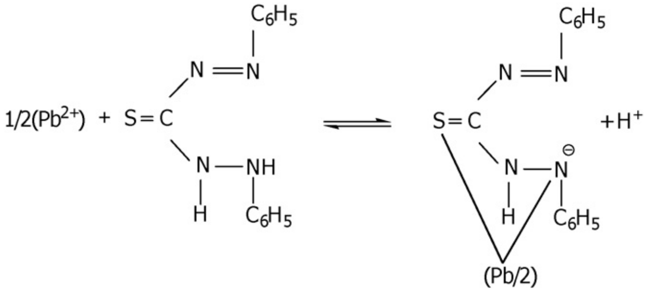

Fig. 2. Proposed mechanism between lead ion and 1,5-diphenylthiocarbazone.

3. Results and discussion

The proposed flow system was undertaken for the development of FI procedure for analysis of lead based on the complexation of lead ions with 1,5-diphenylthiocarbazone in a micellar medium containing sulfuric acid and sodium dodecyl sulfate resulting in intense red–blue complex having an absorption maximum at 500 nm. The present work was developed and optimized by a univariate method. The variable by variable method was applied to select the appropriate conditions for the flow injection spectrophotometric determination of lead.

It is well known that lead ions react with 1,5-diphenylthiocarbazone to form an intense red–blue complex, which is insoluble in water and soluble in organic solvents.

Thus, previously conventional spectrophotometric determination of metal ions, including lead (II) ions based on their dithizonated employed solvent extraction to improve the sensitivity of the method. This sample pretreatment (solvent extraction) could lead to time-consuming, a relative large amounts of toxic and/or expensive organic solvent consumption and also chemical waste produced in order to avoid solvent extraction, then various micellar systems have been developed [8,26–28]. Khan et al. [8] have first reported a spectrophotometric procedure for lead (II) determination based on the complexation of lead (II) with 1,5-diphenylthiocarbazone in a micellar media consisting of cationic surfactant (cetyltrimetylammonium bromide, CTAB) in hydrochloric acid. To date, no previous paper published on lead (II)-dithizonate formed in the presence of anionic surfactant, e.g. sodium dodecyl sulfate (SDS) but trace mercury was successfully determined using 1,5-diphenylthiocarbazone in the anionic surfactant/sulfuric acid media [26]. Therefore, in the present work, attempts were made to investigate whether lead (II) could be complexed with 1,5-diphenylthiocarbazone in anionic surfactant/sulfuric acid medium as well as mercury (II) and use as the basis for the development of a novel FI procedure for trace lead (II) determinations.

3.1. Stoichiometry of lead (II)–1,5-diphenylthiocarbazone complex

The metal ligand ratio was found to be 1:2 using mole ratio and continuous variation method. The formation of the resulted complex was shown in Fig. 2 [27,29,30]. Interestingly, the lead ions and 1,5-diphenylthiocarbazone complex in the presence of aqueous micellar (sodium dodecyl sulfate) increase in sensitivity for the proposed method. The mechanism of this sensitizer was reported previously [26–29].

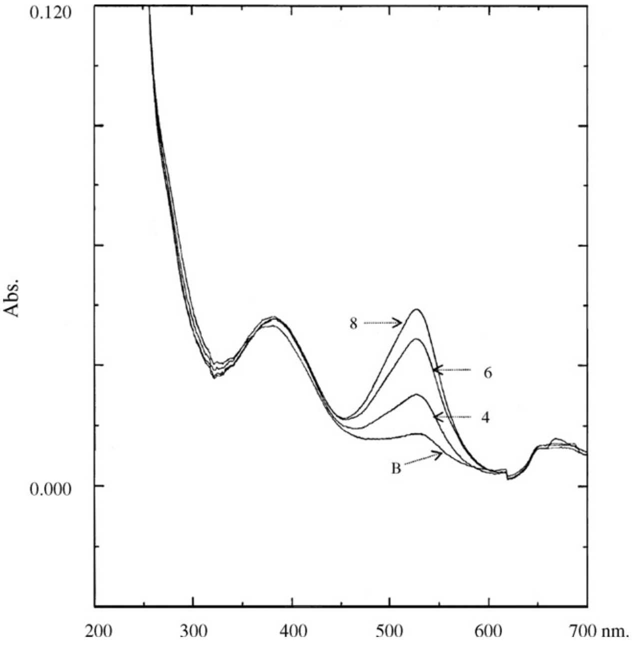

Fig. 3. Absorption spectra of lead–1,5-diphenylthiocarbazone complex in the sulfuric acid solution containing sodium dodecyl sulfate. (B: blank; the numbers on the spectra represent various Pb (II) concentrations (4, 6 and 8 μg ml^{-1}) in standard solutions.)

3.2. *Choice of FI manifold*

Preliminary investigation has been carried out to obtain the most suitable FI manifold for lead (II)–1,5-diphenylthiocarbazone in an anionic surfactant/sulfuric acid medium. Three FI manifolds have been designed namely a three-channel FI manifold, a two-channel designed FI manifold and a single-channel FI manifold. They were tested for determining lead (II) in standard solutions. It was preferable to use the three-channel FI manifold for lead (II) determination since it provided a greatest sensitivity, reproducibility and relative high sample throughput.

3.3. *Effect of absorption spectra*

The absorption spectra of the complexation of lead, sulfuric acid, sodium dodecyl sulfate and 1,5-diphenylthiocarbazone were recorded using a spectrophotometer. The absorption spectra were studied from 200 to 700 nm. In order to achieve the greatest sensitivity, measurements were made at 500 nm in further studies (Fig. 3).

3.4. *Effect of sulfuric acid, sodium dodecyl sulfate and 1,5-diphenylthiocarbazone concentration*

The effect of varying concentration of sulfuric acid solutions between 0.125 and 1.50 mol l^{-1} was examined. The highest peak height was recorded when the concentration of sulfuric acid solution was 0.75 mol l^{-1} and was therefore chosen as optimum concentration. Further increasing the sulfuric acid concentration the peak height decreased gradually up to 1.50 mol l^{-1} (Fig. 4).

The concentration of sodium dodecyl sulfate solution was optimized. Various concentrations over the range 0.05–0.80 mol l^{-1} were investigated. It was found that the peak height increased with increasing sodium dodecyl sulfate concentration and reached a maximum peak height at 0.4 mol l^{-1}, above which the peak height decreased. Thus 0.4 mol l^{-1} of sodium dodecyl sulfate was used subsequently (Fig. 4).

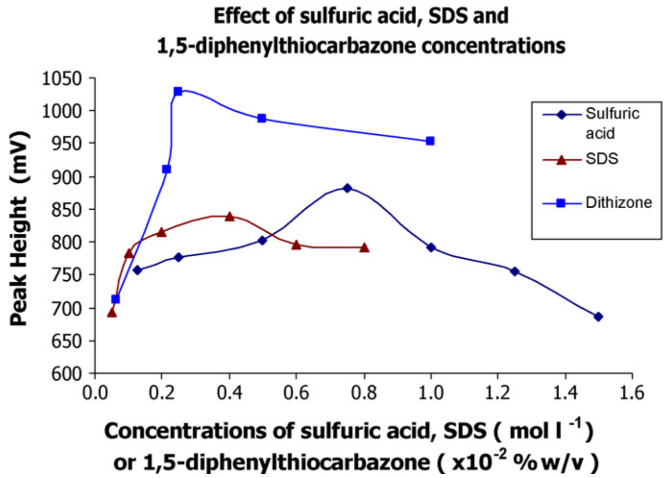

Fig. 4. Effect of sulfuric acid, sodium dodecyl sulfate (SDS) and 1,5-diphenylthiocarbazone (dithizone) concentrations on the mean of peak height ($n = 5$) of 6 μg ml^{-1} lead standard solution.

The effect of various concentrations of 1,5-diphenylthiocarbazone solutions (0.000625–0.01%, w/v) on the absorption of the lead–1,5-diphenylthiocarbazone complex (as peak height) was examined. The 1,5-diphenylthiocarbazone concentration which exhibited the greatest peak height was found to be 0.0025% (w/v) and was therefore chosen as optimum concentration. Further increasing the 1,5-diphenylthiocarbazone concentration the peak height decreased gradually up to 0.01% (w/v) (Fig. 4).

3.5. *Effect of mixing coil length and injection loop volume*

These studies were carried out at various mixing coil lengths between 50 and 250 cm for mixing coil No. 1 (H_2SO_4, sodium dodecyl sulfate) and mixing coil No. 2 (H_2SO_4, sodium dodecyl sulfate, 1,5-diphenylthiocarbazone), injection loop volumes between 50 and 250 μl on the complexation produced were investigated. It was found that the peak height increased with the mixing coil No. 1 and No. 2 lengths up to 100 and 150 cm, respectively. Both mixing coil lengths of 50, 100, 150, 200 and 250 cm provided the peak height of 698, 770, 668, 668, 658 mV and 608, 706, 760, 562, 554 mV, respectively. The optimum mixing coil lengths of No. 1 and No. 2 for subsequence studied were 100 and 150 cm, respectively.

The influence of the sample/standard volume on the absorbance was recorded by injecting volumes in the range 50–250 μl of lead standard solution (6 μg ml^{-1}). It was shown that the peak height increased from 696 to 1320 mV on increasing the injection volume from 50 to 250 μl. It was found that the peak height increased with the injection volumes up to 150 μl, and the injection volume of 50, 100, 150, 200 and 250 μl produced the peak height of 696, 730, 1042, 1218 and 1320 mV, respectively. The appropriate peak height was reached at 150 μl. The most suitable injection loop volume value for further use was 150 μl.

3.6. *Effect of sulfuric acid, sodium dodecyl sulfate and 1,5-diphenylthiocarbazone flow rate*

The effects of sulfuric acid, sodium dodecyl sulfate and 1,5-diphenylcarbazone solutions flow rates were investigated on the determination of lead standard (6 μg ml^{-1}). The peak heights were monitored from the flow rate of 1.0–3.0 ml min^{-1} for all solution streams. The peak height increased with increasing flow rate of each stream up to 2.0 ml min^{-1} for sulfuric acid, 2.0 ml min^{-1} for sodium dodecyl sulfate which were then merged with the flowing stream of 1,5-diphenylthiocarbazone solution with the flow rate of

Table 1
Variable range studies and optimum conditions for the determination of lead.

Parameter studied	Range studied	Optimum level
Wavelength (nm)	200–700	500
Sulfuric acid concentration (mol l^{-1})	0.125, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5	0.75
Sodium dodecyl sulfate concentration (mol l^{-1})	0.05, 0.1, 0.2, 0.4, 0.6, 0.8	0.4
1,5-Diphenylthiocarbazone concentration (% w/v)	0.000625, 0.00125, 0.0025, 0.005, 0.01	0.0025
Sulfuric acid flow rate (ml min^{-1})	1.0, 1.5, 2.0, 2.5, 3.0	2.0
Sodium dodecyl sulfate flow rate (ml min^{-1})	1.0, 1.5, 2.0, 2.5, 3.0	2.0
1,5-Diphenylthiocarbazone flow rate (ml min^{-1})	1.0, 1.5, 2.0, 2.5, 3.0	1.5
Mixing coil [I] (cm) [Pb(II) + H_2SO_4 + sodium dodecyl sulfate]	50, 100, 150, 200, 250	100
Mixing coil [II] (cm) [Pb(II) + H_2SO_4 + sodium dodecyl sulfate + 1,5-diphenylthiocarbazone]	50, 100, 150, 200, 250	150
Injection volume (μl)	50, 100, 150, 200, 250	150

1.5 ml min^{-1} above which the peak height slightly decreased. Thus 2.0 ml min^{-1} of sulfuric acid, 2.0 ml min^{-1} of sodium dodecyl sulfate and 1.5 ml min^{-1} of 1,5-diphenylthiocarbazone solution were regarded as the optimum flow rates.

3.7. Analytical characteristics

Analytical characteristics for the determination of lead were studied under the optimum conditions (Table 1).

3.7.1. Calibration curve

Using the proposed FI manifold for the determination of lead under the optimum conditions, the linear calibration graph over the range of 1.0–12.0 μg ml^{-1} of lead standard solution was established, which could be expressed by the regression equation $y = 127.96x - 69.935$ ($r^2 = 0.9981$) where y represents the peak height in mV and x is lead concentration in μg ml^{-1} after subtraction of blank. Thus, the amounts of lead in sample can be quantified according to the above regression lines of equation. The detection limit was defined as the concentration of analyte that gives the signal that is different from the blank by an amount equal to three times the standard deviation of the blank signal ($s/n = 3$). It was found to be 0.027 μg ml^{-1} (0.027 mg l^{-1}). The quantitation limit (defined as ten times standard deviation) was studied and found to be 0.092 μg ml^{-1} (0.092 mg l^{-1}). It is shown that the present method was very suitable for determining relatively large amounts of lead (II) in waste waters or effluent from industries but it is not suitable for determining trace lead (II) in natural waters that usually does not exceed 0.1 mg l^{-1}. In this case, an on-line preconcentration and separation of trace lead (II) using a mini-column in cooperating with the FIA system is required. This is the author's on-going research which will be published in the next research article.

Table 2
Effect of some interferences on the peak height of 4.0 μg ml^{-1} lead standard solution.

Interference ions[a] (μg ml^{-1})	Percentage of relative height (%); $n = 5$
None of interference (lead standard only)	100.00
Mg^{2+}	89.04
Mn^{2+}	80.82
Ca^{2+}	87.67
As^{3+}	93.15
Hg^{2+}	84.93
Zn^{2+}	90.41
Sn^{2+}	86.30
Al^{3+}	98.04
Cu^{2+}	80.80

[a] Mole ratio of an interference ion:lead standard (10:1).

3.7.2. Reproducibility and accuracy

The relative standard deviation of the proposed method (peak height in mV) calculated from 12 replicate injections of 4.0 and 8.0 μg ml^{-1} of lead was 0.42% and 0.38%, respectively. The recoveries were determined with the standard addition method, in which lead (1.0, 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 μg ml^{-1}) was added and mixed with water samples, the water samples were analyzed using the proposed method. The percentage recoveries of 1.0, 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 μg ml^{-1} ($n = 5$) of lead were found to be 106.00%, 104.50%, 97.25%, 103.00%, 102.75%, 102.80% and 99.08%, respectively, showing that the proposed method could provide acceptable

Table 3
Accuracy of proposed FI method compared with FAAS method for the determination of lead.

Sample[a]	Concentration of lead added (μg ml^{-1})	Concentration of lead found (μg ml^{-1})		
		FI[b]	FAAS[c]	*t*-Test
A	3.50	3.48	3.66	−0.18
B	5.50	5.57	5.41	0.16
C	2.00	2.32	2.30	0.02
D	6.50	6.55	6.66	−0.11
E	1.00	1.32	1.26	0.06
F	6.50	6.62	6.75	−0.13
G	2.00	2.15	2.22	−0.07
H	3.50	3.82	3.67	0.15
I	2.00	2.01	1.98	0.03
J	1.00	1.15	1.32	−0.17
K	4.50	4.41	4.59	−0.18
L	3.00	3.38	3.09	0.29
				$D = -0.0108$
				$S.D. = 0.1547$
				$t = 0.24$
				t-Distribution (95%) = 2.20

[a] Average from five determinations.
[b] Flow injection method.
[c] Flame atomic absorption spectrophotometry.

method efficiency and recoveries of the added lead by this analysis method were satisfactory.

3.7.3. *Interferences*

Effects of some possible interfering ions on the determination of lead were investigated for the maximum (w/w) ratio of interfering ions, which lead up to 10:1. Synthetic sample solutions containing 4.0 μg ml^{-1} of lead and different concentrations of some metal ions were tested, and peak heights obtained were measured. Most cations were interfered, interestingly the foreign-ion that caused an error has been shown in Table 2 with the percentage of relative height for determining the analyte of interest. It was found that the percentage of relative height of some possible interfering ions were in the range of 80.80–98.04%. However, the most serious interferences were from copper (II) and manganese (II).

3.7.4. *Analysis of water samples*

The recommended method has been applied to the determination of lead (II) in water samples. The results obtained were compared favorably with those obtained by FAAS. The accuracy was verified by the Student's *t*-test [31] with calculated Student's *t*-test value (0.24) less than the theoretical value (2.20, n = 12) at a confidence level of 95% (*P* value of 0.05). The comparison between the proposed FI and FAAS method was accepted with reasonable agreement (Table 3).

4. Conclusion

The proposed FI spectrophotometric method has proved to be simple and sensitive for lead determination. The linearity of the calibration graph is in the useful concentration range for quantitation of lead in water samples. The detection limit of this proposed method was more reasonable than those previously reported for spectrophotometric [7], electrochemical method [9], chromatography [15,16] and flow injection [21,23]. The method developed is simple, economic, rapid, providing a good sample frequency of 80 h^{-1}, and is especially suitable for routine analysis.

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