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Preconcentration and solid-phase extraction of beryllium, lead, nickel, and bismuth from various water samples using 2-propylpiperidine-1-carbodithioate with flame atomic absorption spectrometry (FAAS)

K. Suvardhan [c], K. Suresh Kumar [c], D. Rekha [c], B. [illegible]yaraj [a], G. Krishnamurthy Naidu [b], P. Chiranjeevi [c]

[a] *Department of Mathematics, S.V. University, Tirupati 5175[illegible], AP, India*
[b] *Department of Pharmacy, S.V. Govt. Polytechnic, Tirupati [illegible]01, AP, India*
[c] *Environmental Monitoring Laboratory, Department of Chemistry, S.V. University, Tirupati 517502, AP, India*

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Abstract

A facile and novel method has been developed for the determination of beryllium, lead, nickel, and bismuth in various water samples. In the present investigation, the use of syringe was loaded with sorbent for the separation and enrichment of beryllium, lead, nickel, and bismuth prior to their analysis by flame atomic absorption spectrometry was described to substitute the batch and column techniques. The proposed method was compared with column technique with respect to easiness, fastness, simplicity, recovery and risk of contamination. The syringe was loaded with 1.0 g of sorbent in order to retain the analyte elements. Seven millilitres of sample solution (pH 5.0 ± 0.2) was drawn into the syringe in 15 s and discharged over 15 s. Then, [illegible] M HCl eluent, was drawn into the syringe and ejected back to desorb the analyte elements. At the optimum conditions, the percentage recoveries of [illegible] and Bi in the range of 94.28–99.02% with standard deviations (S.D.) of 0.11%. The elements could be concentrated by drawing and discharging several portions of sample successively but eluting only one time. The detailed study of various interferences made the confirmation of the method highly selective. The risk of contamination is less than that with the column technique. The method was successfully applied for the determination of Be, Pb, Ni, and Bi in spiked and natural water samples. The results obtained are in good agreement with the reported methods at the 95% confidence level.

Keywords: Solid-phase extraction; Sorbent; Syringe (20 ml); 2-Propylpiperidine-1-carbodithioate; Flame atomic absorption spectrometry (FAAS) and water samples

1. Introduction

Trace metal analysis is an important part of studies in analytical chemistry. The direct determination of metal traces in various samples usually requires an efficient preconcentration step in order to bring the concentration of the analyte within the dynamic measuring range of the detection and additionally to eliminate matrix effect, intereferences, which cannot be manipulated by the measuring device. In addition, interferences due to complex matrices of many samples cannot always be controlled even with stabilized temperature platform furnace (STPF) concept [1] together with a suitable modifier and separation procedure may be required. As a result, FAAS combined with preconcentration/separation techniques have been widely used for the determination of trace elements. Among the preconcentration/separation techniques, sorption of trace elements on an ion-exchanger or chelating collector has been of greatest interest and various collectors have been

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[*] Corresponding author. Tel.: +91 877 2250556; fax: +91 877 2261274.
E-mail address: chiranjeevi_sai@yahoo.co.in (P. Chiranjeevi).

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proposed for this purpose. These include polymeric resins [1–5], silica [6,7] and activated carbon [8], dithiocarbamates [9–13], and xanthates [14,15] for the determination of trace metal ions in different environmental matrices.

Techniques, such as co-precipitation, ion-exchange [16,17] and more recently cloud point extraction [18] have been successfully employed for a variety of metallic species. These techniques involve several problems like lack of automation, which increases the experimental efforts, and the total time of analysis. Cloud point extraction, although generally simple to apply, it was still prone to the analyst's efficiency [18]. Conventional separation and preconcentration techniques, such as co-precipitation, distillation, liquid–liquid extraction, absorbative columns, and chemical and bio-sorption have been employed for the single or multi elemental extraction of almost every metal from their initial matrices [19–22]. The above reported methods (co-precipitation, distillation, liquid–liquid extraction, absorbative columns, chemical and bio-sorption) suffer from several drawbacks such as low detection limits, employing highly commercial procedures, risk of contamination, and time consuming techniques. For many years, solvent extraction has been a most widely applied method and numerous publications have been presented for the determination and speciation of various elements and in a wide variety of samples-matrices [23–25].

In the present study, a novel method was presented for the extraction and preconcentration of Be, Pb, Ni, and Bi from various water samples. The method is based on the direct complexation of Be, Pb, Ni, and Bi with newly synthesised 2-propylpiperidine-1-carbodithioate. Optimum experimental conditions were investigated with a spiked standard solution of the same matrix, in order to examine the possibility of obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. Under these conditions, preconcentration factor of 100 was achieved. This is an alternative method to the column and batch techniques.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer ® Model 2380 atomic absorption spectrometry (FAAS) with air-acetylene flame and hallow cathode lamps were used for the analysis of beryllium, lead, nickel, and bismuth. All instrumental settings were those recommended in the manufacturer's manual book. A pH meter, Elico Li-129 Model glass-electrode was employed for measuring pH values.

2.2. Reagents and solutions

Doubly distilled water and high purity reagents were used for all preparations of the standard and samples solutions. All the chemicals were purchased from Merck Chemicals, Mumbai, India. Standard stock solutions (1000 mg l^{-1}) of beryllium carbonate, bismuth nitrate (dissolved in 2 ml of 0.5 M HNO_3), lead nitrate and nickel sulphate were prepared individually by dissolving the proper amounts of analyte in doubly distilled water in a 100 ml flask. Dilute solutions were prepared by the appropriate dilution of the stock solution daily in doubly distilled water for reference solutions. The pH adjustment was made by adding 2.0 ml of phosphate buffer solution.

A buffer solution of pH 5.0 ± 0.2 was prepared by adding concentrated sulfuric acid (7.0 ml) to 250 ml distilled water in a 500 ml flask. Then, sodium dihydrogen phosphate monohydrate (20 g) was added and the flask shaken until dissolution was completed. The solution was then diluted to 500 ml. It was stored in a clean metal free polyethylene bottle.

2.2.1. Synthesis of sodium 2-propylpiperidine-1-carbodithioate reagent

Carbondisulphide (1.05 mol) was slowly added to a solution of 2-propylpiperidine (1.43 mol) in 25 ml of water at 5 °C with constant stirring, followed by 1.0 mol of sodium hydroxide dissolved in 20 ml of water to form sodium 2-propylpiperidine-1-carbodithioate as shown in Fig. 1(a). The product was warmed to room temperature and washed 2–3 times with purified acetone. The reaction product was recrystallized from warm acetone. The purified compound had a melting point of 303–308 °C at 740 mm pressure. Crystallization of water is less in 2-propylpiperidine-1-carbodithioate when compared with other carbodithioate, therefore, the extractability of the complex become easier. The metal salt of this reagent is a resonance hybrid of the structures, which contributed to the stability of metal complexes as shown in Fig. 1(b).

2.3. General procedure

A cleaned porous disk filter was placed on the bottom of a 20 ml syringe. The syringe was filled with 1.0 g of (1 cm of height) 2-propylpiperidine-1-carbothioate (Fig. 2). The pH of the sample was adjusted to the desired value with phosphate buffer (5.0 ± 0.2) solution. Seven millilitres of sample solution was drawn into the syringe in about 15 s and discharged again in 15 s. To find the retention yields, Be, Pb, Ni, and Bi in the discharge were analysed by FAAS. Before elution, one or two times of doubly distilled water was drawn and ejected to wash the collector. Then, 3.0 M HCl as the eluent was drawn into the syringe and ejected back to desorb the analyte elements. The analyte elements in the discharge were determined by FAAS and recoveries were calculated. For a better contact between sample solution and sorbent, all the solution should be drawn above the top of sorbent.

In order to concentrate the analyte elements, different sample portions (7.0 ml) were passed through the sorbent successively but eluted with only 7.0 ml of 3.0 M HCl in

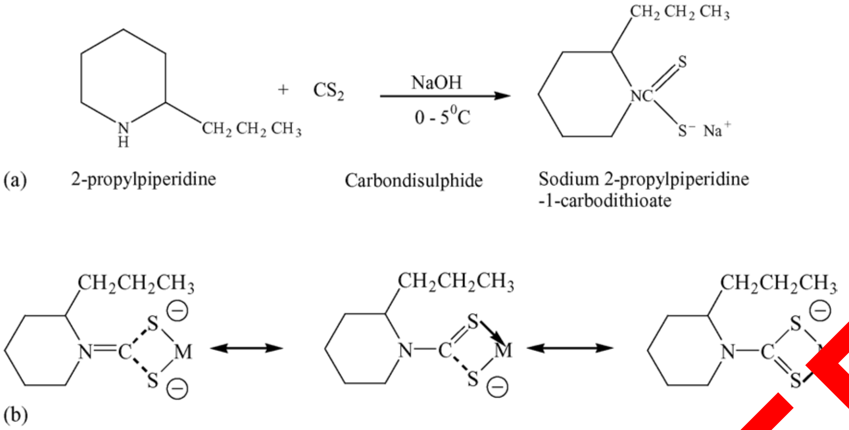

Fig. 1. (a) Synthesis of sodium 2-propylpiperidine-1-carbodithiodate reagent. (b) Resonance hybrid of the 2-propyl piperidine-1-carbodithioate with metal.

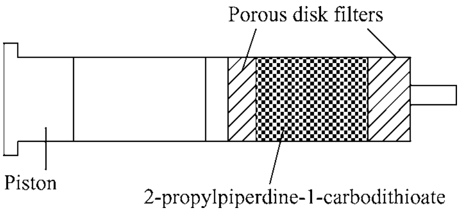

Fig. 2. Diagram of the syringe (20 ml).

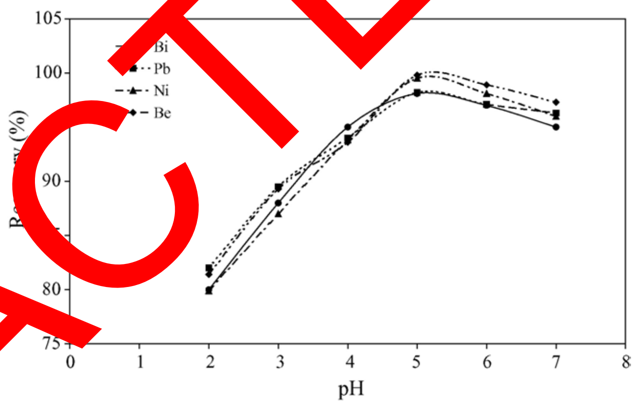

Fig. 3. Effect of pH on the complexation of trace metals with 2-propylpiperidine-1-carbodithioate.

one time. The spiked, natural water samples, standards, and blanks were treated in the same manner. The washing steps before elution process is especially important to remove the matrix present in natural water samples. Otherwise, the analysis was not interference free and recoveries were low.

2.3.1. Determination of trace metals in water samples

The extraction efficiency was studied using spiked water samples for the recovery of trace metals (Be, Pb, Ni, and Bi). Doubly distilled water was spiked with known amounts of multielemental standards (7.0, 21.0, and 42.0 μg l^{-1}) and allowed to stand overnight. The concentrations of metals in spiked water samples were determined as described in the aforesaid general procedure.

Natural water samples were collected in and around the Tirupati area. Water sample (200 ml) filtered through a 0.45 μm cellulose membrane filter was taken and pH was adjusted to 5.0 ± 0.2 with 2.0 ml of phosphate buffer. The concentrations of metals in natural waters were analysed as described in the above general procedure.

3. Results and discussion

3.1. Effect of pH

pH is an important parameter, because it significantly affects the metal—2-propylpiperidine-1-carbodithioate complex formation. The effect of pH on the complexation of metal ions with 2-propylpiperidine-1-carbodithioate was studied by adding 20 μg of each of the elements individually in 60 ml doubly distilled water and determined by complexing with 2-propylpiperidine-1-carbodithioate in the pH range of 2.0–7.0 as shown in Fig. 3. The elemental data are in Table 1. The results show that the maximum recovery was obtained at pH 5.0 ± 0.2 for all the elements. So pH 5.0 ± 0.2 was selected for further investigations.

Table 1
Effect of pH on the complexation of metal ions with 2-propylpiperidine-1-carbodithioate

pH	Recovery (%)[a]			
	Be	Pb	Ni	Bi
2.0	80.86 ± 0.31	82.31 ± 0.29	79.98 ± 0.43	81.49 ± 0.30
3.0	88.42 ± 0.43	89.54 ± 0.33	87.01 ± 0.44	89.32 ± 0.29
4.0	95.28 ± 0.61	94.33 ± 0.22	93.80 ± 0.69	93.66 ± 0.36
5.0	98.14 ± 0.11	98.26 ± 0.26	99.55 ± 0.67	99.84 ± 0.83
6.0	97.0 ± 0.51	97.05 ± 0.43	98.11 ± 0.30	98.90 ± 0.69
7.0	95.28 ± 0.26	96.38 ± 0.34	97.0 ± 0.3	97.39 ± 0.30

[a] Mean ± standard deviation ($n = 4$).

Table 2
Effect of sample volume on elution of metal ions

Volume of water (ml)	Recovery (%)[a]			
	Be	Pb	Ni	Bi
20	92.01 ± 0.25	93.18 ± 0.72	90.22 ± 0.09	93.64 ± 0.99
40	96.30 ± 0.33	97.42 ± 0.34	96.73 ± 0.44	97.90 ± 0.72
60	99.26 ± 0.18	99.38 ± 0.92	99.10 ± 0.93	99.19 ± 0.20
80	98.82 ± 0.31	98.89 ± 0.31	97.88 ± 0.11	98.46 ± 0.22
100	98.21 ± 1.03	98.17 ± 0.47	96.99 ± 0.28	98.12 ± 0.15

[a] Mean ± standard deviation ($n = 4$).

3.2. *Effect of sample volume*

The effect of sample volume on the elution of Be, Pb, Ni, and Bi was studied by taking different volumes of water samples, 20, 40, 60, 80, and 100 ml. The extraction was carried out as described in the general procedure. The results are reported in Table 2. In all cases, the recovery obtained was higher than 98.0% for all these elements. However, the efficiency of recovery slightly decreased when the sample volume was more than 60 ml. Hence, 60 ml of water sample was chosen for the present study.

3.3. *Effect of HCl concentration on the back extraction*

The sample was drawn into the syringe passing through the sorbent and discharge passing through the sorbent again one more time. The pull and push process was employed to obtain equilibrium in 30 s as one cycle. During this procedure, the analyte elements were sorbed (retained) by the sorbent.

The effect of HCl concentration on the back extraction of trace metals was studied and the results are presented in Table 3. Results depict that the extraction was dependent on the concentration and performed in the range of 1.0–5.0 M HCl with 7.0 ml capacity. Highest recoveries were obtained for 3.0 M HCl solution. Therefore, 7.0 ml of 3.0 M HCl was selected for further studies.

3.4. *Effect of volume of HCl on percentage of elution of metal ions*

Data for the effect of volume of HCl on elution of metal ions from various water samples studied at 30–35 °C are shown in Table 4. It was observed that the elution of metal ions gradually increased with the increase in the volume of an eluent to certain extent. Further increasing the volume of an eluent, the elution percentage slightly decreased. Thus, 7.0 ml of HCl was chosen for maximum recovery of metal ions.

Table 3
Effect of HCl concentration on extraction of metals

HCl concentration (M)	Recovery (%)[a]			
	Be	Pb	Ni	Bi
1.0	89.63 ± 0.19	90.24 ± 0.08	91.46 ± 0.08	91.62 ± 0.41
2.0	96.23 ± 0.16	95.47 ± 0.42	95.23 ± 0.18	96.34 ± 0.08
3.0	[illegible].58 ± 0.49	98.72 ± 0.45	99.41 ± 0.35	98.91 ± 0.29
4.0	98.13 ± 0.28	97.18 ± 0.28	98.05 ± 0.35	97.65 ± 0.55
5.0	96.19 ± 0.51	96.24 ± 1.02	97.89 ± 0.24	96.40 ± 0.80

[a] Mean ± standard deviation ($n = 4$).

Table 4
Effect of volume of HCl on elution of metals

Volume of eluent (ml)	Recovery (%)[a]			
	Be	Pb	Ni	Bi
2.0	86.26 ± 0.13	84.30 ± 0.74	87.25 ± 0.84	89.25 ± 0.23
3.0	93.27 ± 0.87	93.45 ± 0.36	91.44 ± 0.79	92.38 ± 0.18
4.0	94.12 ± 0.09	95.90 ± 0.82	94.20 ± 0.41	95.40 ± 0.55
5.0	97.24 ± 0.51	97.89 ± 0.33	96.36 ± 0.42	97.55 ± 0.49
6.0	98.62 ± 0.83	98.11 ± 0.13	98.50 ± 0.69	97.89 ± 0.32
7.0	99.19 ± 0.22	99.28 ± 0.23	99.05 ± 0.77	98.90 ± 0.74
8.0	98.25 ± 0.13	98.0 ± 0.83	97.86 ± 0.29	97.67 ± 0.68

[a] Mean ± standard deviation ($n = 4$).

Table 5
Influence of excipients on the determination of trace metals

Excipient ions	Tolerance limit[a] (µg ml^{-1})
Na^+	45
K^+, Mg^{2+}	40
Cl^-, $SO_4{}^{2-}$	28
CH_3COO^-	25
$Cr_2O_7{}^{2-}$	4
Ca^{2+}	35
$PO_4{}^{3-}$, $NO_3{}^-$	25
$Co_2{}^+$	2.0
Bi^{3+}, Mn^{2+}	2.0
Fe^{3+}	1.5

[a] Tolerance limit, which caused upto ±2% error.

3.5. Detection limits

The detection limit of each of the elements was expressed as the amount of analyte in µg l^{-1} giving a signal to noise ratio of 3. The limits of method for the elements Be, Pb, Ni, and Bi were 0.30, 0.25, 0.20, and 0.34 µg l^{-1}, respectively.

3.6. Influence of excipient ions

The influence of excipient ions on the determination of Be, Pb, Ni, and Bi was studied by multielemental solution (100 µg × 100 ml^{-1}) containing different amounts of metal solutions (both cations and anions). The results are presented in Table 5. It revealed that the ions commonly present in water, such as calcium, magnesium, sodium, potassium, chlorides, nitrites, sulphates, bicarbonates, and phosphates, do not interfere in the determination of trace metals [illegible] to 30 µg ml^{-1}. This indicates the validity of the method for the preconcentration and solid-phase extraction of trace metal ions [illegible] various water samples.

3.7. Application of the proposed method and statistical comparison with reported methods

The data obtained with the proposed method for the preconcentration [illegible] solid-phase extraction employed for spiked and natural water samples were presented in Tables 6 and 7.

Table 6
Recovery of trace metals from spiked water samples

Elements	Proposed method (concentration added)									Reported method [12]		
	7 µg l^{-1}			21 µg l^{-1}			42 µg l^{-1}			Recovery (%)[a]		
	Recovery (%)[a]	*t*-test	*f*-test	Recovery (%)[a]	*t*-test	*f*-test	Recovery (%)[a]	*t*-test	*f*-test			
Be	94.28 ± 0.20	2.95*	0.12*	97.14 ± 0.11	12.3*	0.038*	[illegible]	3.49*	1.30*	93.50 ± 0.59	96.0 ± 0.65	98.41 ± 0.24
Pb	94.57 ± 0.52	3.86*	1.08*	98.14 ± 0.48	14.26*	[illegible]	[illegible]	4.71*	2.98*	93.21 ± 0.50	97.10 ± 0.48	98.05 ± 0.22
Ni	94.0 ± 0.74	2.49*	0.396*	96.42 ± 1.1	5.10*	[illegible]	[illegible]	4.58*	1.31*	92.93 ± 0.76	95.18 ± 0.48	97.05 ± 0.57
Bi	95.0 ± 0.80	2.42**	3.87**	96.14 ± 0.40	[illegible]	0.99	98.55 ± 0.20	5.10*	0.30*	93.98 ± 0.40	95.52 ± 0.33	98.25 ± 0.37

[a] Mean ± standard deviation ($n = 4$).
[*] 1% level of significance.
[**] 5% level of significance.

Table 7
Trace metal content in natural water samples collected from two different sources in and around the Tirupati area

Element	Present method		Standard Method [26]	
	Natural water sample I (µg l^{-1})	Natural water sample II (µg l^{-1})	Natural water sample I (µg l^{-1})	Natural water sample II (µg l^{-1})
Be	6	6	5	5
Pb	[illegible]	27	31	26
Ni	23	24	25	23
Bi	32	27	34	25

Table 8
Comparison of reported methods with present method for determination of trace metals

Complexing agent	Detection limits (µg l^{-1})	Remarks	References
Phenylpiperazine dithiocarbamate	17	Low detection limit, commercial reagent, less sensitive	[10]
Ammonium pyrroline dithicarbamate	0.82	Low detection limit, high reagent consumption	[11]
Piperidine dithiocarbamate	25	It is a column technique and needs elaborate procedure, time consuming, risk of contamination.	[12]
Ammonium hexamethylene dithiocarbamate	15	Low sensitive and selective	[13]
Potassium propyl xanthate	10	Low detection limits, $PO_4{}^{3-}$, Mn^{2+} and Fe^{3+} interfer's seriously	[14]
Potassium ethyl xanthate	12	Less sensitive and suffers from interference effect	[15]
2-Propylpiperidine-1-carbodithioate	0.25	Sensitive, selective, facile, economical reagent, free form interference and contamination	This work

The obtained results were compared with the reported method [12] in terms of Student's *t*-test and Variance ratio *f*-test. The analytical data summarised in Tables 6 and 7 suggest that the percentage recovery of Be, Pb, Ni, and Bi from various water samples ranges from 94.28 to 99.02% which is more reliable and sensitive than the reported method [12].

It is evident from the data in Table 8 that the proposed method is rapid and more sensitive.

4. Conclusion

Syringe filled with sorbent was used for the separation and enrichment of traces of beryllium, lead, nickel, and bismuth in various water samples prior to their analysis by FAAS. The method has added advantages over reported methods [12] owing to its:

(i) Syringe method is more handy, more practical, faster, and easier than the column technique.
(ii) The risk of contamination is quite low.
(iii) The synthesis of metal chelating agent at ordinary laboratories was simple and more economical.
(iv) Synthesised organic reagent is distinct in terms of sensitivity, selectivity towards metal ions.
(v) 2-Propylpiperidine-1-carbodithioate possesses a high electric dipole moment. The propyl substituent at C_2 carbon of piperidine ring being influences the +I effect, leads to the free-electron-releasing tendency of the N-group into sulphur atoms. Therefore, the electron donating capacity of 2-propylpiperidine-1-carbodithioate increases, permitting the formation of strong complexes with metal ions.
(vi) Foreign ions do not interfere in proposed method, making the method more selective.

Finally, it can be concluded that the syringe method is superior to the column technique in many respects for the separation and enrichment of beryllium, lead, nickel, and bismuth in environmental samples.

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