

A novel slurry sampling analysis of lead in different water samples by electrothermal atomic absorption spectrometry after coprecipitated with cobalt/pyrrolidine dithiocarbamate complex

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Abstract

A preconcentration/separation technique based on the coprecipitation of lead with cobalt/pyrrolidine dithiocarbamate complex (Co(PDC)_2) and subsequently its direct slurry sampling determination by electrothermal atomic absorption spectrometry (AAS) was described. For this purpose, at first, lead was coprecipitated with cobalt/pyrrolidine dithiocarbamate complex formed using ammonium pyrrolidine dithiocarbamate (APDC) as a chelating agent and cobalt as a carrier element. The supernatant was then separated and the slurry of the precipitate prepared in Triton X-100 was directly analyzed by electrothermal atomic absorption spectrometry with respect to lead concentration. The effects of experimental conditions on coprecipitation of lead with gathering precipitate as well as homogeneity and stability of the slurry were investigated. After the optimization of experimental parameters, a 100-fold enrichment of the analyte with quantitative recovery (>90%) and high precision (<10% R.S.D.) were obtained. By using the proposed technique, the lead concentrations in heavy matrices of Certified Sea-water and wastewater samples could be practically and rapidly determined in the range of 95% confidence level. The detection limit of the described method for lead using sample-matching blanks was 1.5 ng/L (3σ , $N=10$).

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1. Introduction

In the determination of trace elements by atomic absorption spectrometry (AAS) as well as by other methods, if the concentration of the analyte is too low to be determined directly and/or interferences due to matrix cannot be eliminated, the use of a separation/enrichment procedure prior to the measurement step is compulsory. For this purpose, one of the most commonly applied methods is the collection of the analyte on a suitable material by ion-exchange or chelation and subsequently its elution by means of a convenient reagent. Another common technique is the coprecipitation of the analyte with a gathering precipitate and subsequently its transferring (completely or partially) into solution phase using a suitable eluent or dissolving the precipitate completely by means of a solvent for

quantification. The literature is full of papers on preconcentration/separation of trace elements by coprecipitation technique using different carriers. In order to coprecipitate various analytes different gathering precipitates such as naphthalene [1], manganese dioxide obtained by the reduction of KMnO_4 [2], cerium(IV) hydroxide [3], lanthanum hydroxide [4], yttrium phosphate [5], 2,3-dihydroxypyridine [6] yttrium hydroxide [7], nickel diethyldithiocarbamate [8], and cobalt diethyldithiocarbamate [9] were used but in all of these studies as well as many others, an elution (leaching)/dissolution step was necessarily applied in order to transfer the analyte into solution phase for its measurement. However, elution step or dissolving the main precipitate may have some drawbacks and risks due to incomplete and/or irreproducible extracting yield causing poor recoveries and precisions, irreproducible blank values from eluents, pollution of laboratory atmosphere and environment especially due to acidic eluents. In addition, acids used as the eluents reduce the lifetime of the graphite furnace. Therefore, it is desired the elution procedure to be fast, quantitative, reproducible enough and

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the eluents to be available, inexpensive and non-hazardous for instrument and health. In this case, if possible, the best solution is the elimination of elution step.

If the elution step or dissolving process is eliminated, the above-mentioned drawbacks and risks are necessarily eliminated or at least diminished. However, the number of studies to eliminate the elution step in coprecipitation and sorption methods have been very limited.

In order to eliminate elution step, Nukatsuka et al. proposed a solid-phase extraction system in which cellulose nitrate was loaded with thallium and then suspended in a small volume of aqueous solution to be introduced directly into the furnace of atomic absorption spectrophotometer to determine the analyte [10]. Bakircioglu et al. used a water soluble polymer, polyacrylic acid, to coprecipitate cadmium, copper and zinc in acetone and subsequently dissolved the precipitate in water prior to their determination by flame AAS [11]. Since the precipitate was dissolved in water rapidly and completely, many drawbacks of coprecipitation methods due to dissolution of the carrier precipitate with acids or chemicals were eliminated or diminished.

In this study, lead was coprecipitated with cobalt/pyrrolidine dithiocarbamate complex (Co(PDC)_2) formed using ammonium pyrrolidine dithiocarbamate (APDC) as the chelating agent and cobalt as the carrier element. The precipitate was then slurried and directly introduced into the graphite furnace atomic absorption spectrophotometer. Slurry sampling has been widely and successfully used for the determination of trace elements by ETAAS directly without dissolving the samples [12–15]. In this method, the granulated solid sample is dispersed using an appropriate diluent and directly introduced into ETAAS or flame AAS (FAAS) or inductively coupled plasma (ICP). Slurry method has many advantages of solution technique, e.g. there is no loss of time for sample dissolution or leaching; the risk of contamination as well as analyte loss during sample preparation is at minimum level; there are hardly the risk of environmental pollution and instrument corrosion from acidic solutions used for elution and finally it is more economical as no reagent and heat are used to dissolve the sample. Moreover, slurry can be diluted; successive injections from the same slurry can be made; standard addition method with aqueous standards can be applied; modifier can be used. The only problem with slurry technique is the preparation of a slurry staying homogeneous at least during the whole analysis which need careful optimization of some experimental parameters such as size of particles, slurry volume,

effective mixing, addition of dispersants, the ratio of solid matter to total slurry volume, etc.

The most important advantage as well as the novelty of this method is the elimination of the elution step or dissolving of the precipitate. However, slurry sampling is not free from problems. Many factors can affect the homogeneity and stability of the slurry, and consequently, the results of determination. The experimental conditions for both quantitative coprecipitation of lead on Co(PDC)_2 and a homogeneous and stable slurry were optimized.

2. Experimental

2.1. Apparatus and reagents

A PerkinElmer 3030 Zeeman atomic absorption spectrophotometer equipped with an HGA-600 graphite furnace was used for the determination of lead. Lead hollow cathode lamp was used as the spectral radiation source. Lamp current, wavelength and slit width were set to 10 mA, 283.3 nm and 0.7 nm, respectively. Pyrolytic graphite coated tubes with pyrolytic L'vov platforms were used throughout this work. Vortex-2-Genie was used for homogenous mixing. A mixture of magnesium nitrate (10 μg) and palladium nitrate (32.5 μg) was used with every sample introduction as a modifier. All chemicals were of analytical grade (Merck, Germany) while APDC and Certified Reference Materials [Sea-water (CRM-SW) and wastewater (CRM-WW)], were bought from Fluka (Switzerland) and High-Purity Standards (USA), respectively. The CRM sample solutions sold, as 10.0 mL of concentrates were further diluted appropriately. Results were given as the averages of at least three independent replicate analyses.

Stock solution (1000 mg/L) of Pb was prepared from Titrisol (Merck) and further diluted with distilled–deionized water daily. Samples were introduced into graphite furnace as 20 μl with an Eppendorf micropipette. All quantifications were performed exclusively by means of integrated absorbance values (peak area) for all determinations. Graphite furnace program for the determination of lead in slurry determination is given in Table 1.

2.2. Procedure for slurry sampling

Firstly, cobalt/pyrrolidine dithiocarbamate complex collecting lead was precipitated by mixing 0.5 mL of 0.1% Co^{2+} (as the nitrate), 5.0 mL of 0.1% APDC and the sample (or standard).

Table 1
Graphite furnace programme for the determination of lead in slurry^a

Step	Furnace temperature (°C)	Time (s)		Internal gas flow (mL/min)
		Ramp	Hold	
Drying	110	10	15	300
Drying	120	5	15	300
Pyrolysis	900	10	20	300
Atomization	1800	0	3	0
Cleaning	2650	1	5	300
Cooling	20	2	6	300

^a In the presence of 10 μg of magnesium nitrate and 32.5 μg of palladium nitrate as the modifier.

The pH of the mixture was adjusted to 8.0 using 0.01 mol/L HCl or NH_4OH . The mixture was vortexed for about 2 min at 2000 rpm. The solid part was precipitated by centrifugation for 5 min at 2000 rpm. The supernatant was removed by decantation. The precipitate, collecting the analyte element, was washed with distilled–deionized water three times to remove the matrix traces and the last solution traces were removed by Pasteur pipette. The slurry of the collecting precipitate was prepared in 500 μL of 1.0% Triton X-100 and further homogenized mechanically stirring with vortex before each sampling. Blanks, standards and samples were subjected to the same experimental procedure.

2.3. Loading capacity

In order to determine the loading capacity of the gathering $\text{Co}(\text{PDC})_2$ precipitate, various amounts of lead from 1 mL of 1 mg/L to 1 mL of 300 mg/L were coprecipitated with 0.5 mL of 0.1% Co^{2+} and 5.0 mL of 0.1% APDC and the concentration of lead in the supernatant, i.e. non-precipitated lead, was determined. The loading capacity was determined from the threshold lead concentration value when lead was first detected in the supernatant or alternatively the gathering precipitate was overloaded and loading capacity was determined from the difference between lead concentrations in the beginning and remaining in the supernatant.

3. Results and discussion

This work is the combination of coprecipitation and slurry techniques. Thus, in order to obtain quantitative recovery with high precisions and enrichment factors, the experimental parameters belonging to both techniques should be optimized. It should be stated that the experimental conditions for coprecipitation of lead (i.e. retention of lead by the carrier precipitate) were optimized compulsorily before those of slurry. Therefore, in the beginning, at first, the parameters influencing the completeness of coprecipitation were investigated by measuring the lead remained in the supernatant and later the slurry conditions were optimized.

Elci et al. [9] proved that formed by the interaction of cobalt with sodium diethyldithiocarbamate was useful to gather various elements from large sample volumes as well as hardly coprecipitates the most possible matrix ions such as alkali and alkaline-earth elements. At first glance, the gathering precipitate in our study and that proposed by Elci et al. [9] seem to be similar. However, their chelating agent was diethyldithiocarbamate whereas in this study pyrrolidine dithiocarbamate was used for this purpose. Moreover, they used flame AAS for the quantification after a traditional elution step whereas in this study much higher sensitivity of electrothermal atomization and the elimination of elution step using slurry sampling in low volumes provided superiorities such as much lower limit of detection, fastness, no risk of environmental pollution and instrument corrosion from acidic solutions used for elution, etc. Therefore, the procedure applied in this paper is completely different from that described by Elci et al. [9].

3.1. Optimization of coprecipitation conditions

3.1.1. Effect of pH on the coprecipitation of lead

First of all, the optimum pH range was determined for the quantitative coprecipitation of lead with cobalt/pyrrolidine dithiocarbamate complex. The lead in matrix-free aqueous solution was quantitatively collected on the gathering precipitate at $\text{pH} \geq 8.0$. Moreover, on condition that the other experimental parameters were optimized, quantitative recoveries were obtained for all the samples studied at $\text{pH} \geq 8.0$ as well. Therefore, the pH values of all sample solutions were adjusted to 8.0 throughout this work.

3.1.2. Effects of the amount of precipitating agents and sample volume

The lead in samples was coprecipitated with cobalt/pyrrolidine dithiocarbamate complex formed upon mixing of Co^{2+} and APDC. At first, the effect of the amount of gathering precipitate on the coprecipitation of a definite amount of lead was investigated.

Both the APDC and Co^{2+} were prepared as 0.1% (w/v) to form the gathering precipitate. The volume of cobalt was kept constant as 1.0 mL whereas APDC was changed from 2.0 mL to 10 mL which covered a range from excess of Co^{2+} to that of APDC. When the volume of 0.1% of APDC was greater than 4.0 mL (or 4.0 mg), 50 mL of 10 $\mu\text{g}/\text{L}$ of lead (i.e. 0.50 μg of lead) could be quantitatively (>95%) coprecipitated. The maximum coprecipitation was attained with 5.0 mL of 0.1% APDC. Therefore, in this work, cobalt/pyrrolidine dithiocarbamate complex obtained from the mixture of 0.5 mL of 0.1% Co^{2+} + 5.0 mL of 0.1% APDC, corresponding theoretically to 2.7 mg of $\text{Co}(\text{PDC})_2$, was benefited to coprecipitate the analyte in all applications.

Later, the effect of sample volume on the completion of coprecipitation was investigated. The effect of sample volume containing 10.0 $\mu\text{g}/\text{L}$ of lead on the coprecipitation of the analyte with $\text{Co}(\text{PDC})_2$ obtained from 0.5 mL of 0.1% Co^{2+} + 5.0 mL of 0.1% APDC was investigated. As depicted in Fig. 1, the analyte could be quantitatively coprecipitated up to 200 mL. However, as the sample volume is increased, the completion of precipitation as well as the separation of the precipitate from solution took more and more time becoming gradually less practical. Therefore, we preferred to work with relatively smaller volumes as far as possible for the sake of simplicity and fastness. In all applica-

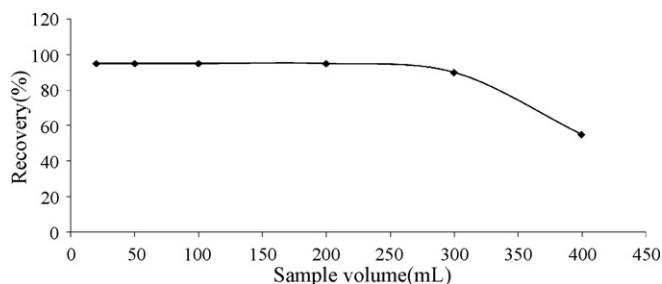


Fig. 1. The effect of the sample volume on the completion of the coprecipitation of 0.010 $\mu\text{g}/\text{L}$ lead with $\text{Co}(\text{PDC})_2$.

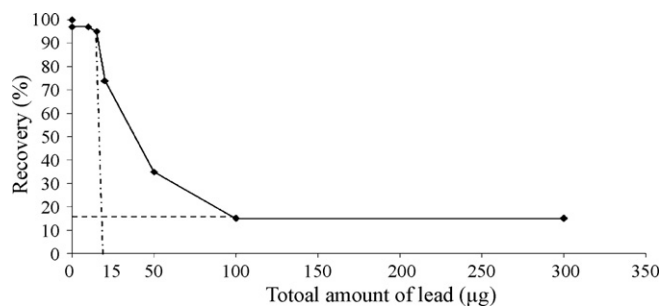


Fig. 2. Loading capacity of Co(PDC)_2 precipitate with respect to lead.

tions, the sample volumes were not exceeded 50 mL. However, as can be seen from Fig. 1 clearly, if necessary much higher volumes can be used as well. As explained previously, optimization of coprecipitation conditions including loading capacity were performed according to lead concentration remaining in the supernatant on the gathering precipitate collecting the analyte. Therefore, the term recovery percentage in Fig. 2 represents the completeness of coprecipitation.

It should be noted that despite $10 \mu\text{g/L}$ of lead is commonly determined by ETAAS without requiring enrichment, the aim of the optimization of coprecipitation conditions was not to test the limits of enrichment factors as well as slurry conditions. Therefore, in this set of experiments, the lead concentration was high enough to be detected directly. The lead in the supernatant which detected without problem directly was determined for all the experiments regarding the optimization of coprecipitation conditions. On the other hand, the concentrations of lead in CRM samples used for validation tests were below the capacity of direct ETAAS.

3.1.3. Standing time for coprecipitation

The effect of standing time on the completion of the coprecipitation procedure of lead including the precipitation of the gathering precipitate was investigated and it was found that the standing time was related with sample volume. Principally, in all validation tests and applications and most of the optimization studies, 50 mL of sample solutions was used. In optimized conditions, 50 mL of lead was quantitatively coprecipitated with cobalt/pyrrolidine dithiocarbamate complex in less than 5 min. As mentioned previously, the completion of coprecipitation was decided when no analyte was detected in the supernatant. Obviously, the completion of whole precipitation procedure was so short that the effect of standing time on the recovery was not investigated in such a very short time of interval. However, it should be noticed that when higher sample volumes were used, the prolonged standing times were needed for the settlement of the precipitate. Moreover, the separation of precipitate from the supernatant needed much more time and became unpractical.

3.2. Optimization of slurry conditions

3.2.1. The choice of gathering precipitate for slurry sampling

It should be mentioned that every kind of solid material cannot be homogeneously suspended. Whatever is done, the

particles of some materials precipitate rapidly into the bottom of the cup so that the slurry prepared does not stay homogeneous during the analysis, in fact between two successive injections. In this case, it is useless to deal with this material for slurry sampling. For example, silica is not suitable for this purpose because it tends to be rapidly precipitated into the bottom of the cup and hardly suspended homogeneously. On the other hand, some solid particles float and tend to remain on the surface of the liquid phase. Again, they are not suitable to be used in slurry analysis. Finally, the particle size of the solid material and its size distribution are equally important to prepare homogeneous and stable slurry. Cobalt/pyrrolidine dithiocarbamate complex was suitable both to collect the analyte and to prepare homogeneous slurry staying stable during the analysis.

3.2.2. Interference effect of the gathering precipitate on the determination of lead

From a series of study, it was found that the sensitivity of lead in the slurry of the precipitate was somewhat ($\sim 10\%$) lower than that in matrix-free aqueous standard even in the presence of modifier. This means that if lead in slurry is compared with that in matrix-free aqueous standards, some errors around 10% should unavoidably occur. Therefore, for the optimization of slurry conditions and recovery tests, in order to eliminate any sensitivity difference between matrix-free standard and slurried sample, the standards were prepared in the presence of cobalt/pyrrolidine dithiocarbamate complex matrix. In addition, in all determinations the blanks, standards and samples were subjected to the same experimental procedure described here.

3.2.3. Effect of slurry volume and addition of surfactant

In order to prepare a homogeneous slurry, to keep its stability during the whole analysis as well as to introduce it precisely and reproducibly into the atomizer, slurry volume was carefully optimized, Triton X-100 as a dispersant was added and the precipitate carrying lead was dispersed using a vortex.

In a series of study, the effect of slurry volume on the repeatability of results using 50 mL of $1.0 \mu\text{g/L}$ lead in the presence of Triton X-100 and after vortexing for about 20–30 s was investigated (Table 2). The low precisions obtained for $<300 \mu\text{L}$ of total slurry volumes may be attributed to the fact that the slurry density (actually the amount of solid material per total slurry volume) was too much to be completely introduced into the furnace. Slurry was so dense that it could not be delivered (drawn and/or discharged) completely, repeatedly and precisely. On the other hand, at large slurry volumes ($\geq 700 \mu\text{L}$), i.e. the ratio of solid-phase to slurry volume was low, the homogeneity could

Table 2
The effect of slurry volume on the recovery of 50 mL of $1.0 \mu\text{g/L}$ lead^a

Total slurry volume (μL)	Recovery of Pb (%) ^a
100	75 ± 8
300	90 ± 5
500	105 ± 3
700	76 ± 10

^a Mean \pm S.D. (N: 3).

not be maintained in every part of the slurry even in short-terms causing relatively poorer precisions (high standard deviations). Most probably, the density of the particles in the slurry at relatively upper part of the sample vial, from where the sample was normally taken, is lower compared to average of the slurry. On the other hand, when the slurried sample was taken from bottom of the vial, the recoveries were higher than 100% which shows that the slurry is not homogeneous at different depths of the vial and confirmed the above-mentioned proposal. When the total slurry volume was 300–500 μL , the precision of the sequential pipettings especially was quite satisfactory and recoveries were quantitative which shows that the slurry is homogeneous and stable at optimum conditions (short-term stability).

After their preparation, the measurement procedure of all slurried samples in ETAAS with three repetitions did not exceed 1 h. To be sure of the homogeneity of the slurried samples during whole analysis period (long-term stability), the measurements were repeated by taking samples from chosen vials from time to time and reproducible results <10% R.S.D. were obtained in 1 h. These results show that when the above-mentioned experimental conditions were applied, the slurry was homogeneous and stayed stable (in short-term and a 1 h of long-term) until the end of the analysis. Since the procedure after coprecipitation of lead including preparation of slurries from gathering precipitates and pipetting of at least three replicates for a series of analysis was completed less than 1 h, we did not investigate the effect of time on stability longer than 1 h. Finally, it should be stressed that the above-mentioned conditions and relating explanations are valid for the experimental conditions and the amounts applied in this study.

In this study, the slurries were introduced into the furnace manually which need care, experience and skillfulness. In order to draw and deliver the sample by the pipette conveniently as adjusted as well as the absorbance and peak shapes of repetitive pipettings for the same solution should be identical as much as possible. After each injection, the position of sample drop on the platform and its drying procedure were observed with a special mirror. In case of any problem during injection or drying, the furnace program was stopped and after thermally cleaning the tube, the injection was repeated. The peak shapes were smooth and similar to those obtained with solutions and absorbances were

reproducible represented with low R.S.D. values. The reason for manual pipetting was to avoid clogging risk of auto-sampler tip with any slurry particle.

3.2.4. The effect of diverse ions

The interference effects of the most common ions on the recovery of the 1.0 $\mu\text{g/L}$ lead at optimum conditions were investigated. Of course we did not investigate the interference effects of all elements. The results are shown in Table 3. The tolerance limits were chosen up to $\pm 10\%$ relative error. Obviously, Co/pyrrolidine dithiocarbamate complex could be successfully used without problem for the enrichment/separation of lead in the presence of diverse ions studied. The tolerance concentrations of foreign ions in the table are above their concentrations in most commonly studied samples which predicted that the method could be successfully applied for the determination of the analyte in complex matrices. As will be seen later on, lead in matrices of certified Sea-water and wastewater matrices could be accurately determined, as well.

3.2.5. Loading capacity of Co(PDC)₂ precipitate

The loading capacity was determined as described previously in Section 2. The retention of the gathering precipitate at elevated concentrations of lead was depicted in Fig. 2.

As shown in the figure, when the total amount of lead treated with 2.7 mg of Co(PDC)₂ was greater than 15 μg , corresponding to 5.6 mg of lead per gram of precipitate, the lead in the supernatant was begun to be detected in the supernatant which was decided as the threshold value for the saturation of precipitate. The loading capacity of the gathering precipitate found is high enough to collect lead in many matrices without being saturated.

3.3. Validation test

The validation of the method in complicated matrices was made by testing the recovery and precision of the ultra-trace analyte in Certified Reference Materials. It should be stressed one more time that samples blanks and standards were subjected to the same coprecipitation/slurry procedure throughout this study to eliminate any possible interferences and thus

Table 3
The effects of the most abundant and common ions on the recovery of 1.0 $\mu\text{g/L}$ of lead

Species	Added as	Concentration of the diverse ion (mg/L)	Recovery, % mean (range)
Na ⁺	NaCl	9,800	110 (105–115)
	NaNO ₃	400	110 (105–115)
	Na ₂ SO ₄	3,200	89 (85–92)
K ⁺	KCl	520	108 (105–110)
Mg ²⁺	MgCl ₂	250	96 (95–98)
Ca ²⁺	CaCl ₂	360	108 (105–110)
Cl ⁻	NaCl	15,000	110 (105–115)
	KCl	470	108 (105–110)
	CaCl ₂	320	108 (105–110)
	MgCl ₂	370	96 (95–98)
NO ₃ ⁻	NaNO ₃	1,100	110 (105–115)
SO ₄ ²⁻	Na ₂ SO ₄	6,700	89 (85–92)

Sample volume: 5 mL; slurry volume: 0.50 mL; the amount of precipitate was as in Table 2; N: 3).

Table 4

Recoveries for lead in Sea-water (CRM-SW) and Waste-water (CWW-TM) Certified Reference Materials (sample volume: 50 mL, slurry volume: 0.5 mL; N:3)

Sea-water (ng/L)	
Certified value	40
Found ^a	41 ± 2
Wastewater (ng/L)	
Certified value	25
Found ^a	24 ± 2

^a Mean ± 95% confidence limits.

sensitivity differences. In this case, quantitative recoveries with high precisions were obtained even in complex matrices.

The optimized procedure was applied for the determination of lead concentrations in Certified Reference Materials [Sea-water (CRM-SW) and wastewater (CRM-WW)]. The analytical results are shown in Table 4. The CRM sample solutions bought as 10.0 mL of concentrates were further diluted appropriately in order to test the recoveries after 100-fold of enrichment. As can be seen from the results in the table, the differences between the mean concentrations of lead found and those given as the certified values are insignificant in the 95% confidence range for both the samples. It should be noted that R.S.D. values for the lead concentrations of the CRMs used in this study were not given by the producer. Therefore, it was tested if the certified concentrations of lead were between 95% confidence limits of the mean values found experimentally. The recoveries and precision of the method are satisfactory and there is neither constant nor proportional error in the method. It seems the capacity of the gathering precipitate is enough to collect all the analyte from complicated matrices.

The detection limit of the described method for lead using sample-matching blanks after 100-fold enrichment was 1.5 ng/L (3σ ; $N = 10$).

4. Conclusion

The method described in this paper is based on coprecipitation of lead with Co/pyrrolidine dithiocarbamate complex and subsequently determination of the analyte by slurry sampling-electrothermal atomic absorption spectrometry. It was simple, fast, easy and free from drawbacks and risks of elution step.

The most remarkable advantage of this method is the elimination of elution step which has some drawbacks and risks such as waste of both time and reagents, incomplete, and irreproducible elution causing poor recoveries and precisions, pollution of laboratory atmosphere and environment especially due to acidic eluents, etc. However, despite its above-mentioned advantages, the slurry sampling of the precipitate has some drawbacks and difficulties such as homogeneity and stability of the slurry. Many factors can affect the homogeneity and stability of the slurry and, consequently, the results of determination. Therefore, the method needs careful optimization of experimental conditions for the coprecipitation of the analyte on the carrier precipitate

quantitatively and reproducibly as well as the preparation of a homogeneous slurry staying stable at least during the whole analysis. In this study, after optimization of experimental parameters, superior enrichment factors up to 100 fold could be very easily and practically reached without any problem which was enough for the determination of lead in samples studied.

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