ORIGINAL ARTICLE

A C G publications *J. Chem. Metrol.* XX:X (202X) X-XX

journal of chemical metrology

Determination of lead and beryllium in boron samples using 4-sulfamoylphenyl dithiocarbamate salt by ICP-OES

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(Received April 25, 2024; Revised May 1, 2024; Accepted May 8, 2024)

Abstract: Today, high amounts of boron waste are generated due to the widespread use of boron and boron compounds. Boron waste in boron-producing enterprises in Türkiye reaches six hundred thousand tons annually. The utilization of boron wastes includes various stages, such as storage of refuse in appropriate places, recovery of boron from boron wastes, and utilization in proper sectors. In this study, the amounts of lead (Pb) and beryllium (Be) in three different boron samples (boron waste, boron ore, and processed boron ore) obtained from Kütahya-Emet region were determined by ICP-OES spectroscopic technique by cloud point extraction (CPE) method using 4-sulfamoylphenyl dithiocarbamate salt complexing agent. Colemanite was used as a boron ore in the study. According to the results, the optimum conditions for the recovery of lead and beryllium ions from aqueous media were found as pH=9, 0.12% (w/w) ligand, and 0.1% (w/w) surfactant concentration, 45 ^{o}C incubation temperature and 60 min incubation time. The RSD % of the method under the optimum conditions found were 2 and 2.5 for Pb^{2+} and Be^{2+}, respectively. The procedure was successfully applied to boron waste samples, and Pb^{2+} and Be^{2+} recoveries between 96-105% were obtained.

Keywords: Boron waste; boron ore; processed boron ore; 4-sulfamoylphenyl dithiocarbamate salt; ICP-OES; cloud point extraction.

1. Introduction

Boron is an essential element for the survival of living things. Compared to other industrial branches, boron and boron compounds have minimal environmental harmful effects [1]. It is widely used to meet the needs of humans and other living beings and reduce the damaging effects of radioactive rays after chemotherapy [2]. It is considered an environmentally friendly element. Boron also exhibits beneficial properties in the field of agriculture [3].

Boron is necessary for daily intake due to its effects on brain and bone development, allergies, menopause, and metabolism. The scarcity of boron in animals and plants can lead to various problems [4]. The World Health Organization estimates that an acceptable safe range of boron intake for adults is 1–13 mg/day [5].

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The article was published by ACG Publications
http://www.acgpubs.org/journal/journal-of-chemical-metrology Month-Month 202X EISSN:1307-6183
DOI: http://doi.org/10.251135/jcm.110.2404.3183
Available online: May30, 2024

Lead and beryllium preconcentration and determination by ICP-OES

Around 230 types of boron ores are found in nature, some of which can be used for commercial purposes. Among them, various valuable boron compounds include colemanite ($Ca_2B_6O_{11}$-$5H_2O$), tincal ($Na_2B_4O_7$-$5H_2O$), and ulexite ($NaCaB_5O_9$-$8H_2O$). [6]. With the rapid increase in production and consumption, there is a need for an additional source of raw material, and boron waste has been identified as a potential source [7]. There are several methods to recover boron from liquid or solid waste, such as gravity methods, electrostatic separation, soaking, magnetic separation, soda leaching, flotation, solution, flocculation, and heat treatment (calcination, decrypting) processes [8].

Heavy metals are defined as metals with a density greater than 5 g/cm^3. Although some metals are necessary for the growth of plants, they can become toxic when present in high concentrations [9]. Heavy metals, which comprise a significant portion of the earth's crust, threaten the environment as they cannot be destroyed or dissolved naturally. They also accumulate in living organisms, harming human health [10].

Lead is primarily used in batteries, and another significant consumption area is the insulation of underground communication cables with lead. Lead oxide, which prevents corrosion, has multiple uses in the coating of wires and paints, in the protection of x-rays since it is a metal that transmits very little radiation, in the production of color television tubes, and in the production of ammunition [11]. Lead is one of the oldest occupational toxins known to humanity. Its production dates back to at least 5000 years ago, and evidence of lead poisoning cases can be traced back to ancient times. Exposure to lead can cause a range of problems, including reproductive toxicity, neurotoxicity, carcinogenicity, hypertension, renal dysfunction, immunological effects, developmental effects, and hematological effects. [12]. The World Health Organization recommends a tolerable weekly limit of 3.57 µg Pb/kg body weight/day for lead intake [13].

Beryllium finds applications in a wide range of fields such as ceramics, electronics, metallurgy, dental health, nuclear, and especially in the space and weapons industries, as alloys or oxides, because of its properties such as corrosion resistance, transparency for the absorption of x-rays, and transmission of neutrons [14]. Although beryllium was predicted to be a non-toxic metal in the 1940s, adverse effects of this element on human health have emerged over the years. While beryllium forms a compound with a black structure, inhaling or skin contact with beryllium in dust can cause an acute disease called 'berylliosis' [15]. This disease, which can occur in the lungs, has been observed to cause lung cancer over the years. The World Health Organization recommends a tolerable weekly limit of 2 µg Be/kg body weight/day for lead intake [16].

Environmental organizations like the World Health Organization (WHO) are tightening heavy metal regulations daily. As a result, it is necessary to have analytical methods to identify and remove heavy metals from the environment accurately [17]. Even though analytical materials are highly sensitive, most samples have heavy metal concentration levels below the detection limit. Therefore, to determine trace elements, preconcentration treatment is essential. This process reduces the matrix effect in the sample, enhances the limit of determination, and provides precise results on the sample [18]. Various precipitation methods are employed today, including liquid-liquid extraction, ion exchange, solid phase extraction, co-precipitation, and cloud point extraction [19-21]. Cloud point extraction is more effective than liquid-liquid extraction. This method has advantages like high extraction efficiency, precipitation, low-cost usage, and the use of non-toxic chemicals [22].

ICP-OES is a method for analyzing elements by emitting excited free atoms or ions in a plasma environment formed by argon gas [23]. This technique is mainly used for qualitative and quantitative analysis of water-soluble materials. It has numerous applications in mineralogy, plant and geology, agriculture, environmental sciences, medicine, and the food industry. [24] Inductively coupled plasma optical emission spectrometry (ICP-OES) is highly suitable for determining heavy metals and is preferred in many research studies. [25]

In this study, the amounts of lead (Pb) and beryllium (Be) elements in 3 types of boron (boron waste, boron ore, and processed boron ore) obtained from Kütahya-Emet region will be analyzed by cloud point extraction (CPE). The heavy metals to be extracted will be chelated with (4-sulfamoylphenyl) dithiocarbamate salt, a hydrophobic complexing agent, trapped as micelles in Triton X-114 surfactant and pre-concentrated. ICP-OES determined the metal concentration in boron samples.

2. Experimental

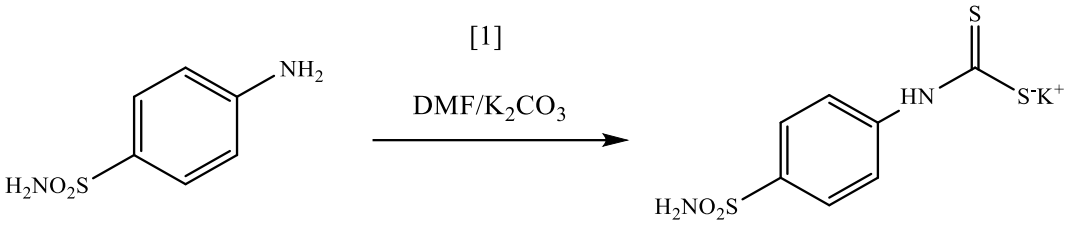
2.1. Materials and Methods

The experiment used chemical substances of analytical purity. To create metal solutions of the desired concentration, 1000 mg/L Pb^{2+} and Be^{2+} solutions (Merck, Darmstadt) were diluted daily. The pH of the solutions was adjusted using 0.05 mol/L NaOH and 0.05 mol/L HNO_3 (Merck, Darmstadt) solutions. For this study, 4-sulfamoylphenyl dithiocarbamate salt was used as a hydrophobic complex-forming agent, and a surfactant called (1,1,3,3-Tetramethyl butyl) phenyl-polyethylene glycol (Triton X-114) was used. Their chemical formulas are shown in Figure 1 and Figure 2. To obtain a 0.1 mol/L solution of (4-sulfamoylphenyl) dithiocarbamate salt, 2 g of the solid was dissolved in 50 mL of DMSO (dimethyl sulfoxide). To obtain a 5% (v/v) Triton X-114 solution, 5 mL of analytically pure Triton X-114 was dissolved in boiling water, and then the volume was completed to 100 mL. The surfactant-rich phase was dissolved in ultrapure 2 mol/L HNO_3 solution (Merck, Darmstadt) to obtain the surfactant-rich phase. Finally, the solutions were prepared with distilled de-ionized water (Milli-Q Millipore 18.2 M cm^{-1} resistance).

2.2. General Procedure for the Synthesis Of 4-Sulfamoylphenyl Dithiocarbamate Salt (2)

Carbon sulfur (2.5 mmol) and 4-aminobenzenesulfonamide (1 mmol) were dissolved in DMF (6 mL), and K_2CO_3 was added to the mixture [26]. The reaction mixture was mixed for 12 h at 5 ºC temperature. After the reaction was completed, the mixture was poured into ice-cold water. It was then filtered, dried, and crystallized from acetone. ^{1}H NMR, ^{13}C NMR, and IR analysis characterized the prepared compound shown in scheme 2.

Yield 86 %, m.p. 241 ºC; IR (KBr, ν, cm^{-1}): 3288 (NH_2), 3007 (NH), 1183 (C=S): ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 10. 38 (1H, s, NH), 8.19 (2H, d, =CH), 7,61 (2H, d, =CH), 7.14 (2H, s, -NH_2). ^{13}CNMR (75 MHz, DMSO-d_6, ppm): 216.8, 145.8, 136.8, 126.1, 121.1.



1 **2**

Figure 1. Synthesis scheme of 4-sulfamoylphenyl dithiocarbamate salt (**2**)

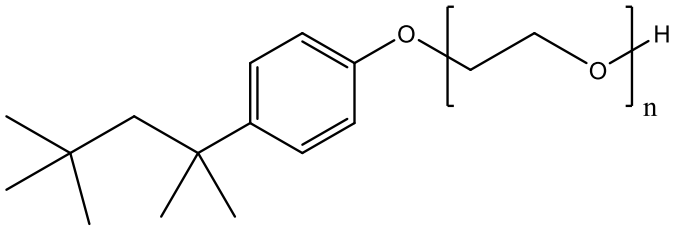


Figure 2. Structure of (1,1,3,3-Tetramethyl butyl) phenyl-polyethylene glycol (Triton X-114)

2.3. Cloud Point Extraction Procedure

In this experiment, which was carried out by applying the cloud point extraction method, parameters such as ligand concentration, surfactant concentration, pH, incubation temperature, and time were optimized. Under optimum conditions, 1 mL of 0.1 mol/L dithiocarbamate (4-sulfamoylphenyl) salt was diluted to 50 mL by adding 5 mL of 5% (v/v) Triton X-114 solution. By adding 0.05 mol/L HNO_3

and 0.05 mol/L NaOH to these prepared solutions, the solutions were adjusted to pH=9. Afterward, these solutions were heated in a water bath at 60ºC for 60 minutes. After heating, the test tubes were centrifuged at 4000 rpm for 30 min. After centrifugation, these tubes were kept in an ice bath for 60 minutes, and the surfactant-rich phase of the solution and the liquid phase were separated from each other with the help of a micropipette. Since the surfactant-rich phase was collected at the bottom of the test tube after the viscous cooling process, the separation process was carried out easily. The surfactant-rich phase separated from the liquid phase was diluted with 4.5 mL of 2 mol/L HNO_3 solution to read the device.

2.4 Preparation of Boron Samples

A gram of each boron waste, boron ore, and processed boron sample was taken and ground in agate and mortar. 0.5g of the ground samples were weighed. The mixture was prepared by adding 4 mL of HCl of 30%, 2 mL of HNO_3 (Merck Suprapure, Darmstadt) of 65%, and 2 mL of $HClO_4$ of 70% to these weighed samples. After treatment, this mixture was allowed to cool; then, the mixture was filtered and diluted to 100 mL in flasks.

2.5. Devices

Standard measurements and determination of metal concentrations after preconcentration were performed with Spectro Arcos brand ICP-OES instrument. pH measurements of the studied solutions were made with a Thermo Scientific brand Orion 2-Star Plus pH meter. Nüve brand NF 400 centrifuge device was preferred for centrifugation processes. All plastic and glass materials used in the experiment were kept overnight in a 10% v/v HNO_3 solution and washed with distilled deionized water. Nüve brand NB 20 water bath was used for the heating process. The operating conditions of the ICP-OES instrument used are given in Table 1. Melting points were determined by a Yanagimoto micro-melting point apparatus (Surrey, UK) and were uncorrected. IR spectra were acquired on a Shimadzu Prestige-21 (200 VCE) (Kyoto, Japan) spectrometer. ^{1}H and ^{13}C NMR spectra were acquired at Varian Infinity Plus at 300 and 75 Hz (Palo Alto, California). ^{1}H and ^{13}C chemical shifts are referenced to the internal deuterated solvent. All chemicals were purchased from Merck (Darmstadt, Germany), Alfa Aesar (Ward Hill, MA), and Sigma-Aldrich (Taufkirchen, Germany).

Table 1. ICP-OES instrument operating conditions

Paramaters	**Spectro Arcos**
Visibility Height	12 mm
Wavelength	Pb: 220.553 nm Be: 313.042 nm
Replication	3
RF	1400 W
Plasma Gas Flow	15.0 L min^{-1}
Auxiliary Gas Flow	1.0 L min^{-1}
Pump rate	30 rpm

3. Results and Discussion

3.1. pH Effect

The extraction of metals in surfactant micelles occurs due to the formation of complexes of sufficient hydrophobicity. Since pH is one of the basic parameters in complexation reactions, it is the variable that should be examined first. Therefore, scanning was done between all values in the pH range of 2-9, and the appropriate pH was 9. Dithiocarbamate (4-sulfamoylphenyl) dithiocarbamate salt used as a complexing agent at this pH was observed to form complexes with the highest efficiency with Pb^{2+} and Be^{2+} metal ions. (4-sulfamoylphenyl) dithiocarbamate salt is thought to have higher extraction efficiencies in basic media because it dissolves better in basic media. The effect of pH on the recovery percentages of

metal ions is shown in Figure 3. 1000 mg/mL metal ion, 0.5 mL 5% (v/v) Triton X-114, and 0.05 mol/L HNO_3 for pH adjustment in each volume buffered to different pH.

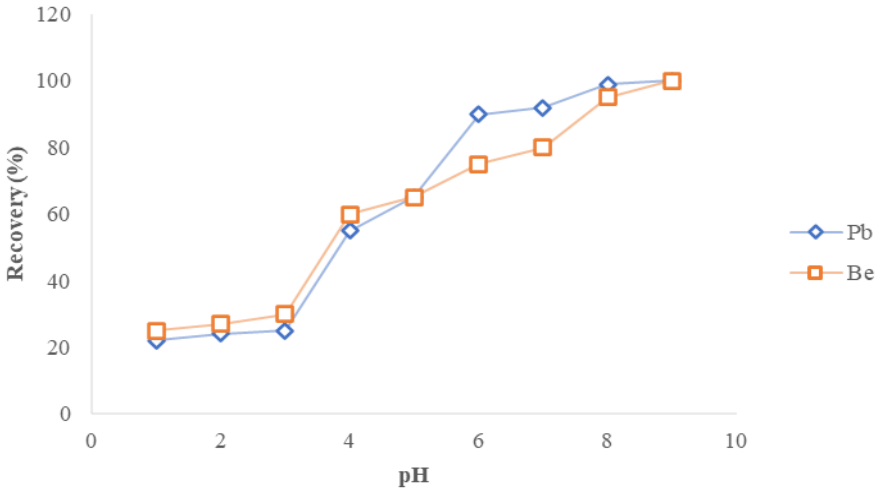


Figure 1. Effect of pH on recovery of metal ions (2 mL of 0.01 M (4-sulfamoylphenyl) dithiocarbamate salt, 2 mL of 5% (v/v) Triton X-114, 50 mL of sample volume, 60 ºC incubation for 60 minutes)

3.2. Effect of Complexing Concentration

In the cloud point extraction method, the complex forming a hydrophobic, fast, and stable structure with metals is an essential criterion for the efficiency of the pre-concentration process. Since all metals in the environment are desired to react with the complexing agent in the formation of the complex, an appropriate amount of complexing agent must be added to the medium. This study observed how the extraction efficiencies of metal ions in the medium at a concentration of 1000 mg/mL vary with different concentrations of complexing agents. The effect of ligand concentration on recovery percentages of metal ions is shown in Figure 4.

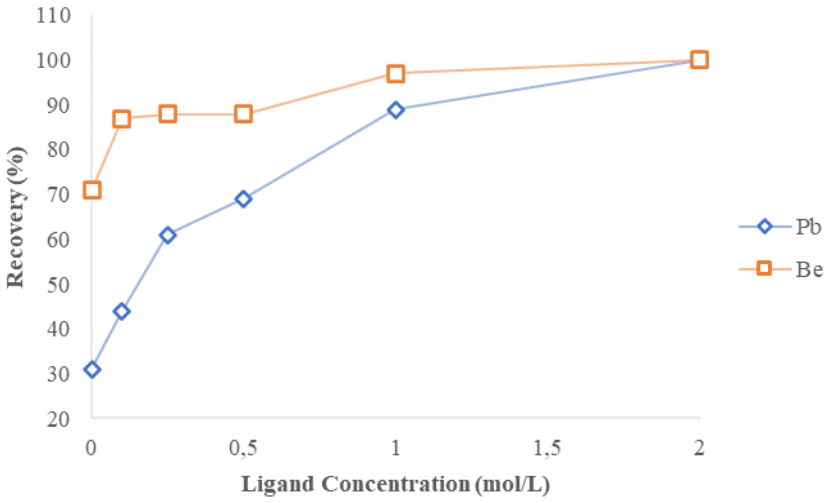


Figure 4. Effect of ligand concentration on percentages of metal ion (pH=9, 2 mL of 5% (v/v) Triton X-114, 50 mL of sample volume, 60 ºC incubation for 60 minutes)

3.3. Effect of Surfactant Concentration

The surfactant concentration is another parameter to be investigated while applying the cloud point extraction method. The surfactant concentration must be at the optimum level in the reaction medium to obtain high-efficiency results. Due to the low amount of surfactant in the environment, the necessary micelle cannot be formed completely, so the metal-ligand complexes cannot pass into the hydrophobic micelle phase. At high surfactant concentrations, a decrease is observed in pre-concentration processes since the micelle volume will increase. In Figure 5, the effect of surfactant concentration on the recovery percentages of metal ions was observed.

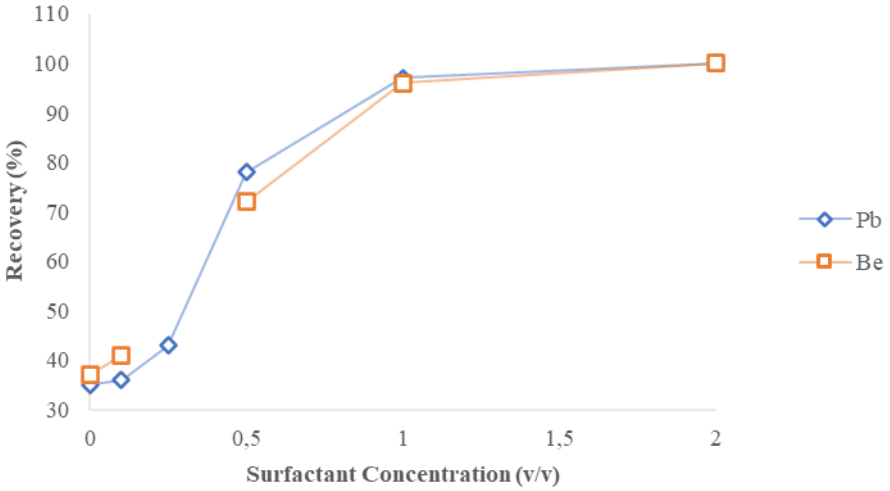


Figure 5. Effect of surfactant concentration on recovery of metal ions (pH=2, 2 mL of 0.01 M (4-sulfamoylphenyl) dithiocarbamate salt, 50 mL of sample volume, 60 ºC incubation for 60 minutes)

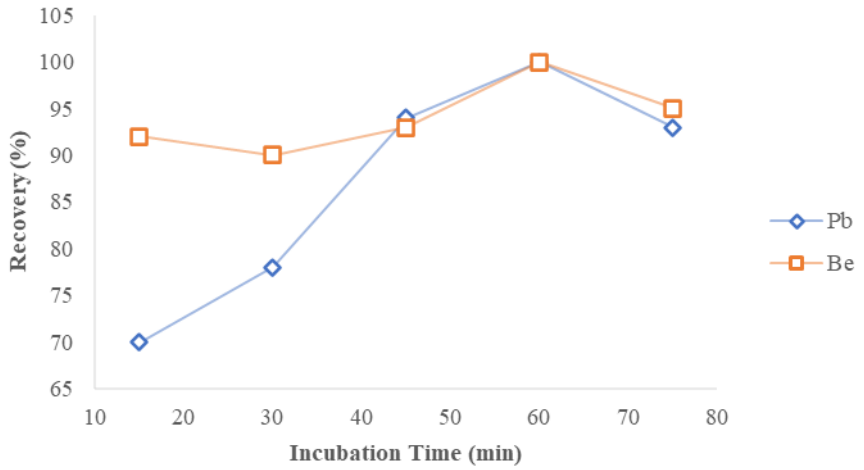


Figure 6. Effect of reaction time on percentage of (pH=2, 2 mL of 0.01 M (4-sulfamoylphenyl) dithiocarbamate salt, 2 mL of 5% (v/v) Triton X-114, 50 mL of sample volume, 60 ºC incubation)

3.4. Incubation Time and Temperature

Another critical parameter for preconcentrating metals is the reaction time and temperature. For the complex formation to be completed and the surfactant to cloud and trap the hydrophobic complexes, it is necessary to reach the required temperature and wait for a specific time at this temperature. Low

extraction efficiencies may be encountered since complex formation cannot occur completely or the surfactant cannot be completely clouded at low temperatures. Since the structures formed may become unstable at high temperatures, these two parameters should be optimized most appropriately. The study observed that the extraction efficiency increased gradually at longer reaction times and reached the maximum extraction efficiency at 60ºC.

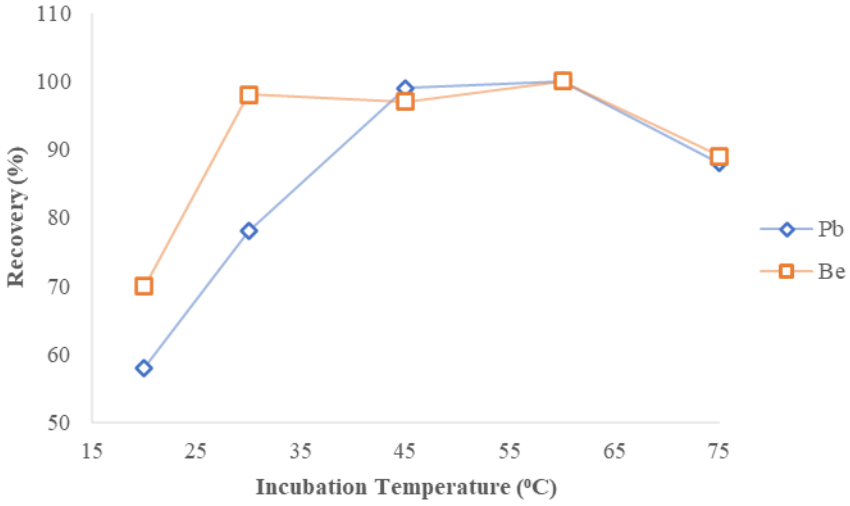


Figure 7. Effect of reaction temperature on percentage of recovery (2 mL of 0.01 M (4-sulfamoylphenyl) dithiocarbamate salt, 2 mL of 5% (v/v) Triton X-114, 50 mL of sample volume, 60 minutes incubation)

3.5. Interfering Ion Effect

Under optimum conditions, the method's selectivity was tested by adding different foreign ions to the solution. Interfering ions produce errors in recovery percentages of the analyte more than ± 5%. If an ion interferes, it changes the recovery percentage of the analyte by more than ± 5%. Table 2 demonstrates the recovery percentages of Pb^{2+} and Be^{2+} at a given concentration and the maximum concentration at which interfering ions can be tolerated. Therefore, it is obvious that the method can be applied to different environmental samples with various matrices despite the presence of large amounts of interfering ions.

Table 2. Interfering ion effect of recovery of lead and beryllium

Interfering ion	Concentration (mg/mL)
Na^{+}	5000
K^{+}	2500
Ca^{2+}	1000
Mg^{2+}	1000
NO_3^{-}	5000
SO_4^{2-}	2500
Fe^{3+}	50
Cl^{-}	5000

3.6. Analytical Performance

After all the optimum conditions for cloud point extraction were completed, analytical performance measures relevant to the method must also be calculated. These criteria are correlation coefficient, qualitative and quantitative detection limit, and precision. A calibration line should be drawn with enriched metal ions after cloud point extraction to obtain these criteria. The enrichment factor is calculated as the ratio of the slope of the calibration line obtained with preconcentration to the slope of the calibration line obtained without preconcentration. Other criteria and results are detailed in Table 3.

Table 3. Analytical performance characteristics of the method used

Parameters	Lead (Pb)	Beryllium (Be)
Correlation coefficient*	0.9023	0.9985
Relative standard deviation (RSD)	2	2.5
Qualitative limit of detection (mg/mL)	107	21
Lineer range (mg/mL)	50-1000	50-1000

*Correlation coefficients obtained after preconcentration

3.7. Uncertainty Assessment

It is essential to assess uncertainty in laboratory testing to guarantee accurate results. Multiple factors, such as equipment calibration and handling, sample collection method, reagent purity, and environmental conditions, can affect the precision of an experiment. Incorporating uncertainty analysis with other validation methods can help identify and prevent potential errors throughout the analytical process. In this research, the NORDTEST approach was deemed more suitable for estimating uncertainty budget, as compared to the EURACHEM CITAC Guide and GUM guidelines for calculations, owing to the use of NIST CRM. This study estimated measurement uncertainty for Be and Pb using the NORDTEST method. The calculations are as follows:

$$u(Rw) = Rw/2 \quad (1)$$

$$RMS_{bias} = (\Sigma(bias)^2/N))^{1/2} \quad (2)$$

$$u(C_{ref}) = \Sigma(C_{ref})^2/N)^{1/2} \quad (3)$$

$$u(bias) = (RMS_{bias}^2 + u(C_{ref})^2)^{1/2} \quad (4)$$

$$u_c = (u(Rw)^2 + u(bias)^2)^{1/2} \quad (5)$$

$$U = 2xu_c \quad (6)$$

The Nordtest methodology employs various parameters to determine a measurement's expanded uncertainty (U). These include the number of rounds (N), standard uncertainty (u(x)), standard uncertainty component for within laboratory reproducibility (u(Rw)), mean of the standard uncertainty of the assigned values (u(Cref)), root mean square of individual bias values (RMSbias), method and laboratory bias (u(bias)), and combined standard uncertainty (u_c). The Nordtest approach displays all parameters in Table 4.

Table 4. Calculated Nordtest guide parameters

	u(Rw)	u(Cref)	RMS_{bias}	u(bias)	u_c	U(%)
Be	15.7	8.32	1.86	8.53	17.87	35.74
Pb	17.7	16.5	3.4	16.9	24.4	48.8

3.8. Application of the Method to Real Examples

The developed cloud extraction method was applied to three different types of boron mine (boron tailings, boron ore, and processed boron) samples. In this study, which was carried out by taking a 50 mL sample, specific concentrations of metal ions were added to the samples, and the results are given in Table 6. Also, the method's accuracy was tested by applying the method to the certified reference materials GBW10011 and GBW10012.

Table 5. GBW10011 and GBW10012 certified reference materials analysis results

	GBW10011			GBW10012		
	Certificated Value mg/kg	**Measured Value mg/kg**	**Recovery %**	**Certificated Value mg/kg**	**Measured Value mg/kg**	**Recovery %**
Be	0.85	0.83±0.16	97.65	1.7±0.4	1.72±0.27	101.18
Pb	0.065±0.024	0.068±0.012	104.62	0.07±0.02	0.069±0.025	98.57

Table 6. Analysis of boron waste sample

Sample	Metals	Added (mg/kg)	Found (mg/kg)	Recovery (%)
Boron waste	Pb (II)	-	0.3	
		0.1	0.4	100
		0.25	0.54	96
	Be (II)	-	BDL	
		0.1	0.1	100
		0.25	0.26	104
Boron ore	Pb (II)	-	0.164	
		0.1	0.268	104
		0.25	0.41	98
	Be (II)	-	BDL	
		0.1	0.102	102
		0.25	0.245	98
Processed Boron	Pb (II)	-	0.119	
		0.1	0.221	102
		0.25	0.372	101
	Be (II)	-	BDL	
		0.1	0.095	95
		0.25	0.242	97

*BDL: Below detection limit

3.7. Comparison with Other Methods

Today, the field of green chemistry is focused on protecting the environment by repurposing materials obtained from waste. It is essential to examine the components of these waste materials for potential toxic effects. This study presents significant contributions to the literature on the analysis of lead and beryllium in three types of boron (boron waste, boron ore, and processed boron ore). The presented study has similar analytical performance values compared to other methods.

Table 5. Comparison of other methods

Method	Metal	Complexing agent	LOD (mg/mL)	RSD	Preconcentration factor	Reference
ETAAS	Be	Cupferron	0.02	6.1	20	[28]
ICP-AES	Be	1,8-dihydroxyanthrone	0.001	2.88	16.7	[29]
Spectrophotometric	Be	Chrome Azurol S	0.05	1.2	25	[30]
FAAS	Pb	-	1.9	3.2	30	[31]
FAAS	Pb	Dithizone	0.08	3.4	53	[32]
ETAAS	Pb	Eriochrome black T	0.04	9	-	[33]
This work	Be	(4-sulfomoylphenyl)	107	2	25	
	Pb	dithiocarbamate salt	21	2.5	25	

4. Conclusions

Although many methods have been developed for metal extraction in recent years, cloud point extraction (CPE) still maintains its value and is frequently used in many studies. In the studies carried out with this method, it is predicted that the metal ions will reach the highest recoveries under the most suitable conditions by optimizing the parameters such as the pH of the environment, the complexing agent concentration, and the surfactant concentration.

In this study, the amounts of Lead (Pb) and Berylium (Be) elements found in 3 types of boron (boron waste, boron ore, and processed boron ore) obtained in the Kütahya-Emet region were easily determined with the help of cloud point extraction (CPE). In this study, the heavy metals desired to be extracted were chelated with (4-sulfomoylphenyl) dithiocarbamate salt, which is a hydrophobic complexing agent, trapped in the micelle Triton X-114 surfactant and subjected to preconcentration.

pH=2, 2 mL of 0.01 M (4-sulfamoylphenyl) dithiocarbamate salt, 2 mL of 5% (v/v) Triton X-114, 50 mL of sample volume, 60 ºC incubation for 60 minutes were found as optimum parameters for metal preconcentration.

The ICP-OES instrument used for the analysis is very suitable for such studies. Although the AAS technique is cheaper than the ICP-OES technique, it is not eligible for the simultaneous determination of metal ions. ICP-OES, on the other hand, allows this quickly, and as can be seen in the study, it could easily determine the ions in 3 samples simultaneously.

The method used in the experiment was also applied to the boron samples, and the accuracy of the way was tested. In this study, boron waste, boron ore, and processed boron samples were recovered by the cloud point extraction method, and the method's applicability in natural samples was proved.

Acknowledgements

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