

Original Research Article

Evaluation of Cadmium (II) and Lead (II) in Marine Soil in Benghazi City Using Atomic Absorption Spectroscopy

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ABSTRACT

This article presents a new approach to measure the concentrations of lead and cadmium in soil marine samples. The technique involves a two-step process: first, the samples are pre-concentrated using liquid-liquid extraction, and then atomic fluorescence spectrometry is used for analysis. In this process, dithizone is used as the chelating agent. During the procedure, a complex is formed between lead and cadmium with dithizone. The researchers also investigated important factors that may affect the efficiency of the extraction, such as pH of the sample and shaking duration.

The results demonstrated that the extraction process yielded optimal results within a pH range of 7 to 9, and the ideal duration of shaking was between 10 to 30 minutes. Through stoichiometry analysis, it was determined that the most probable structure of the extracted ion pair complex consisted of one metal ion bonded to two ligand molecules ($1M^{+2}:2HDZ^{-}$). The influence of organic solvents on the extraction process showed that the distribution ratio (D) for extraction increased with a decrease in dielectric constant. Particularly, carbon tetrachloride demonstrated a higher distribution ratio (D), possibly due to its lower dielectric constant, which aids in the disruption of hydration shell around metal cations (Cd and Pb), allowing for enhanced coordination between the ligand molecules and metal cations. A previously described method for analyzing Cd and Pb in marine soil was adapted for this study.

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GRAPHICAL ABSTRACT



1. Introduction

Urban and agricultural soils are frequently contaminated with heavy metals due to mining, pesticide, and battery use, as well as the discharge of industrial waste. This contamination poses a significant risk as excess heavy metals in the soil have the potential to pollute the environment and harm human health by accumulating in the food chain. Specifically, heavy metals such as cadmium (Cd) and lead (Pb) have been identified as priority pollutants due to their detrimental effects on the brain, kidney, and liver. Furthermore, both North America and China have reported a substantial number of sites contaminated with heavy metals. As a result, the effective control and remediation of heavy metal-polluted soils has become an increasingly important issue that requires attention [1].

Marine soil is a composition that consists of all the elements found in the Earth's crust. Studies have been conducted to determine the concentrations of total lead and cadmium in marine soil, as these elements have been found to have an impact on humans and other living organisms in different areas. Therefore, there has been significant interest and efforts dedicated to study and determine these elements. It is worth mentioning that most of these elements are

typically found in very low levels, often lower than the detection limits of common analytical methods. Spectroscopic methods are commonly used for their determination [2] and chemically interfered with other major constituents. Much effort been tried to solve difficulties of such interferences by the development of various techniques [3]. Solvent extraction is a widely used method for concentrating trace elements by separating them from the sample matrix [4, 5] such as Dithizone and its derivatives [6, 7] and oxine [8]. This technique offers the benefits of a relatively simple experimental procedure and high selectivity. However, it has the drawback of low concentration efficiency [4, 5]. Auxiliary ligands are often employed in conjunction with a primary ligand, such as the combination of KCN and KSCN [9-11].

The dithizone reagent has a high sensitivity towards the presence of heavy metals such as lead (Pb) and cadmium (Cd), as outlined in this research. Inorganic or ionic metals can easily form colored coordination compounds when they react with dithizone [12]. The analysis using atomic spectroscopic methods typically requires the sample preparation, which can be simple or complex. These steps of sample preparation are

crucial in the analysis as they often contribute to the most errors [12-14].

Sample preparations typically consist of several essential steps such as digestion, extraction, and analyte preparation before conducting an analysis. It is important to note that this particular step is time-consuming, accounting for approximately 61% of the total analysis time. In addition, it contributes to around 30% of the total analysis error. In current times, the primary objectives of sample preparation involve achieving the best possible results within a shorter timeframe, while minimizing contamination, reagent consumption, and waste generation. When dealing with solid samples, additional steps such as sampling, sub-sampling, grinding, and dissolution are necessary. It is worth noting that the risk of contamination is typically higher when working with solid samples compared to liquid samples [15]. Flame atomic absorption spectrometry (FAAS) is a well-established analytical technique that is widely used in analytical laboratories for accurate elemental metal determinations. It serves as a reliable method for elemental analysis and is commonly referred to as a staple technique in the field [8].

Typically, solid samples are typically prepared for analysis by dissolving them to create a liquid solution. This solution can then be introduced into a flame or furnace for further analysis. The dissolution process can be carried out using various methods such as mineral acid digestion (also known as wet ashing), fusion of solids with molten salts and subsequent dissolution of the fusion bead, dry ash of organic solids followed by acid dissolution of the remaining residue, combustion in oxygen bombs, and several other techniques that are too numerous to list. However, it is important to note that a major drawback of acid dissolution is the potential risk of losing or contaminating the analyte, particularly when dealing with trace amounts at

parts per million (ppm) or parts per billion (ppb) levels.

2. EXPERIMENTAL

Apparatus and reagents used in this study were of high purity. Double distilled water was used as a solvent. Stock solutions of 1.000 ppm Cd (II) and Pb (II) ions were prepared. Dithizone, obtained from Riedel-De Haën AG, was dissolved in chloroform at 0.02% (w/v) concentration. A potassium cyanide solution of 0.05 M was used as an auxiliary ligand. The pH measurements were conducted using a digital pH meter (Jenway Model 3150). Dissolved oxygen levels were measured using a Corning dissolved oxygen meter, and conductivity measurements were taken using a Corning conductivity meter. Atomic absorption spectrometry was performed using the Nov AA 300 instrument, assembled in the chemistry department laboratory. Samples frequently contain water, either in the form of chemically bound hydrates or as moisture that is trapped or adsorbed on the surface. A majority of solid materials have a tendency to adsorb atmospheric water on their exposed surfaces. The quantity of water adsorbed depends on the chemical composition of the solid [16]. It is necessary to remove this water before weighing the samples and before conducting any analysis [16-18].

The objective of the drying process to completely remove all water from the sample, to make it anhydrous, or to eliminate any adsorbed moisture while retaining chemically bound water [17]. Typically, samples are subjected to drying in an oven within the temperature range of 105 °C to 110 °C for 1-2 hours [16-18]. This process is carried out until a constant weight is achieved, ensuring that the samples are dried without undergoing decomposition [16].

10 grams of the sample were placed in a 250 ml beaker, and then 2.5 ml of concentrated hydrochloric acid (36%) was added, and the mixture was evaporated by heating it on a hot

plate until it became dry. This process was repeated twice with additional 2.5 ml of concentrated hydrochloric acid, allowing the beaker to cool for approximately 2 minutes between each addition. Afterward, 2.5 ml of concentrated nitric acid (65%) was added, and the mixture was heated on the hot plate at around 290 °C until nitrogen oxide fumes were produced. The beaker was cooled again for about 2 minutes after the evaporation. Once cooled, the remaining residue was heated to 40-50 °C with 75.0 ml of 1M hydrochloric acid. The mixture was then filtered through Whatman 52 filter paper into a 100 ml volumetric flask. The filter paper was rinsed with a small amount of 1M hydrochloric acid, and the volume in the flask was made up to 100 ml by adding distilled water. Next, 10.0 ml of the resulting solution was transferred to a separator funnel. After that, 10.0 ml of ammonium citrate reagent, 2.0 ml of

hydroxylamine hydrochloride reagent, and 5 drops of thymol blue indicator solution were added. Concentrated ammonia solution (NH₄OH) was added to make the solution alkaline. Carefully, 4.0 ml of a potassium cyanide (KCN) solution was added, and the pH was adjusted to 8-9 using 1% nitric acid (HNO₃). The mixture was vigorously shaken for 30 minutes with 5.0 ml portions of dithizone solution until the color in the last portion remained unchanged. In the case of using FAAS (Flame Atomic Absorption Spectroscopy), the CHCl₃ extract is transferred into a separate funnel, and then 10 ml of 1% HNO₃ is added to the mixture. The solution is shaken for 30 minutes to ensure thorough mixing. After shaking, the layers are allowed to separate, and the metals' content in the aqueous phase is then measured using FAAS. Using the data provided in [Table 1](#), the metal content in the aqueous phase for both metals is measured using FAAS.

Table1. Operating conditions of AAS and heating programs for a FAAS for both metals

Data of adjust	Lead	Cadmium
Lamp current	3.0 mA	4.0 mA
Analytical mode	Single beam	Single beam
Wavelength line	283.3 nm	228.8 nm
Burner type	50 mm	50 mm
Slit width	1.2 nm	0.5 nm
Burner	9 mm	9 mm
Flame	C ₂ H ₂ /air	C ₂ H ₂ /air

2.1. Diphenylthiocarbazone

Emil Fisher is acknowledged for the identification of dithizone, which is alternatively referred to as diphenylthiocarbazone or H₂DZ [19, 20]. For quite a significant period, dithizone has been extensively employed as a reagent for colorimetric analysis of trace metals [21, 22]. Dithizone has been acknowledged as a remarkable ligand with the ability to create complex ions, even in solutions with alkaline conditions [23].

Under optimal conditions or after eliminating any interference, the interaction between dithizone and twenty-four different metals can produce coordination compounds that exhibit unique colors. By precisely controlling the reaction conditions, it becomes feasible to selectively target and isolate the desired substance [24]. Dithizone, which is the initial chelating reagent utilized for extracting metal ions, continues to be a notable chelating agent in extraction procedures [25]. Only in recent times have we begun to gather evidence pertaining to the

properties and structures of the complexes that are created [26, 27].

2.2. Effect of shaking time

The study measured the time-dependent behaviors of adsorption for Cd (II) and Pb (II) by altering the equilibrium time between the adsorbate and adsorbent, within a range of 5-60 minutes. The concentration of Cd (II) and Pb (II) was maintained at 10 µg/ml, while 0.1 g of calcite was added. The percentage adsorption of Cd (II) and Pb (II) was plotted on a graph as a function of time, indicating that equilibrium between Cd (II), Pb (II), and calcite was achieved within 10 minutes. As a result, a shaking time of 10 minutes was used for all subsequent measurements (Fig 1) [23].

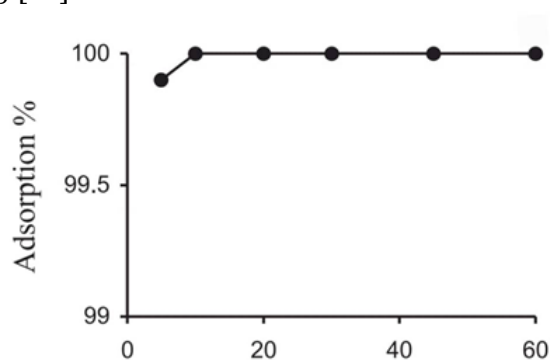


Fig1. Effect of shaking time

2.3. Effect of pH for Metals-Dithizone complex

The pH of a solution affects the formation of metal-dithizone complexes. For instance, in the case of Pb(II) and Cd(II) ions, they can precipitate as hydroxides in strongly basic solutions. By increasing the pH, dithizone can react with other metallic cations. In addition, the pH plays a role in metal extraction, and the efficiency of extraction is studied under different pH conditions. Specific

pH limits are controlled to achieve optimal and consistent color formation. The study results indicate that the extraction of metal-dithizone complexes is most complete between pH levels of 3 and 12. The maximum absorbance is observed at pH levels ranging from 7 to 9 (Table 2 and Fig 2) [23]. Calibration Functions of lead are Slope 0.01205 mg/l, R^2 adjusted 0.999319504 and Detection limit 0.04227 mg/l; (see Fig. 3). Calibration Functions of cadmium are Slope 0.16576 mg/l, R^2 -adjusted 0.999944493, and Detection limit 0.00114 mg/l (see Fig 4).

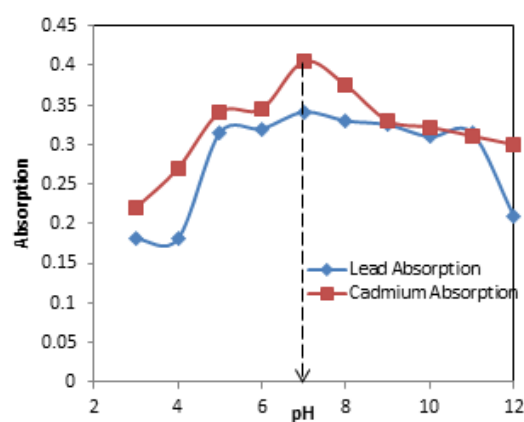


Fig 2. Effect of pH

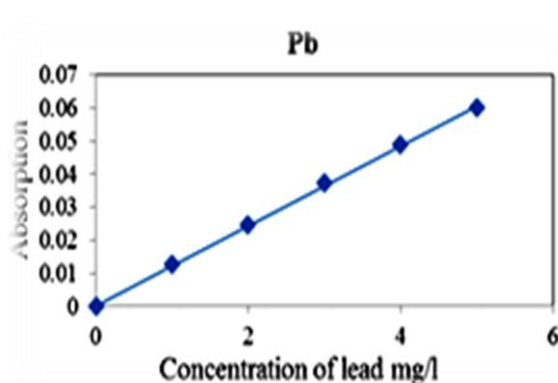


Fig 3. Calibration curve of standard lead solutions

Table2. The relation between the pH and the mean absorbance standard solution of lead and Cadmium 1ppm, (n=4) at 25 °C, using FAAS

pH	Lead Absorption	Cadmium Absorption
3	0.181	0.220
4	0.181	0.270
5	0.315	0.341
6	0.320	0.345
7	0.341	0.405
8	0.330	0.375
9	0.325	0.330
10	0.310	0.322
11	0.315	0.311
12	0.210	0.300

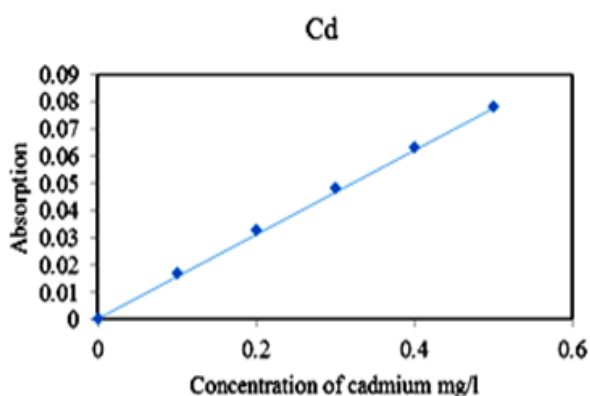
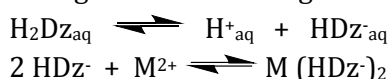


Fig4. Calibration curve of standard cadmium solution

3. RESULTS AND DISCUSSION

Dithizone is well known for its capability to form stable complexes with a wide range of metal ions. When dithizone becomes ionized and transforms into the dithizonate ion, it can effectively bind with a metal ion to generate a complex. Subsequently, this complex can be extracted into an organic solvent using the following method:



During the extraction process, when cyanate ions are present in an aqueous solution as auxiliary ligands, the metal ions initially undergo a

reaction with cyanate ions to form complexes. These complexes then react with HDZ⁻ ions, which are derived from chloroform, resulting in the formation of ternary complexes [18].

Where are: (1) Beside North Benghazi Power Station, (2) Ras-Almaingar coast, (3) near Seaport of Benghazi, (4) Giliana Coast, (5) Eshbilia coast, (6) Alahli Club (in front of Rear Gate of Benghazi University), (7) Nairoaz coast, (8) Abou-Fakhra coast, and (9) Geminis coast. To clarify, the comparison in Table (3) clearly indicates that both samples of marine soil are free from lead and cadmium contaminants.

4. Conclusion

In this study, we performed measurements on small quantities of lead and cadmium. These samples were collected from the coast of Benghazi. Our goal was to increase the concentrations of lead and cadmium in the samples to facilitate analysis using an atomic absorption spectrometer. We achieved this by employing a solvent extraction method with a dithizone complex. We found that the ideal pH range for the formation of the dithizone complex was between 7 and 9.

Table 3. Concentration levels of Cadmium and Lead in Benghazi City coast using FAAS

Symbol	Concentrations	
	Cadmium $\mu\text{g/Kg}$	Lead $\mu\text{g/Kg}$
1	41.62	390.7
2	54.89	311.8
3	54.84	432.4
4	68.85	255.0
5	43.62	306.0
6	34.11	454.4
7	46.94	394.6
8	56.58	461.2
9	93.40	313.8

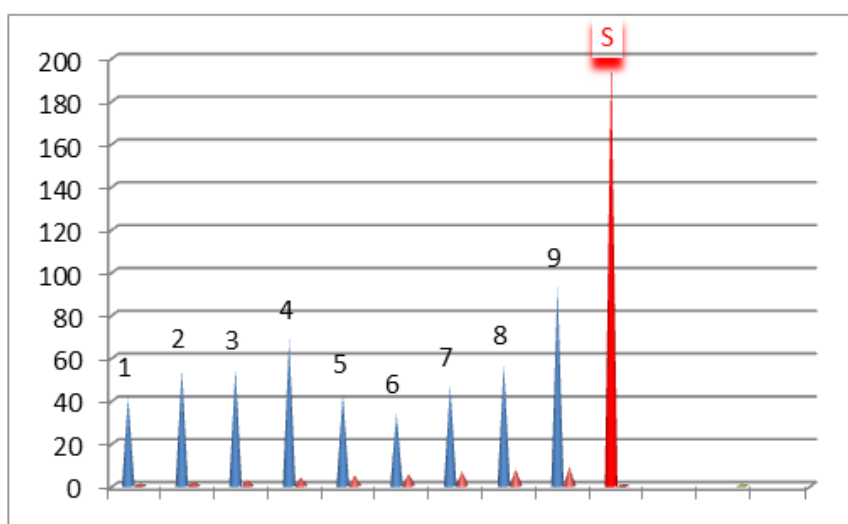


Fig5. Comparison between the international standard in Sweden with results of Lead

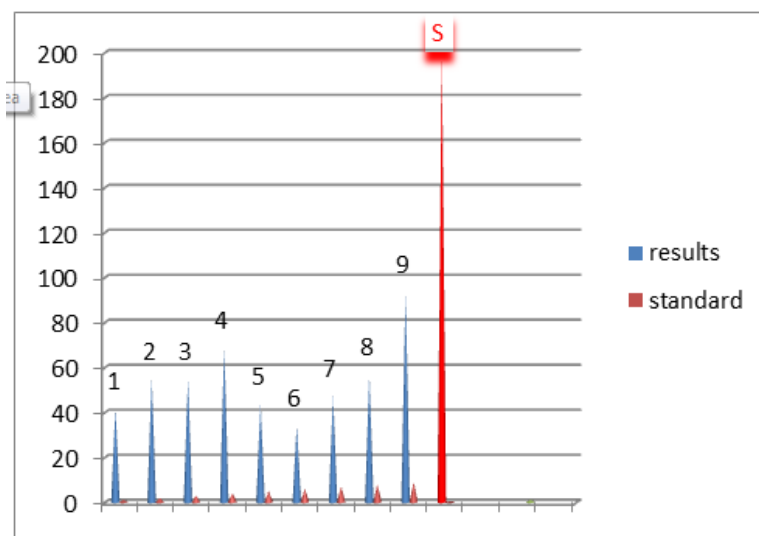


Fig.6. Comparison between the international standard in Sweden with results of Cadmium

In addition, we determined that the extraction process should not exceed 30 minutes to obtain optimal results. In China, the international standard measurement for soil quality regarding lead is 35 mg/kg or less. Meanwhile, in Sweden, the accepted level is below 10 mg/kg (Fig. 5 and 6)[28]. To ensure that not all results obtained exceed the allowed limit according to the soil quality standards, the measurements for cadmium in the soil should not exceed ≤ 0.20 mg/kg. Therefore, it is important to ensure that all obtained results comply with this limit to meet the soil quality. Chronic low-level exposure to various metallic pollutants is a significant public health concern across many areas. It is crucial to understand the underlying mechanisms behind the interactions of heavy metals to assess and manage health risks associated with chemical mixtures. Therefore, further research is necessary to better understand the molecular mechanisms involved and the overall impact on public health caused by human exposure to combinations of toxic metals.

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