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Extraction of Heavy Metals using Dithizone Method on Seawater

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Abstract: Research conducted is related to the preparation and characterization of dithizone method based on extraction of cadmium, lead and zinc trace metals from seawater samples. Inorganic metals or ions can act back with dithizone to produce colourful coordination. The dithizone reagent is highly sensitive to the presence of heavy metals such as plumbum (Pb), cadmium (Cd) and zinc (Zn) as designated in this study. Inorganic metals or ionic can react with dithizone to produce colored coordination compounds. The resulting dithizoneate may be extracted with an organic solvent such as carbon tetrachloride (CCl_4). This study also involves steps such as adjusting the pH value in order to produce the dithizoneate metal product we need. In this study, metal powders were dissolved in seawater samples and extracted with dithizone to enhance the detection and extraction facilities. We analyze trace metals carried out by plasma atomic emission spectroscopy (ICP-OES) to see the efficiency of dithizone extraction methods into seawater samples used. Dithizone extraction method used in extracting Pb element indicates a good performance.

Keywords: Dithizone

Introduction

Malaysia is a country surrounded by the sea, it also has many beautiful beaches. However, the issue of environmental pollution is quite alarming as Malaysia is a developing country. Environmental pollution is caused by the acts of some selfish and irresponsible parties who have dispersed toxic waste into the water without being processed. The act has polluted the water resources and hunted seawater. Wastes of the industrial sector such as fuel contain high heavy metals. As we know, heavy metals are very difficult to get rid of and will continue to be contaminated in our body after we take sea life such as shellfish, fish and others (Jong et al. 2010).

Seagrasses have been known to generally play an important role in the sea in general. Fermentation metals such as iron (Fe) and cadmium (Cd) are very important for the growth of phytoplankton, iron (Fe) are also used in chlorophyll production processes in biogeochemical cycles of marine life, copper (Cu), cadmium (Cd) and lead (Pb) toxic in some circumstances (Lee et al. 2011). Photogravure is an important element in marine life, but traceable metal data on a scale globally is very limited due to difficulties in sampling and analysis. This incident is due to the very low concentration of metals (10^{-9} to 10^{-12} mol L^{-1}) compared to the high salt matrix in sea water. Thus, trace metal analysis requires a pre-concentration process with purification prior to detection such as solvent extraction followed by trace metal qualification using plasma atomic emission spectroscopy (ICP-OES).

There are various methods of extraction of metals from water, but the method of extracting metals from seawater is the most difficult extraction due to disturbances such as chloride ions, high salt concentrations and so on in sea water. In addition, the method of extraction of seepage metal from seawater involves measures or work that is quite complicated and requires much labor, long allocated time and large quantities of seawater samples. In this study, trace metal extraction was performed using the dithizone method. Inorganic metals or ionic can react with dithizone to produce colored coordination compounds. This dithizone reagent is highly sensitive to the presence of heavy metals such as lead (Pb), cadmium (Cd) and zinc (Zn) as provided in this study. This resulting dithizoneate can be extracted with organic solvents such as carbon tetrachloride (CCl_4). This study also involves measures such as adjusting the pH values so as to produce the dithizoneate metal

products we need. For example, when analyzing zinc (Zn) metal, by adjusting the pH value to 4.0 - 5.5, zinc (Zn) will react with dithizone to produce zinc dithizoneate. The metal alloys are defined as toxic metals due to the presence of elements Pb, Cd, As, Ti, and U elements. In the water symbol there are various metals such as Cr, Ni, Mn, Co, Fe and Zn (Alloway 1990). Most of these metals do not affect the environment when present in small quantities. However, however, if it is present in excess quantities, it is said to be toxic because of the contamination effect it will carry. Trace metals or heavy metals will have an impact even within a short period of time, as well as chronic consequences on aquatic life as well as animals or humans that consume the aquatic life. Heavy metals are difficult to decompose and will accumulate in our body such as tissue organisms. The properties of these toxic metals will continue to occur in our bodies, and will cause very serious effects such as causing a person to infect chronic or carcinogenic diseases. In this study, trace metals aimed at being extracted are cadmium (Cd), lead metal (Pb) and zinc metal (Zn).

Method

Preparation of Standard Solution Dithizone

30 mg dithizone dissolved in 1000 mL of chlorophyll. Solution dithizone shaken until no visible sedimentation under volumetric flask. It then added 5.0 mL of ethanol before being stored in the laboratory refrigerator under 12 ° C. Before use, incorporate 5.0 mL of HNO_3 into the solution and shake to avoid precipitate the volumetric glass flask.

There are many types of standard methods that have been used in determining the concentration of heavy metals in seawater samples. However, only a few studies have been able to effectively extract the traceable metal and the results of this study are more pronounced than seawater. Among such studies were carried out by Lim and Shahru (2002), made using the Cadmium method, the hydronium method. Both methods are an ideal method for assessing the content of heavy metals. However, both methods require a considerable length of time and complicated measures. Additionally, these methods involve high risk reagents besides requiring high costs of either cost or maintenance costs.

In this study, metal extraction traction was carried out using the dithizone method. Dithizone or known as diphenylthiocarbazone or 1,5- diphenylthiocarbazone is a compound containing sulfur (S) and a good ligament. Dithizone is prepared with dithizone's reaction to react with various metals such as lead (Pb) and cadmium (Cd) and produce colored complexes. With the pH value adjustment, the results for the determination of heavy metals such as lead (Pb), cadmium (Cd) and zinc (Zn) will be easier and faster. For example, when conducting zinc (Zn) metal analysis, by adjusting the pH value to 4.0 - 5.5, zinc (Zn) will react with dithizone to produce zinc.

Results and Discussion

Table 1 and figure 1 show the percentage of zinc metal extraction and the concentration of zinc metal which is stirred by using 10 mL of 5.0 ppm Zn $(NO_3)_2$ and 10.0 ppm Zn $(NO_3)_2$ and diluted solution. It can be seen that the extraction method of dithizone for 10.0 ppm of Zn $(NO_3)_2$ solution using distilled water can obtain the highest concentration of trace metal, which is 0.615 mg / L with the highest extraction percentage of 30.8%. Meanwhile, extraction by sea water obtained the lowest concentration of trace metals for 10.0 ppm of Zn $(NO_3)_2$ solution was 0.349 mg / L with 17.5% percentage of recovered extraction.

This condition occurs due to the suitability of pH value which is less suitable for Zn metal. The pH value of the buffer provided was impaired by the addition of acetic acid during the experiment as the production of Zn was required to have a relatively low pH adjustment of 2.5 - 3.0. This incident is also due to the loss of most Zn metal during solvent evaporation through spinning evaporation and drying before being sent to ICP-OES. Zn (1040.15 K) has a lower boiling point compared to Pb (2022.15 K) and Cd (1180.15 K) under 1.0 atm pressure. This feature shows Zn is a more volatile metal and is easily lost during heated.

Table 1. Percentage of zinc metals extracted using dithizone method

Type	Extraction (%)	
	5ppm	10ppm
Distilled Water	30.0	30.8
Artificial Seawater	28.9	21.9
Seawater	21.4	17.5

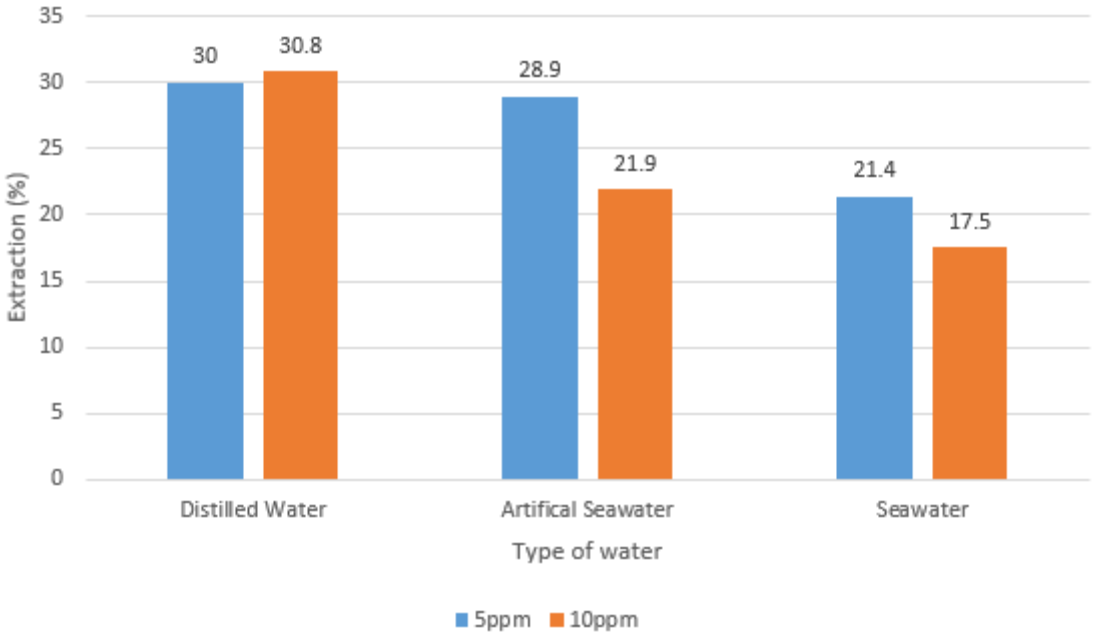

Figure 1. Comparison of percentage of zinc metal extraction using 5.0 ppm and 10.0 ppm Zn $(NO_3)_2$ solution

Table 2 and Figure 2 show the percentage of cadmium metal extraction and the concentration of cadmium metal which is displaced by using 10 mL of standard solution of 5.0 ppm Cd $(NO_3)_2$ and 10.0 ppm Cd $(NO_3)_2$ with diluted solution. Cadmium metal is the most successful traceable metal to be extracted from water samples using the method of treatment. Overall, we can see that the method is highly sensitive to the cadmium metal through the percentage of metal extraction obtained is the highest among the three trace metals. The highest extraction of metals is 10.0 ppm Cd $(NO_3)_2$ solution using distilled water, which is 1.835mg / L. It is also the closest percentage of extraction to the perfect, by 99.2%. The lowest percentage of extraction is by extraction by natural sea water, ie 70.7% or 1.414 mg / L recovered using 10.0 ppm of Cd $(NO_3)_2$ solution used with 0.0707mg Cd extracted from 0.10005mg as entered early research.

This incident occurs due to the pH value in the solution during titration, which is about 3.0 corresponding to cadmium metal according to Table 1. According to Lohan et al study, the pH value is very important for the recovery of trace metals where the effectiveness of the extraction percentage is 99.2%. In addition, cadmium metal element contamination can be determined through this analysis through a percentage of metal extraction as high as 84.3% for 5.0 ppm and 70.7% for 10.0 ppm standard metal solution for water blank types. Air blank means no added oceans in the sample. The contamination is likely to come from the contamination of the instrument which is the contamination of the rotating evaporator or in the beaker during the solvent drying process.

Table 2. Percentage of cadmium metals extracted using dithizone method

Type	Extraction (%)	
	5ppm	10ppm
Distilled Water	90.4	99.2
Artificial Seawater	87.0	82.9
Seawater	84.5	82.7

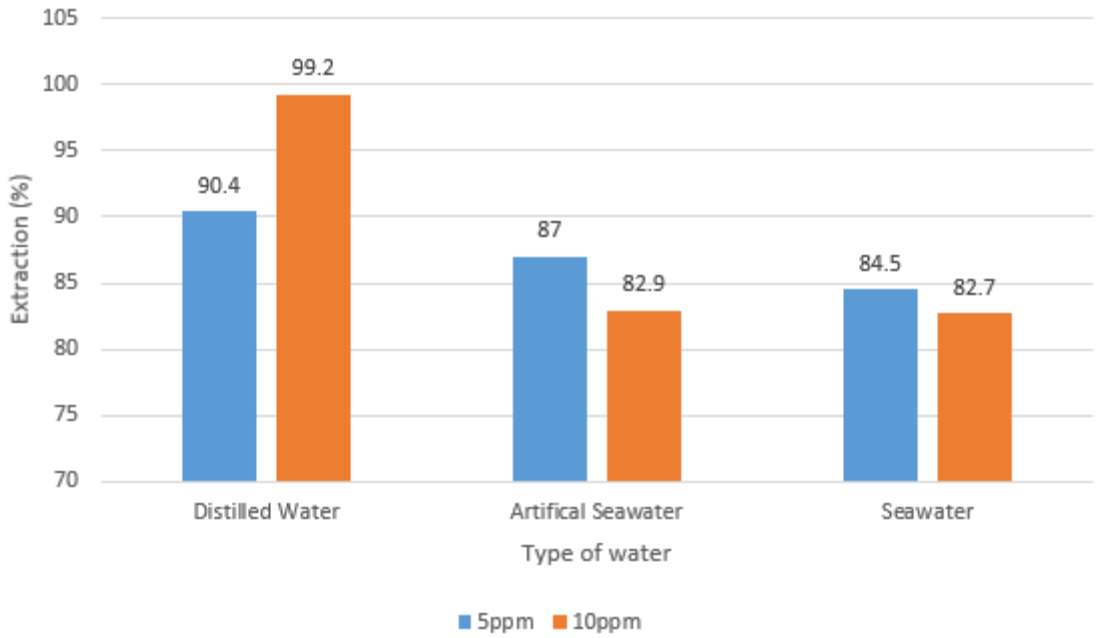

Figure 2. Comparison of percentage of cadmium metal extraction using 5.0 ppm and 10.0 ppm Cd $(NO_3)_2$

Table 3 and figure 3 shows the percentage of extraction and concentration of the extracted metal for Pb $(NO_3)_2$ by using 5.0 ppm and 10.0 ppm of the standard Pb $(NO_3)_2$ solution in 10.0 ml. The percentage of metal extraction and the concentration of extraction metal against the trace metals using artificial sea water samples was higher than the extraction of trace metals using seawater samples. For Pb elements, artificial sea water sample has reached 66.2% effectiveness of metal recovery with 5.0 ppm of standard metal solution and reached 62.6% for 10.0 ppm of standard metal solution. The percentage of metal extraction is low due to the presence of large ion disruption of ion chloride and salt matrix in water, thus affecting the effective extraction of the method. Dithizone extraction method used in extracting lead element indicates a good performance.

Table 3. Percentage of lead metals extracted using dithizone method

Type	Extraction (%)	
	5ppm	10ppm
Distilled Water	74.6	79.8
Artificial Seawater	66.2	62.6
Seawater	61.8	55.8

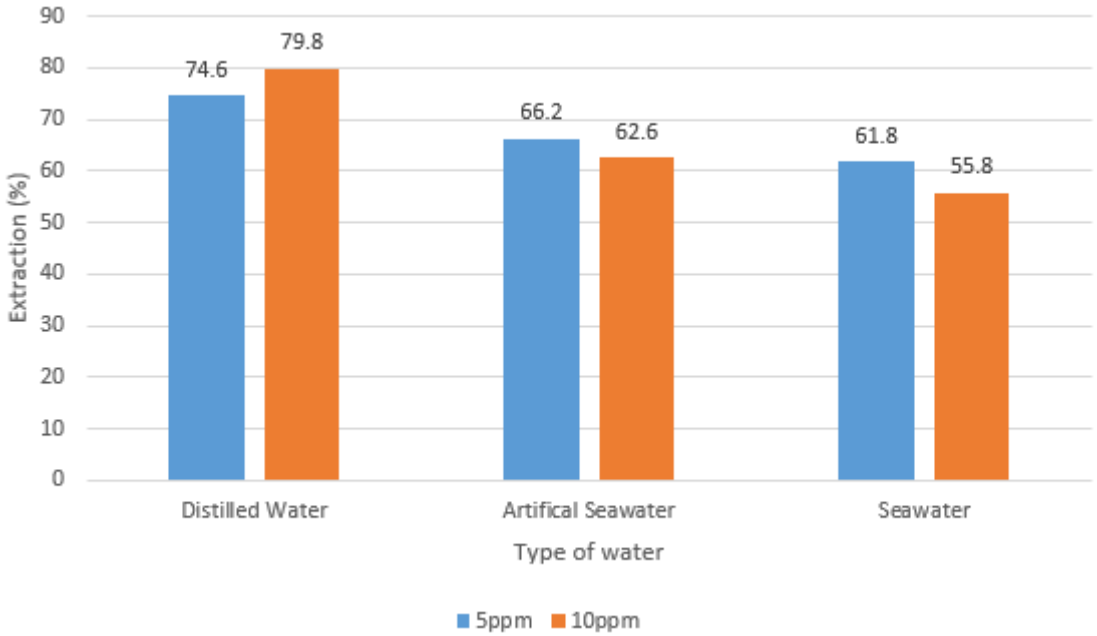

Figure 3. Comparison of percentage of lead metal extraction using 5.0 ppm and 10.0 ppm $Pb(NO_3)_2$

Conclusion

Studies show that simple extraction methods such as dithizone can produce trace metals from seawater samples with ICP-OES determination. This method only uses about 180 - 220 mL of sea water sample volume for each concentration of a standard metal solution, for 5.0 ppm with 10.0 ppm. This study also shows that the simultaneous analysis potential of some elements (Cd, Pb and Zn) can be carried out through spiking extraction on samples by using several standard solutions. This method can be useful for the analysis of large quantities of trace metals. This is because this method can be used to measure the analysis of various elements by simply using a small sample volume. This can help in the collection of samples, sample storage and analysis on samples become easier. Given more attention to the pH value analyzed, it is believed that the reading or value of the extracted trace metal concentration for each element obtained from the experiment is further enhanced. Using the dithizone method, the extracted metal concentration was 1.414 mg / L for Cd, 0.038 mg / L for Pb and 0.473mg / L for Zn.

Recommendations

Revision of chemicals and radar tools and instruments such as pH meter, rotary evaporation machine used is very important. Ensure that the chemicals and equipment used are always in good condition to improve the effectiveness of the analysis and also save time allocated. The provided standard solutions should not be used for more than 2 weeks. It should be provided every 2 weeks to improve the sensitivity and reagent selection of metal elements. In this way, contamination and elemental contamination can be avoided, the extraction decision can be reversed.

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