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The Comparison of Optimum Conditions for Lead (Pb) Analysis Method using DITHIZONE and EDTA Complex in Seaweeds (*Eucheuma spinosum*)

M Syahrir[1], M Wijaya[1], and R Irmayani[1]

[1] Chemistry Department, Makassar State University, Jl. Dg Tata 2 Kampus FMIPA Parangtambung, Makassar 90222, Indonesia

e-mail: syahrirunm@ymail.com, syahrir_gassa@yahoo.com

Abstract. The comparison of optimum conditions for lead (Pb) analytical method using dithizone and EDTA complexes in Eucheuma Spinosum (Eucheuma Sp.) was measured using a standard addition method, where the standard solution of Pb^{2+} was added to the sample to reduce noise. Additionally, UV-Vis spectrophotometer was used with dithizone and EDTA complexes in Eucheuma Spinosum, where Pb^{2+} ions in both complexes were measured. Both complexes were first developed to determine the optimal pH that would measure Pb^{2+} level in Eucheuma Spinosum. The most favorable pH level for such measurement was pH 8, at which pH activity was most stable, and the most favorable complex was dithizone complex, with a regression value closer to one than that of EDTA complex.

Keywords: Eucheuma Spinosum, Standard Addition Method, Dithizone, EDTA.

1. Introduction

The bulk of Indonesian people lives off the marine owing to the country's numerous extensive seas. One of its marine natural products that is mostly marketed is seaweed. However, the seas have become increasingly contaminated as shipping and domestic activities that produce waste containing heavy metals aggravate water pollution. When large quantities of metal pollutants are released, large-scale mortalities of aquatic organisms, including seaweeds, are likely to occur. Seaweed cells, albeit dead, have been found to have great capacities for adsorption of heavy-metal ions [1],[2].

Eucheuma seaweed is a group of algae species that commonly has smooth and cylindrical thalli and grows attached to a substrate with a disc-shaped holdfast [3]. Extensive studies have found that the functional groups, typically present in seaweeds, are capable of metal-ion binding [1], [2]. These particularly can consist of carboxyl, hydroxyl, amine, sulfate, and sulfonate groups present within cytoplasm cells that contribute to metal binding [4]. Seaweeds adsorb and accumulate heavy metals from seawater in thalli. As a consequence, heavy metals displace essential ions in the plant cells.

These metal-contaminated seaweeds along with the increased exposure to lead (Pb) also result in perilous effects on human. Acute and chronic poisoning occurs with such symptoms as burning sensation in the mouth and diarrhea associated with a stimulus in the gastrointestinal system [5]. Another research by [1],[2] found the lead concentration in seaweeds from Takalar and Sinjai was 0,250-0,260 ppm and 0,0450-0,0470 ppm, respectively. High concentration of lead and abundant presence of PAHs that bind to metals along with other types of pollutant result from human activities, most notably shipping (loading-unloading operations) and industrial activities along the coastal water

[6], [7]. These metals can be especially harmful when they bind to ligands. Dithizone and EDTA, as chelating agents, may reduce the concentration of these toxic elements. Both have different chelating capacities, which can be measured by determining the absorbance ranges using spectrophotometric procedure. This depends on the pH optimum and standard calibration curve of Pb^{2+} ions.

This study aimed to measure optimal analytical condition for lead (Pb) in *Eucheuma Spinosum* with spectrophotometric determination by the comparison between two different complexes-dithizone and EDTA.

2. Experimental section

2.1 Equitment
The equipment includes UV-Vis spectrophotometer, blender, procelain cup, analytical balance, 20 mL pipette, bulp, 50 mL volumetric flask, 100 mL volumetric flask, spray flask, hot plate, oven, spatula, 50 mL beaker, pH meter, 10 mL measuring cup, vial bottle and regular funne**l.**

2.2 Materials
The substances include seaweeds, lead (II) nitrate ($Pb(NO_3)_2$), nitric acid ($HNO_{3(p)}$), dithizone, sodium ethylene diamine tetra acetate (na_2edta), 10% ammonium hydroxide (NH_4OH), potassium cyanide (KCl), chloroform ($CC1_3$), aquades (H_2O) and Whatman quantitative filter 42.

2.3 Procedure

2.3.1 Dithizone and EDTA solutions. Dithizone and EDTA solutions were prepare Pb Standard [8]. Pb standard solution was prepared at 100 ppm concentration and diluted to 1 ppm, 2 ppm, and 3 ppm.

2,3.2 Sample preparation of seaweeds. Samples of seaweeds were taken from the coastal water in Wajo Regency, where, by far, the largest seaweeds of South Sulawesi are found. The location is shown in Figure 1.

Figure 1. Map of Wajo Regency.

Prior to dissolution, the samples were washed, dried, blended into a fine purée and weighed to ± 5 grams. After weighing, the samples were loaded into a porcelain cup and dissolved with 20 mL of $HNO_{3(p)}$. The solution was heated over a hot plate. Heating proceeded until white fume appeared. Then, the solution was cooled for a few minutes and filtered through Whatman filter 42.

2.3.3 Determination of pH optimum. pH optimum was determined at pH 6, 7, 8, 9, 10 of the reagents. Afterward, the absorbance for dithizone complex was tested at 515 nm wavelength and EDTA complex at 421 nm.

2.3.4 Determination of Pb2+ concentration in seaweeds. The concentration of Pb^{2+} was determined using standard addition method [9]. The solution of EDTA proceeded in the same manner.

2.3.5 Data analysis: technique and method. Standard addition method was used to minimize errors that might result from differences in environmental conditions (matrix) of the samples and the standards. The fundamental formula that led the spectrophotometric analysis was Lambert-Beer law.

3. Result and discussion

3.1 Determination of pH optimum

pH optimum was determined by adding 2 ppm standard solution of Pb^{2+} to the sample. Dithizone and EDTA were used to form Pb-Dithizone that yielded dark red complex and Pb-EDTA that yielded yellow complex. The pH of Pb solutions ranged from 6 to 10 to allow the complex compounds of Pb-Dithizone and Pb-EDTA to achieve constant absorbance, as shown in Table 1.

Tabel 1. The mean values of absorbances for pH optimum of Dithizone and EDTA.

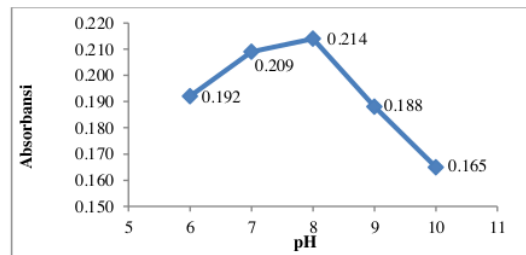| pH	Mean values of absorbances	
	Dithizone	**EDTA**
6	0,192	0,211
7	0,209	0,238
8	0,214	0,249
9	0,188	0,215
10	0,165	0,190

Figure 2. Calibration curve of absorbances for pH aptimum of Dithizone.

The curve shows that dithizone generated pH 8, at which pH was most stable, with absorbance of 0,214 at λmax 515 nm wavelength.
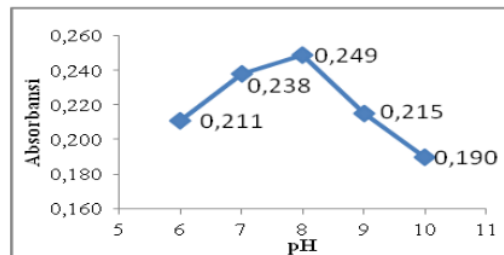

Figure 3. Calibration curve of absorbances for pH optimum of EDTA.

Dithizone reagent is one of chelating agents with high selectivity and sensitivity to Pb in a base atmosphere, where OH^- ions bind to one of H^+ ions in dithizone that forms dithizonate anions. These anions will yield a stable complex with Pb^{2+}. In an acidic atmosphere, Pb^{2+} ions will compete with H^+ ions to bind to dithizone [1], [10].

These two competitive ions lead to different result in terms of the dithizone binding. Dithizone-binding H^+ would result in dithizonate acid, while dithizone-binding Pb^{2+} would result in unstable dithizone-Pb^{2+}. Complexes tend to show maximum adsorption at 520 nm wavelength [11].

Similar to the prior curve, pH optimum of EDTA was pH 8, at which pH was most stable. However, unlike dithizone, the absorbance was 0,249 at λmax 421 nm wavelength. The reaction of complex formation between metal ions and EDTA is extremely sensitive to pH. The complex-forming reaction constantly releases H^+ ions, which in turn will lead to the increasing level of H^+ in the solution, thus rendering decline in complex stability in the atmosphere. Buffer solution is therefore necessary.

3.2 Determination of Pb^{2+} concentration in seaweeds

pH optimum in both dithizone and EDTA was pH 8 as to determining Pb^{2+} concentration using standard addition method, i.e. adding 1, 2 and 3 ppm of Pb^{2+} standards into the sample solution. Table 2 describes the mean values of absorbance for the determination of Pb^{2+} concentration in seaweeds using dithizone and EDTA.

Table 2. The mean values of absorbance for the determination of Pb^{2+} concentration in seaweeds with Dithizone and EDTA.

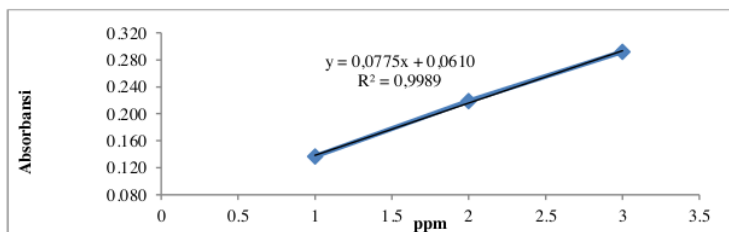| Sample	Mean values of absorbance	
	Dithizone	**EDTA**
A_1 + 1 ppm	0,137	0,158
A_2 + 2 ppm	0,219	0,253
A_3 + 3 ppm	0,292	0,334

Figure 4. Calibration curve of the absorbance for the determination of Pb^{2+} concentration with Dithizone.

Figure 4 illustrates that the curve of Pb^{2+} concentration using Dithizone generated linearity value y= 0,0775x + 0,0610 and R^2 = 0,9989 or correlation coefficient r = 0,9994.
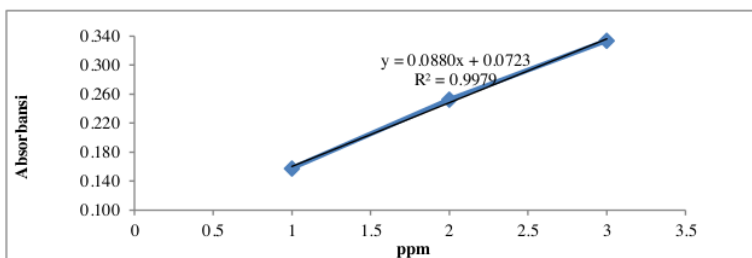

Figure 5. Calibration curve of the absorbance for the Determination of Pb^{2+} concentration with EDTA.

Figure 5 illustrates that the curve of Pb^{2+} concentration using EDTA generated linearity value y = 0,0885x + 0,0717 and R^2 = 0,9979 or correlation coefficient r = 0,9989. Despite slight difference in regression output where that of dithizone was slightly closer to one than that of EDTA, both indicated a near-perfect positive fit or near-one regression.

4. Conclusion

A spectrophotometric procedure for the determination of optimum condition in analytical method for Lead (Pb) in Eucheuma Spinosum using Dithizone and EDTA has been presented. The most favorable pH optimum in terms of determining Pb^{2+} concentration in Eucheuma Spinosum using dithizone and EDTA was both pH 8. Though both showed near-one regression value, the most favorable complex for such determination was dithizone, with a regression value closer to one

Acknowledgements

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