The use of solid phase spectrophotometry for control toxic metal ion content in milkfish cultivation

S Saputro, L Mahardiani and Ninda DCD
Chemistry Education, Faculty of Teacher Training and Education, Sebelas Maret University, Jl. Ir. Sutami 36A Surakarta, Central Java-57126, Indonesia
E-mail: sulistyos@staff.uns.ac.id

Abstract. Solid-Phase Spectrophotometry (SPS) has been widely used in the study of trace element speciation in water. This spectrophotometer has advantages that have a high sensitivity, a small device (portable), and easy to use in the analysis process. This study aims to: (1) increase the use of SPS values in controlling toxic ions in water used for milkfish cultivation, and (2) determine SPS sensitivity for the determination of Cd(II) in pond water samples analyzed. The method used is laboratory experiment. The result showed that the SPS method can be used in the analysis of the content of Cd(II) in the pond water with such a high enough sensitivity results obtained LoD of 0.51 µg/L, RSD < 5% and recovery of 95-105%.

1. Introduction
Fish has a high nutrient content, especially protein and unsaturated fats. Milkfish is one of the cultivated fish commodities that are popular with people because of its high protein content (20-24%) and other ingredients (amino acids, fatty acids, minerals and vitamins) that are high. Milkfishes cultivation is a lucrative industry sector. The development of milkfish cultivation has a good trend with the yield of milkfish production from milkfish ponds in Central Java reaching 64,305 tons with a production value of Rp. 643,052,700,000. in 2011[1].

Ponds Milkfish is mostly in coastal areas (estuary water) and most are mixed brackish water ponds from sea water and river water (downstream of the river). Heavy metals are increasingly found in natural water sources and rivers and sea water. Based on previous research on the content of Cd(II), many seawater showed high yields of pollution. Downstream has a wide possibility of pollution from upstream, midstream and downstream (the pollution accumulates downstream (as long as there is no metal sedimentation). This is consistent with Harsono's research about the content of heavy metals in the river in Juwana which are famous for producing milkfish has a highly toxic heavy metal content [3]. The location of milkfish cultivation that is susceptible to pollution causes periodic monitoring of the content of toxic metal in pond water to ensure the quality of the milkfish produced.

The toxic ion content is usually a very small concentration. Atomic absorption spectroscopy, a device commonly used to measure metal content for the µg/L level, so it needs a more accurate method. In addition, a more practical analysis method is needed so that it can be used to periodically control heavy metal content. In 1976 a new analytical method was reported, namely Solid-Phase Spectrophotometry [6]. After the analytical method, more advanced research and development has emerged with various chemical species. Solid-Phase Spectrophotometry has been Solid-Phase...
Spectrophotometry (SPS) is a sensitive measurement method in the determination of trace element metal ion content that has been proven in previous studies to examine Cr (VI), Pb (II) and As III ion content and also SPS is a sensitive method used in pharmaceuticals for example in determining phenol concentrations [9] [8] [7] [5]. SPS is also a practical method with a relatively small tool size and does not require preconcentration of the sample to be tested so that it can be used for in-situ analysis [10]. Therefore, in this study, the authors tried to use SPS to determine the Cd (II) in the water of the ponds milkfish.

2. Methods

2.1 Tools and Materials

The tools used are a Solid-Phase Spectrophotometry (SPS) K-MAC Lab Junior (figure 1), Satoda Science, Japan; analytic balance; timer; Magnetic stirrer; pipette drops; volumetric equipment; measuring flask; micro pipette; volumetric pipette aliquotting device assembled using a syringe, teflon capillary pipe and other devices used to extract 0.06 ml of resin and beaker glass. Material used are the standard solution of Cd(NO₃)₂ 1000 mg/L; 1 M NaOH; ditizon powder (Merck); muromac AG 50W X2 100-200 mesh resin and aquadest.

![Simple Spektrofotometer SPS](image)

2.2 Methods

2.2.1 Sample Collection and Preparation. Pond water is measured DO, pH and temperature first. Samples of pond water were taken by dipper (figure 2) at a depth of about 30 cm, then filtered with a cellulose acetate filtering unit, after that, put the sample into a PTFE bottle.

![Dipper](image)

2.2.2 Making Resin solutions. Muromac AG 50 W X2 100-200 mesh resin was dissolved in a distilled water and left for a while until the resin becomes more bubbly.

2.2.3 Manufacture of Ditizon Complexing Solution. Ditizone powder weighing 5 mg was dissolved into 100 ml of chloroform.

2.2.4 Preparation of Cd(II) Standard solution of 100 mg/L. Cd(II) stock solution 1000 mg/L 2.5 mL was dissolved in a distilled water until the volume is 25 ml.

2.2.5 Preparation of standard solution of Cd(II) 1 mg/L (1000 μg/L). Cd(II) solution of 100 mg/L weighing 5 grams was added to aquadest until weighing 50 grams.
2.2.6 Preparation of Cd(II) Standard Solution 100 μg/L. Cd(II) 1000 μg/L 10 mL in volume was dissolved in a distilled water until the volume is 100 mL.

2.2.7 Preparation of standard solution of Cd(II) 0 μg/L, 20 μg/L, 40 μg/L, and 80 μg/L. Standard solutions of Cd(II) 0μg/L, 20μg/L, 40μg/L, and 80μg/L, were prepared by diluting Cd 100μg/L solution with distilled water.

2.2.8 Procedure for Determining Cd(II) Calibration Curves. Into 20 mL standard Cd (II) solution 0 μg/L, 20 μg/L, 40 μg/L, and 80 μg/L, 0.2 mL 1M NaOH was added. Then, 1 mL of dithizone was added. After that, 0.06 mL resin was added and stirred using a stirrer for 20 minutes and the samples were analyzed using Solid Phase Spectrophotometry with a wavelength of 485 nm and 615 nm. Then the difference in absorbance of two wavelengths is taken, namely ΔA = A 485nm - 615nm where ΔA is used in making the standard curve Cd (II) (ΔA vs. concentration).

2.2.9 Procedure for Determining Cd(II) Species in a Sample. Into 20 mL standard Cd (II) solution 0 μg/L, 20 μg/L, 40 μg/L, and 80 μg/L, 0.2 mL 1M NaOH was added. Then, 1 mL of dithizone was added. After that, 0.06 mL resin was added and stirred using a stirrer for 20 minutes and the samples were analyzed using Solid Phase Spectrophotometry with a wavelength of 485 nm and 615 nm. Then the difference in absorbance of two wavelengths is taken, namely ΔA = A 485nm - 615nm where ΔA obtained has been substituted into the standard curve equation Cd (II) so that the species Cd (II) in the sample is known.

2.2.10 Determination of Detection Limit. The limit of detection is calculated using the method 3σ (standard deviation), which is taken 20 ml of aqueous solution 5 times, then 0.2 mL of 1M NaOH is added, 1 mL of dithizone solution and 0.06 mL of resin has been stirred for 20 minutes and the samples were analyzed with Solid Phase Spectrophotometry with a wavelength of 485 nm and 615 nm. Then the difference in absorbance of two wavelengths is taken, namely ΔA = A 485nm - A 615nm, where ΔA is substituted into the standard Cd curve, then the concentration and detection limits can be calculated.

2.2.11 Determination of recovery. Recovery was determined by making a standard solution of Cd(II) 0μg/L, 40μg/L, 80μg/L, and 160μg/L with solvent is one sample solution. Then 0.2 mL of NaOH 1 M, 1 mL dithizone and 0.06 mL resin were added. After that the solution was stirred using a stirrer for 20 minutes and the samples were analyzed using Solid Phase Spectrophotometry with a wavelength of 485 nm and 615 nm. Then the absorbance difference from the two wavelengths is taken, namely ΔA = A 485nm - A 615nm, where ΔA is substituted into the standard Cd(II) curve. The obtained concentration then compared between the level of readability of the instrument and the results of the calculation.

3. Result and discussion

3.1 Collecting samples
Sample P1 is taken from the pond with the closest distance from the residential area, the P2 is taken out of the pond with a distance of 2 plots of P1, P3 is taken out of the pond with a distance of 2 plots of P2, P4 is taken out of the pond with a distance of 2 plots of P3.

| Sample | Temp °C | pH   | DO    |
|--------|---------|------|-------|
| P1     | 37.8    | 6.64 | 10.20 |
| P2     | 38.5    | 6.10 | 9.85  |
| P3     | 39      | 5.90 | 10.40 |
| P4     | 38.8    | 6.14 | 10.84 |
Table 1 contains data of temperature, pH and DO water sample. The data demonstrate that the temperature of the pond water when sampling is quite hot. This is explained by the fact that the sampling time is during the day. pH from 4 pond water shows a value of <7. This shows that pond water is slightly acidic. The pH of pond water should be neutral, so that pH neutrality is needed. The value of dissolved oxygen (DO) of all pond water is very high. This is not suitable for normal conditions at a pressure of 1 atm with an average temperature of 38°C where normal DO in this condition are around 6.62 mg/L while the DO content in the sample ranges from 10 mg/L or in other words there is a condition of supersaturation. This is influenced by samples carried out during the day. According to Jeffries and Mills, this is because during the day the release of oxygen in the photosynthetic process which runs intensively and dissolved oxygen levels can exceed saturated oxygen levels and the water experience supersaturation [2].

3.2 Determination of Cd(II) calibration curve

From the standard curve (figure 3) is obtained an equation that is $y = 2.2928x + 0.1546$ where y is $\Delta A$ and x are the concentration. These equations will be used to determine the metal concentration of Cd (II) metal ions in samples and test solutions.

3.3 Determination of Cd(II) levels in water sample

Based on data in table 2, the concentration of Cd (II) in pond water samples ranged from 0.044 mg/L (sample P4) to 0.10 mg/L (sample P2). The difference in the concentration of Cd (II) in each sample can be seen from the physical condition of the sample where the P2 sample with the largest Cd (II) content has a more dirty water color and there are even some milkfish that die and float on the surface of the water. P2 sample has the smallest DO value. It is appropriate that at relatively low DO water organism will have difficulty surviving.

| Sample  | $\Delta A$ | Concentration of Cd(II) (mg/L) |
|---------|------------|-------------------------------|
| Sample P1 | 0.357456   | 0.089                         |
| Sample P2 | 0.386113   | 0.10                          |
| Sample P3 | 0.318853   | 0.072                         |
| Sample P4 | 0.256329   | 0.044                         |

3.4 Determination of detecting limit

One way to verify the analysis method is by determining the detection limit (limit of detection) and recovery. Detection limit (LoD) is the smallest limit test parameter owned by a tool/instrument. The
valuation and determination of detection limits depend on the analysis carried out or what tools/instruments are used in the analysis. In the experiments that have been carried out, the detection limit value is 0.00051 mg/L or 0.51 μg/L. This shows that at a concentration of Cd (II) of 0.51 μg/L, the sample is still legible.

3.5 Determination of Precision

Precision tests were carried out to measure the level of accuracy of the test method. Precision is measured through the distribution of individual results from the average if the procedure is applied repeatedly in samples taken from a homogeneous mixture [4]. Precision testing is performed by calculating RSD from the detection limit data. Based on the calculation results obtained RSD amounted to 3.68%. These results have met the required accuracy of RSD ≤5% [9].

3.6 Determination of recovery

The accuracy of a measurement can be defined as the suitability between the determination and the actual value. Accuracy is stated by recovery calculation. Recovery is expressed as the ratio between the results obtained and the actual results. The results of this study to comply with the requirements recovery value 95-105%.

4. Conclusion

Based on the results of the research conclusions that can be taken, solid phase spectrophotometry can be used to determine the concentration of Cd(II) in pond water samples with a low detection limit (0.51 μg/L) and have an accuracy and precision that meet the criteria of measurement instruments. Solid phase spectrophotometry is a suitable method to control Cd(II) levels in milkfish ponds regularly because of the ease in the analysis.

References

[1] Andriyanto S 2013 Kondisi terkini budidaya ikan bandeng di Kabupaten Pati, Jawa Tengah Media Akuakultur 8(2) 139-144
[2] Effendi, Hefni 2003 Telaah kualitas air: bagi pengelolaan sumber daya dan lingkungan perairan Yogyakarta Penerbit Kanisius
[3] Harsono D R S 2002 Analisis tingkat pencemaran air sungai di daerah estuari Jawa Tengah Badan Penelitian dan Pengembangan Propinsi Jawa Tengah
[4] Harmita H 2012 Petunjuk pelaksanaan validasi metode dan cara perhitungannya Pharmaceutical Sciences and Research (PSR) 1(3) 117-135
[5] J Vucovic, S Matsuoka, K Yoshimura, R J Grubecic, D Kremer, N Santic 2012 Analytical Sciences 28(4) 397-402
[6] S Matsuoka K Yoshimura 2010 Recent trends in solid phase spectrometry: 2003–2009. A Review Analytica Chimica Acta 664 1-18
[7] S Saputro, M Masykuri, L Mahardiani, B Mulyani, I Qorina, K Yoshimura, K Takehara, S Matsuoka 2017 The usage of activated carbon from teak sawdust (tectona grandis l.f.) and zeolite for the adsorption of Cr(VI) and its analysis using solid-phase spectrophotometry (sp). In IOP Conf. Series: Materials Science and Engineering Vol 176 No 1 p 012019
[8] S Saputro, K Yoshimura, S Matsuoka, K Takehara, J Aizawa and Y Tennichi 2014 Chemical Geology 364 33-42
[9] S Saputro, K Yoshimura, K Takehara, S Matsuoka, and Narsito 2009 Analytical Sciences 25 1445-1450
[10] Sarenqiqige, S Saputro, S KAI, M Satoda, S Matsuoka and K Yoshimura 2013 *Analytical Sciences* **29** 677-680

[11] A Sasongko, K Yulianto, D Sarastri 2017 Verifikasi metode penentuan logam kadmium (Cd) dalam air limbah domestik dengan metode spektrofotometri serapan atom *Jurnal Sains dan Teknologi. 6*(2) 228-237

**Acknowledgement**

The author would like to thank the Chemistry Laboratory of Faculty of Teacher and Training Education and the Integrated Center Laboratory of Sebelas Maret University for giving permission to conduct this research.