Method validation of As, Cd, Cr, Cu, Mn, Ni, Se, and Zn metals in Citarum River sediment using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

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Abstract. The Citarum River has a volcanic catchment area in West Java Province. It is also one of the nationally strategic rivers in tropical Indonesia due to its roles in water supply and power generation. However, the Citarum River has experienced a decline in quality in which one of the causes is pollutants containing heavy metals. This research is aimed to validate the ICP-OES method in analyzing metals in sediment. Several parameters have been taken into account and evaluated for the validation of method, namely: linearity, the minimum detection limit, the limit of quantification, accuracy, and precision. The linearity of As, Cd, Cr, Cu, Mn, Ni, Se, and Zn was found satisfactory with coefficient of correlation (r) > 0.9995. The precision of all metals was calculated as relative standard deviation (RSD) and was found that the RSD value was < 2/3 CV Horwitz. The recovery value of all metals was found between 80-95%. The limit of detection (LOD) value for all metals was below 10 ug/L except for Zn and Mn. The method was validated using CRM PACS-3. Metal concentrations in the Citarum River sediment for all stations after being compared with the quality standard of ANZECC are still below the threshold values.

Keywords: Citarum River, heavy metals, ICP-OES, method validation, sediment

1. Introduction

The Citarum River has been extremely polluted by agricultural, residential, and industrial wastes. The Citarum River passes through the Southern part of Bandung—the third largest city in Indonesia, which is heavily populated and industrialized. The area to the South of the Citarum River has predominantly industrial and residential use, whereas the area to the North of the Citarum River is predominantly used for agriculture[1]. The region where the Citarum River is located has a tropical climate with a high rainfall and humidity throughout the year. For Bandung, the average annual temperature is 26.8°C, while the average annual rainfall is 2120 mm [2]. In the higher elevations in the Southern part of Bandung, however, the average annual rainfall could be as high as 4000 mm [1]. For this study, the sediment sample was collected from the downstream of the Citarum River. Industrial wastes usually consist of heavy metals [3], and these heavy metals often comes from anthropogenic activities [4]. The heavy metals that go along into the river will be transported to the sediment [5]. The amount of heavy metals in sediment will increase when the industrial and human activities are also increasing [6]. Sediment,
quantitatively, is known to be a major compartment for metal storage in aquatic environment. Concentration of metals in sediment is the first step to indicate the condition of the environment and provide a base line information on a possibility of metal contaminants bioavailability to biota [7]. The harm of heavy metals increase as they are not chemically or biologically degradable and once they are in the environment, they can remain exist for hundreds of years. Moreover, if they are accumulated with some inferior organisms, they can easily incorporated into the food chain and can cause serious disorders or diseases [3]. Metal analysis usually measured by atomic absorption spectrophotometer (AAS). Previous researchers have analyzed metals in water and sediment using AAS [8,9]. Measurement of arsenic (As) in sediment using Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES) was developed by Kasan [10]. The basic differences between AAS and ICP OES techniques is that one relies upon an atomic absorption process while the other is on an atomic/ionic emission spectroscopic technique. ICP-OES have much higher temperatures for emission to take place for most of the elements. Many metals have sensitive ionic emission lines, one of advantages of ICP-OES, compared to the AAS technique, provides higher detection sensitivity [11]. Furthermore, other advantages of using ICP-OES in measuring metals compared to AAS, include lower detection limit, faster (metals measurement can be conducted simultaneously), and rapid sample preparation. The low metal concentration levels in sediment samples impose the need to have very sensitive analytical techniques like ICP OES [12]. This work aims to implement ICP OES for metals measurement namely As, Cd, Cr, Cu, Mn, Ni, Se, and Zn in sediment samples. Method validation is done to assure that the measurements will produce accurate and precision results within the predetermined specifications.

2. Method

2.1 Sampling and sample preparation

The sample was collected from three stations of Citarum River which was potentially polluted on May 2018, the coordinate of sample collection is shown in Table 1. Once collected, the sediment sample from each Station were bought to the laboratory for sieving using 100 mesh size sieve, the stored brown glass bottle.

| Station | Sample coordinate | Location     |
|---------|-------------------|--------------|
| 1       | 6°58′47.7″S-107°37′05.3″E | Dayeuhkolot |
| 2       | 6°58′44.6″S-107°37′03.0″E | Dayeuhkolot |
| 3       | 6°58′24.4″S-107°37′27.0″E | Katapang Andir |

2.2 Analytical measurement

The sample preparation is based on EPA method number 3050B [13]. One gr of dried sample must be weighted accurately, add 10 ml of nitric acid, and heat the sample at 95 °C for 10-15 minutes. Allow the sample to cool, then slowly add 10 ml of peroxide and 5 ml hydrochloric acid. Cover the vessel with a watch glass. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 ml (usually this amount can be achieved by heating the sample at 95 °C for 2 hours). After cooling, dilute to 100 ml with water. Particulate in the digestate should then be removed by filtration, by centrifugation at 2000-3000 rpm for 10 minutes or by filtering using Whatman No. 40 filter paper and collect the filtrate in a 100 ml volumetric flask, make to volume and analyzed by ICP-OES (ThermoScientific iCAP 7000 Series). A similar process was conducted to PACS-3 certified reference materials. Method blank was carried throughout the entire sample preparation. This blank will be useful in determining the limit of detection. Determination of moisture content was conducted as follows: two gr of sediment sample was weighed accurately in an aluminium plate, the sample was heated in 105 °C oven for 2 hours, cooled, and weighted. The process was repeated until a constant weight of dry sample is obtained. The calibration curve were prepared by measuring dilutions from standard stock solution of 1000 µg/ml. The reagent quality used were “Pure for Analysis”. Deionized water with conductivity less than 0.05 µS/cm
was used. The parameters studied in the validation were: linearity, repeatability, accuracy, and detection and quantification limit. Linearity: the calibration curve were prepared with five points: 25; 50; 100; 200; 500 µg/l of all metals concentration (As, Cd, Cr, Cu, Mn, Ni, Se and Zn). Accuracy: certified reference material PACS-3 were used to analyze six replicates. The recovery was calculated by comparing the analysis result with the value of CRM PACS-3 certificate of each metal multiplied by 100. Repeatability: a blank solution was used to analyze six replicates. Relative standard deviation was calculated by the value of standard deviation of each metal, divided by the average concentration of each metal, and multiplied by 100. The predicted relative standard deviation for each concentration was calculated as Horwitz coefficient of variation (CV Horwitz), \(2^{1-0.5 \log C}\), where \(C\) is a fraction concentration of the analyte. HorRat value was calculated by RSD divided by CV Horwitz value. Detection and quantification limits: the LOD and LOQ was measured from 6 repeated blank method and the concentration was calculated by the average concentration from the graph plus 3 times standard deviation and 10 times standard deviation, respectively.

3. Result and discussion

The moisture content for sediment sample collected from Station 1, Station 2, and Station 3 was 10.95%, 14.13%, and 11.78%, respectively. The moisture content of sediment sample collected from Station 2 was found higher compared to other stations, due to the condition of Station 2 which is wider than the other Stations. All metals measurement result was based on dry weight, so the moisture content of the sample is very important to identify.

3.1 Method validation of ICP-OES

Method validation is basically the process of defining an analytical requirement, and confirming that the method under consideration has capabilities consistent with what the application requires [14]. Linearity: the coefficient of correlation \((r)\) of all metals (As, Cd, Cr, Cu, Mn, Ni, Se and Zn) was found higher than 0.9995. The ICP-OES method found to be very suitable for measuring metals in a wide working range of concentration (0-500 µg/l).

| Table 2. Method validation results of ICP-OES metals measurement |
|------------------|--|--|--|--|--|--|--|--|
|                  | As | Cd | Cr | Cu | Mn | Ni | Se | Zn |
| Coefficient of correlation \((r)\) | 0.9999 | 0.9999 | 0.9999 | 0.9998 | 0.9988 | 0.9999 | 0.9999 | 0.9995 |
| % RSD            | 2.32 | 1.23 | 0.86 | 0.96 | 0.58 | - | 0.37 | 0.37 |
| CV Horwitz       | 14.14 | 8.73 | 5.13 | 10.00 | - | - | 7.10 | 7.10 |
| 0.67 CV Horwitz  | 9.43 | 5.82 | 3.42 | - | 6.67 | - | 4.73 | 4.73 |
| % Recovery PACS-3 certificate value (mg/kg) | 95.31 | 74.96 | 94.33 | 92.84 | 95.39 | 99.27 | - | 95.36 |
| LOD (µg/L)       | 6.93 | 6.93 | 8.7 | 12.49 | 30.37 | 8.82 | 6.12 | 17.50 |
| LOQ (µg/L)       | 11.54 | 11.55 | 14.52 | 20.82 | 50.62 | 14.70 | 10.20 | 29.17 |

Repeatability or precision was represented by relative standard deviation (RSD). The RSD value for all metals was below 10 % and below 0.67 CV Horwitz. Where Horwitz coefficient of variation was calculated from \(2^{1-0.5 \log C}\), \(C\) is fraction concentration of the analyte. In this research the HorRat value was below 0.3. Recovery value of each metal was found acceptable by AOAC and Pharmacopeia for sample concentration of 1-10 mg/kg (80-110%), and 10-100 mg/kg (90-107%). However, the recovery value of Cd was found lower, as the Cd metal might be evaporated during the digestion process. No information on Se metal value on PACS-3 CRM certificate. The LOD for As, Cd, Cr, Ni, and Se metals was found below 10 µg/l, except for Zn, Mn and Cu.
3.2 Heavy metals measurement
Cd and Se metals in Citarum River sediment sample was found below the LOD value (not detected). The concentration of metal in sediment occurred in Station 1 gave higher value compare to Station 2 and 3, as shown in Figure 1. The metals measurement results was compared to Australian and New Zealand Environment and Conservation Council-Interim Sediment Quality Guideline (ANZECC ISQG) standard [15]. The Ni metal concentration was 27.7 mg/kg higher than ANZECC ISQG low standard of 21.0 mg/Kg. Zn metal concentration was found 389.4 mg/kg compared to ANZECC ISQG low standard of 200.0 mg/kg. Mn metals value in sediment sample was 795 mg/kg, no information value in ANZECC ISQC standard. Zn and Mn metals are major metal in sediment samples, while other metals are heavy metals. Chromium (Cr) is used as a pigment in paint and in processes such as manufacturing stainless steel, treating timber (tanalised wood), tanning leather, and electroplating. In our study, the highest Cr concentration (61.5 mg/kg) occurred in the Station 1 and the lowest (39.8 mg/kg) occurred in Station 3.

Table 3. Metals concentration (mg/kg) in Citarum River sediment samples

|       | As  | Cd  | Cr  | Cu  | Mn  | Ni  | Se  | Zn   |
|-------|-----|-----|-----|-----|-----|-----|-----|------|
| Station 1 | 1.92* | 61.5 | 51.7 | 795 | 27.7* | 389.4 |
| Station 2 | 1.80* | 56.7 | 27.0 | 518 | 21.4* | 122.2 |
| Station 3 | 2.65* | 39.8 | 34.1 | 731 | 18.5* | 122.1 |
| ANZECC ISQG low | 20.0 | 1.5 | 80.0 | 65.0 | - | 21.0 | - | 200.0 |
| ANZECC ISQG high | 70.0 | 10 | 270.0 | 270 | - | 52.0 | - | 410.0 |

*: below LOD value (not detected)

Figure 1. Comparison heavy metal concentration between station and standard

4. Conclusions
When using validates methods the following rules are recommended to ensure that acceptable performance is achieved. Firstly, the analyst should be completely familiar with the new method before using it for the first time. Secondly, an assessment needs to be made of how many samples can be conveniently handled at a time. It is better to analyze a few samples well than to try to analyze a large number and have to repeat most of them. Finally, make sure everything needed for the method is
available before work started. This involves gathering together the right equipment, reagents and standards.

From this study, there are clear differences in the metal concentrations in the Citarum River sediment between sampling site, Station 1, Station 2, and Station 3. Recorded metal concentrations from all Stations in May 2018 were below the relevant ANZECC ISCG low trigger value so they are not harmful for the environment. Concentration of heavy metals at Station 1 are potentially concerning for the industrial waste and human activities. We recommend to continues to monitor contaminant concentration at Citarum River by sampling frequently to determine if concentrations are increasing.

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