Pre-concentration of Pb, Cd, and Ni in river water using back extraction method

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Abstract. Dissolved heavy metals such as Pb, Cd and Ni in natural water can be the source of harmful contaminant for human health and aquatic life in aquatic systems. Particular treatment is needed for low concentration of metals in water samples using Flame Atomic Absorption Spectrophotometer (FAAS) measurement. The sample was collected from Cikapundung River in Siliwangi and Dayeuhkolot, Bandung. Back-extraction procedure was used as an alternative method for pre-concentration in trace metal analysis. Ammonium Pyrrolidine Dithiocarbamate (APDC) and Diethylammonium Diethyldithiocarbamate (DDDC) in Methyl Isobuthyl Ketone (MIBK) were used as chelating agent. In this study, the application of back-extraction procedure using APDC/DDDC chelating agent in MIBK resulted the detection limit of 2.2 µg/L for Pb; 1.6 µg/L for Cd; and 1.0 µg/L for Ni. The result showed that sensitivity was increased 4 times for Pb, 6 times for Ni, and none for Cd. The highest concentration of Pb in Cikapundung River was found 8.0 µg/L. All Ni concentration in water samples were under limit of detection. Method validation was conducted in this study and found that the value of correlation coefficient (r) for Pb, Cd and Ni was 0.9995, 0.9960 and 0.9994, respectively. The recovery value for Pb, Cd and Ni were 112.0, 81.5 and 85.9%, respectively in Cikapundung River, and 119.0, 83.5 and 85.9%, respectively, in groundwater samples. The value of Relative Standard Deviation (RSD) for Pb, Cd and Ni in Cikapundung River were 2.01, 2.15 and 6.40%, respectively. On the other hand, the value of RSD of Pb, Cd and Ni in groundwater were 2.70, 3.30 and 7.69%, respectively. In conclusion, back-extraction method can be applied as pre-concentration for low concentration of Pb and Ni in river water samples.

1. Introduction

Water analysis is very important to quantify the heavy metals water pollution. Analytical method should be developed to get an accurate and precision result. Sample preparation is usually needed in chemical analysis to convert analytes to a more suitable detectable form, to separate them from the sample matrix or to concentrate species for trace analysis. This step is the most difficult part in chemical analysis, due to the risks of analyte losses, sample contamination and incomplete sample decomposition as well as analyte extraction. In addition, sample preparation is often the most time-consuming step in analytical procedures. It is contrasting with the impressive development of modern instrumental techniques that significantly improved detectability and reduced the analysis time. In spite of this development, sample treatment is still needed to improve its selectivity and to minimize...
matrix effects. Sample preparation techniques such as hot plate and microwave digestion widely used for this purpose and as the established standard methods for years [2], ISO standard 11466 [3], and preparation for material standard in The Community Bureau of Reference (BCR) [4,5] for trace element dissolution from a large number of matrices. The digestion techniques, however, require the use of concentrated mineral acids, high temperatures and, in the case of microwave applications, high pressures.

Another pre-concentration techniques for metals include solid-phase extraction (SPE) has received much attention in recent years for the analysis of trace concentrations in samples. This technique reduces consumption and exposure to solvent, disposal costs, and extraction time [6,7]. Octadecyl-bonded silica (ODBS) membrane disks have been utilized for the extraction and analysis of many different organic and environmental matrices [8,9]. Moreover, these membrane disks modified by suitable ligands are also successfully used for the separation and sensitive determination of metal ions [10,11].

Metal exchange back-extraction was developed by Lo et al. [12], using Hg to overcome the slow kinetics of acid back-extraction. This method required a single 20-min extraction into chloroform to pre-concentrate (> 90%) of Cd, Co, Cu, Fe, Ni, Pb and Zn. Improvements to this method were recently made by Sachsenberg et al. [13] of which a 90-s single extraction into di-isobutyl ketone (DIBK), with Pd back-extraction is required to quantitatively determine Pb, Cu, Ni and Cd in seawater. This technique produced high pre-concentration factors from relatively small sample volumes, but was limited by the range of metals determined. Back extraction method is an alternative method which was used for water samples. APDC/DDDC as chelating agent in Freon-TF at pH 5 was used in back extraction method. Dithizone was used as chelating agent for Pb and Cd extraction in xylene solvent [11]. The detection limit of Pb and Cd were 0.4 and 0.008 µg/L, respectively. GFAAS is used in back extraction method to determine soluble Cd, Cu, Ni, Pb, and Zn in water sample. The chelating agent was mixture of APDC/DDDC in MIBK solvent and reached the detection limit of 0.001 µg/L [14].

FAAS is as still widely used in Indonesian laboratories to measure metal concentration in water. However, pre-concentration is needed to improve the detection limit. In this study, heavy metals such as Pb, Cd and Ni from river water were measured using back extraction method. Chelating agents used in this study were APDC-DDDC in MIBK solvent at pH 5.

2. Experimental

A total of 12 samples were collected from 6 different areas along Cikapundung River, Bandung City, West Java, as shown in Table 1. The collection method was based on Indonesian National Standard (SNI 06-2412-1991) [15]. Temperature and pH were measured at the sampling sites. Pb, Cd, and Ni analysis was done at an analytical laboratory, Research and Development Center for Water Resources, Bandung.

The extraction was carried out based on Moelyo, et.al. [14]. Prior to analysis, all samples was stored in refrigerator. The sample was filtered using Whatman filter paper 0.45 µm. For every 500 mL volume of filtrate 0.5 mL of concentrated HNO₃ was added. Prior to extraction, the sample was added with 1% ammonium acetate buffer to get pH 4-5. The sample was put in separation funnel, then added with 1 mL of chelate mixture solution of 1% APDC/DDDC and 20 mL of MIBK. The mixture was mixed for 2 min and allowed into two layers. One mL of concentrated HNO₃ was added to the organic layer. The solution was mixed slowly for 20 min, then 9 mL of aqua-millipore was added and mixed for another 30 sec, allowed the mixture to separate, water layer was transferred to a bottle, and measured by FAAS (Hitachi Zeeman 2300 with auto-sampler systems). The FAAS working condition is showed in Table 2.

Validation was carried out by measuring linearity, precision, accuracy, LOD and LOQ. To obtain linearity equation, the instrument respond was plotted in different standard concentration of each analyte. Precision was measured six times for sample concentration of each analyte. The accuracy was measured by adding standard solution to the sample solution and the accuracy of the method was calculated as % recovery. LOD and LOQ was determined by measuring the reagent blank.
Table 1. Sample location and measured parameter on site.

| No | Location                      | pH  | Temp     | Local Time | Weather | Geography Position |
|----|-------------------------------|-----|----------|------------|---------|--------------------|
|    |                               |     |          |            |         | South              |
| 1  | Cikapundung River-Gandok      | 6.80| 25.1°C   | 10.10      | Clear   | 06° 51’ 47,52”    |
|    |                               |     |          |            |         | 107° 37’ 13,5”    |
| 2  | Ground water-Gandok           | 6.19| 23.8°C   | 10.20      | Clear   | 06° 52’ 51,24”    |
|    |                               |     |          |            |         | 107° 36’ 56,34”   |
| 3  | Cikapundung River -Siliwangi  | 6.86| 23.9°C   | 10.50      | Clear   | 06° 53’ 4,8”      |
|    |                               |     |          |            |         | 107° 36’ 27,24”   |
| 4  | Ground water -Siliwangi       | 7.07| 24.6°C   | 10.55      | Clear   | 06° 53’ 3,48”     |
|    |                               |     |          |            |         | 107° 36’ 28,44”   |
| 5  | Cikapundung River -Wastukencana| 7.13| 24.2°C   | 11.33      | Clear   | 06° 54’ 19,56”    |
|    |                               |     |          |            |         | 107° 36’ 27,48”   |
| 6  | Ground water -Wastukencana    | 7.05| 24.0°C   | 11.48      | Clear   | 06° 54’ 19,32”    |
|    |                               |     |          |            |         | 107° 36’ 32,4”    |
| 7  | Cikapundung River -Dalem kaum | 7.09| 24.0°C   | 12.25      | Clear   | 06° 55’ 23,76”    |
|    |                               |     |          |            |         | 107° 36’ 31,32”   |
| 8  | Ground water -Dalem kaum      | 7.09| 24.0°C   | 12.35      | Clear   | 06° 55’ 23,76”    |
|    |                               |     |          |            |         | 107° 36’ 31,32”   |
| 9  | Cikapundung River -Soekarno Hatta| 7.22| 25.7°C   | 13.02      | Clear   | 06° 56’ 57”       |
|    |                               |     |          |            |         | 107° 37’ 18,78”   |
| 10 | Ground water -Soekarno Hatta  | 6.97| 24.0°C   | 13.58      | Clear   | 06° 56’ 55,26”    |
|    |                               |     |          |            |         | 107° 37’ 17,94”   |
| 11 | Cikapundung River -Dayeuh kolot| 7.03| 26.9°C   | 14.23      | Clear   | 06° 59’ 3’        |
|    |                               |     |          |            |         | 107° 37’ 48,3”    |
| 12 | Ground water -Dayeuh kolot   | 7.10| 26.1°C   | 14.34      | Cloudy  | 06° 59’ 2,7”      |
|    |                               |     |          |            |         | 107° 37’ 47,28”   |

Precision method was carried out by measuring the water samples 6 times. The standard deviation (s) and relative standard deviation (RSD) were calculated and the result was compared to the coefficient of variation (CV) Horwitz of $2^{1.05 \log C}$. Accuracy of method was carried out by adding standard solution to water sample. The percentage of recovery was calculated and compared with the acceptable recovery value based on AOAC [16].

Table 2. FAAS condition.

|                  | Pb   | Cd   | Ni  |
|------------------|------|------|-----|
| Lamp current (mA)| 7.5  | 7.5  | 10  |
| Wavelength (nm)  | 217.0| 228.8|232.0|
| Slit (nm)         | 1.3  | 1.3  | 0.2 |
| Burner head       | Standard | Standard | Standard |
| Burner height (mm)| 7.5  | 5.0  | 7.5 |
| Fuel gas support  | Air-acetylene | Air-acetylene | Air-acetylene |
| Oxidant gas pressure (Kpa)| 160  | 160  | 160 |
| Fuel gas flow rate (L/min) | 2.0  | 1.8  | 1.8 |
3. Result and discussion

The range of all metal concentration for standard calibration curve was between 10 to 100 µg/L. Table 3 showed the correlation coefficient for Pb, Cd and Ni and their linearity equations. The correlation coefficient for all metals were found higher than 0.99.

Table 3. Calibration curve for each metal-
(Standard range 0.01-0.10 mg/L).

| Metal | Linearity equation | Correlation coefficient (r) |
|-------|--------------------|-----------------------------|
| Pb    | y = 1.327x         | 0.9995                      |
| Cd    | y = 9.060x         | 0.9960                      |
| Ni    | y = 2.014x         | 0.9994                      |

LOD value using back extraction method for Pb, Cd and Ni was found as 2.2, 1.6 and 1.0 µg/L, respectively whereas LOQ was found 7.3, 5.2 and 3.2 µg/L for Pb, Cd and Ni, respectively (Table 4). Those values were 4 and 6 times lower than acid sample preparation. LOD was calculated as three times of standard deviation of the reagent blank. The LOQ was calculated as 10 times standard deviation of the reagent blank measurement. Back-extraction method had successfully improve the detection limit for Pb and Ni metals to 0.002 and 0.001 mg/L, respectively, while for Cd, there is no significant difference.

Relative standard deviation (RSD) was calculated from standard deviation divided by average concentration multiplied by 100%. RSD value was between 2.0-7.7 % for all metals. Recovery was calculated from final concentration minus sample concentration divided by standard concentration added multiply by 100%. The recovery value was found between 81-119%. This value was acceptable by AOAC for low concentration (65-120%) [16]. Accuracy and precision results as showed in Table 5.

Table 4. LOD and LOQ value using back-extraction method for Pb, Cd and Ni metals.

| Metal | LOD  (µg/L) | LOQ  (µg/L) |
|-------|-------------|-------------|
| Pb    | 2.2         | 7.3         |
| Cd    | 1.6         | 5.2         |
| Ni    | 1.0         | 3.2         |

Table 5. Accuracy and Precision data for Pb, Cd and Ni metals.

| Metal     | % Recovery | % RSD | 0.67 x CV Horwitz |
|-----------|------------|-------|-------------------|
| River water sample |           |       |                   |
| Pb        | 112        | 2,01  | 18,89             |
| Cd        | 81,5       | 2,15  | 19,82             |
| Ni        | 85,9       | 6,40  | 19,66             |
| Ground water sample |          |       |                   |
| Pb        | 119        | 2,70  | 18,74             |
| Cd        | 83,5       | 3,30  | 19,75             |
| Ni        | 91,1       | 7,69  | 19,49             |
Table 6. Heavy metal concentration.

| No | Location                  | Pb (µg/L) | Cd (µg/L) | Ni (µg/L) |
|----|----------------------------|-----------|-----------|-----------|
| 1  | Cikapundung River-Gandok   | ND        | ND        | ND        |
| 2  | Cikapundung River -Siliwangi| ND        | ND        | ND        |
| 3  | Cikapundung River -Wastukencana| ND      | ND        | ND        |
| 4  | Cikapundung River -Dalemkaum| ND        | ND        | ND        |
| 5  | Cikapundung River -Soekarno Hatta| ND    | ND        | ND        |
| 6  | Cikapundung River -Dayeuh kolot| 8.0     | ND        | ND        |
| 7  | Ground Water-Gandok       | ND        | ND        | ND        |
| 8  | Ground Water -Siliwangi   | ND        | ND        | ND        |
| 9  | Ground Water -Wastukencana| ND        | ND        | ND        |
| 10 | Ground Water -Dalemkaum   | 13.0      | ND        | ND        |
| 11 | Ground Water -Soekarno Hatta| ND       | ND        | ND        |
| 12 | Ground Water -Dayeuh kolot| ND        | ND        | ND        |

ND = not detected

Table 6 shows, Pb concentration in Cikapundung River from Dayeuhkolot area was found 8 µg/L, below the permissible level of water quality class 1 of 30 µg/L based on the Indonesian Government Regulation (Table 7). As Dayeuhkolot area is surrounded by textile industries, Pb concentration was found higher than other area which is mostly housing area. On the other hand, Pb concentration for Ground Water from Dalemkaum area was below the acceptable level of 13 and 15 µg/L, respectively, according to the Indonesian Government Regulation and the USEPA. As Dalemkaum is a Central Business District (CBD) for Bandung, water quality could be polluted from transportation and electroplating industry nearby the Bandung CBD.

Table 7. Allowable metal concentration in water samples (µg/L).

| Metal   | Internasional Standard* | Indonesian Standard ** |
|---------|-------------------------|------------------------|
|         | Class 1 | Class 2 | Class 3 | Class 4 |
| Arsen   | 10      | 1.0     | 2.0     | 2.0     | 5.0     |
| Lead    | 15      | 30      | 30      | 30      | 1000    |
| Cadmium | 10      | 10      | 10      | 10      | 10      |
| Nikel   | 100     | -       | -       | -       |
| Cobalt  | 100     | -       | -       | -       |
| Mangan  | 50      | 100     | -       | -       |
| Chrom   | 100     | 50      | 50      | 50      | 10      |
| Iron    | 300     | 300     | -       | -       |

Source: * USEPA [16]
** Indonesian Government Regulation [17].

4. Conclusion

The back-extraction method can be used as an alternative method for determination of Pb, and Ni in water sample. Back-extraction method was found more sensitive compared to both USEPA and ISO
11466 methods for determination of Pb and Ni metal in water sample by FAAS. The LOD for Pb and Ni was lower 4 and 6 times, respectively. However, the extraction method using APDC/DDDC was not demonstrated for the determination of cadmium in water sample. Water sample taken from Cikapundung was classified as class 1 and confirm to use for drinking water or any other use with the similar requirements.

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