Cadmium in Water Samples determined by Atomic Absorption Spectrometry after Solid Phase Extraction using DOWEX 50WX2 resin

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Abstract

The Pre-concentration of Cd(II) in water samples was carried out by using column solid phase extraction DOWEX 50WX2 prior to flame atomic absorption spectrometry analyzed. The analytical parameters consist of pH, flow rate, volume of eluent and volume of sample were determined. The optimum conditions were obtained pH was 5, sample flow rate was 1 mL min^{-1}, volume of eluent nitric acid 1N was 10 mL and sample volume was 50 mL. The optimum conditions obtained were used to determine the detection limit and the accuracy of the method using tap water samples. Determination of detection limit used tap water which contain Cd 0.001 mg L^{-1} and the accuracy (recovery,%R) with concentration of Cd 0.01 mg L^{-1}. The detection limit was found 0.2697±0.0899 μg L^{-1} (n=7) and accuracy (n=7) was 93±6%. The result showed the accuracy still meets the acceptance criteria for accuracy (70%-125%) and the RSD 6% is smaller than the Horwitz value of 20.8%. Based on the accuracy (R%) and % RSD values obtained, it can be concluded that this method provides effective results for pre-concentration to increase the detection limit of Cd (II)in clean water using SSA-flame.

Keywords: SPE,Cd, Dowex 50WX2, Flame-SSA

Abstrak (Indonesian)

Pre-koncentrasilogam Cd (II) dalam sample air keran telah dilakukan menggunakan kolom ekstraksi fase padat dengan resin DOWEX 50WX2 sebagai adsorben sebelum dilakukan analisis secara spektrofotometri serapan atom-nyala. Parameter analisis yang terdiri dari variasi pH, laju alir, volume eluen, dan volume sampel telah ditentukan. Diperoleh kondisi pH optimum 5, laju alir sample 1 mL min^{-1}, volume eluen asamnitrat 1N 10 ml dan volume sample 50 mL.Kondisi optimum yang diperoleh, digunakan untuk menentukan limit deteksi metode dan akurasi metode menggunakan sample air keran. Untuk penentuan limit deteksi digunakan air keran dengan konsentrasi Cd 0.001 mg L^{-1} dan penentuan akurasi dengankonsentrasi Cd 0.01 mg L^{-1}. Diperoleh limit deteksi metode 0.2697±0.0899 μg L^{-1} (n=7) dan rekoveri (n=7) 93±6%. Nilai akurasi yang diperoleh masih memenuhi kriteria keberterimaan akurasi yaitu masih berada pada kisaran 70-125% dan RSD 6% lebih kecil dari nilai keberterimaan table Horwitz yaitu 21.7%. Berdasarkan nilai akurasi dan % RSD yang diperoleh disimpulkan bahw ametode ini memberikan hasil yang efektif untuk pre-konsentrasi guna meningkatkan limit deteksiCd(II) dalam air bersih secara SSA-nyala.

Kata Kunci: SPE, Cd, Dowex 50WX2, SSA-Nyala

INTRODUCTION

The release of Cadmium heavy metals to the environment from industrial waste generally comes from the electroplating, smelting, metal alloys, pigments, plastics, batteries, mining, and refining processes [1]. Although heavy metals are present in food, rivers and sea water in low concentrations, they will accumulate in the human body and damage human health. Several heavy metals such as iron, copper, manganese, cobalt, zinc, molybdenum, vanadium and selenium are vital to living organisms and are found in enzymes, hormones and vitamins. However, other elements such as aluminum, arsenic,

lead, mercury, and cadmium are toxic even at very low concentrations[2].

The World Health Organization allows the highest 3 μg L^{-1} Cd(II) contents in drinking water guidelines [3] and the maximum permissible levels set by US Environmental Protection Agency (EPA) are 5 μg L^{-1} Cd(II) as contaminants for national primary[4]. Therefore, it is needed to develope a sensitive method for determinations of cadmium in drinking and waste waters[5].

Direct and accurate determinations of cadmium at trace levels by analytical techniques such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) are difficult due to the analyte concentrations below the limit of detection of these methods and also matrix interferences. Hence, before determining the analytes at these levels, generally the pre-treatment steps including separation and also pre-concentration of analytes from the sample matrix are required[5]

Several studies have been carried out to increase the limit of metal detection testing using solid phase extraction (SPE) techniques on various sample matrices. Among them are research using carbon nanotubes [6], amberlyst-15 resin [5], Chromosorb-102 resin for Bi, Cd, Co, Cu, Fe, Ni and Pb metals. in drinking water, seawater and sediment [7], Dowex Marathon C (DMC) resin for Cd and Pb metals in food and water [8], modified C18 for Cd, Cu and Pb metals in water [9], polystyrene-divinylbenzene is functioned with 2-hydroxyacetophenone for Cd, Co and Ni metals in sediments [10], octadecyl silica membrane discs are modified with 8-hydroxyquinoline for Cd and Pb metals In seafood [11], ferrous magnetite nanoparticles are modified by SDS and 2-mercaptobenzothiazole [12], Nano Graphene modifies 2-propyl-piperidine-1 carbodithioate [13]. The results showed that SPE is an effective method for the pre-concentration of metals in various sample matrices or to increase the detection limit of metal.

MATERIALS AND METHODS
Materials

All chemicals and reagents were of analytical grade.Ultrapure water was used in all experiments. Cd(II) Standard solution and calibration solutions of Cd(II) were prepared from Cd(II) standard solution 1000 ppm traceable NIST SRM, purchased from Merck (Darmstadt, Germany) in acidic medium diluted to 100 mL with ultrapure water. Nitric acid (65%) were purchased fromMerck (Darmstadt,

Germany). Dowex 50WX2 hydrogen form resin beads purchased from Sigma-Aldrich, USA with particle size100-200 mesh.

Methods

Shimadzu, AA-7000 model flame atomic absorption spectrometer was used. Background correction was made with a deuterium lamp. The operating conditions for Cd lamp was 8 mA lamp current wavelength 228nm.

A glass column (length, 30 cm and inner diameter,1.0 cm) was used. A piece of glass wool, 500 mg of Dowex resin 50WX2 and again a piece of glass wool were placed. Dowex50WX2 resin was preconditioned before use by treating 50 mL of blank solution which has been adjusted to pH 3 using 0.1 mol L^{-1} HNO_3 and/or NaOH solutions and this solution was passed through the columnat a flow rate of 1 mL min^{-1}.

The effect of pH was observed by passing 50 ml of model solution containing Cd 100 μg L^{-1} at a flow rate of 1 mL min^{-1} with pH ranges from 1 to 6. The retained Cd(II) ions on the resin were eluted by using 5 ml of 1 mol L^{-1} HNO_3 solutio (n=3). Eluent was analysed using flame-SSA.

The effect of the flow rate was observed by passing 50 ml of model solution containing Cd 100 μg mL^{-1} at the optimal pH that obtained from the results of previous experiments with a flow rate from 0.6 to 2.8 ml min^{-1}. The retained Cd(II) ions on the resin were eluted using 5 ml of 1 mol L^{-1} HNO_3 solution (n=3). Eluent was analyzed using flame-SSA.

The effect of volume of eluent HNO_3 1N was observed using 5 ml and 10 ml of HNO_3 1N to elution the retained of Cd(II) ions on the resin (n=3).

The optimum conditions of pH, Flow rate and volume of eluent, used to determination of tap water samples spiked with Cd 10 μg L^{-1}. The variation of samples volume are 50, 100, and 200 ml (n=3).

Determination of the detection limit by measuring the sample solution containing1μg L^{-1} (n=7). Accuracy and precision were carried out by measuring the sample solution spiked with CRM Cd solution traced to NIST 10μg L^{-1} under optimum conditions (n=7).

Data Analysis

Data evaluatin use equation as follows:

$$\% R = \bar{x}/\mu\ 100\% \dots\dots\dots\dots\dots\dots\dots (1)$$

where is:
$\bar{x}$= avarage result test

μ = target value of model or sample solution

$$\%RSD = \frac{sd}{\bar{x}} \, 100 \ldots\ldots\ldots\ldots.(2)$$

Requirement: RSD ≤ 0.67 x $2^{1-0.5 \, \log C}$

$$LoD = 3sd \ldots\ldots\ldots\ldots\ldots(3)$$

$$LoQ = 10sd \ldots\ldots\ldots\ldots\ldots(4)$$

where is:
LoD= Limit of Detection
LoQ=Limit of Quantification

RESULTS AND DISCUSSION
pH Effects

Effect of pH in solid phase extraction is an important parameter. Therefore, in this experiment the effect of pH solution to adsorb of Cd(II) on the recovery was studied firstly. The effect of pH was observed with pH ranges from 1 to 6 (n=3).
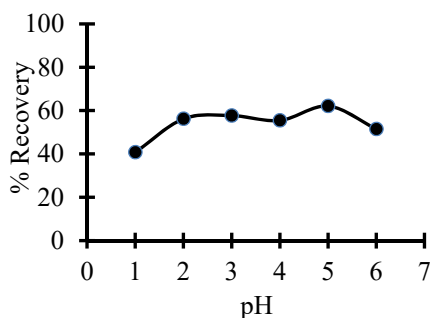

Figure1. Effect of pH on the recoveries of Cd (n=3)

Effect of pH was observed by passed through the Dowex 50WX2 resin 50 ml of 100 µg L⁻¹Cd(II) solution with a flow rate 1 ml men⁻¹. The retained Cd(II) on the Dowex 50WX2 resin was eluted by 5 ml of 1 mol HNO₃. The results can be seen in Figure 1.

The adsorption Cd(II) encreased in pH range 1-5 and the higher pH than 5 adsorption decreased.The low adsorption at pH below 5 is due to competition from H⁺ and Cd(II) ions in the solution to bind with sulfonate active groups of DOWEX 50WX2 resin. At pH 5, the protonated sulfonate groups release H⁺ and form negatively charged active sites that capable to adsorb Cd(II) effectively. At pH 6, the adsorption of Cd(II) ions decreased, because of forming Cd(OH)⁺and Cd(OH)₂in the solution[1].

Flow Rate Effect

The solution flow rate in the column will greatly affect the interaction time between the solution and the resin. The faster the flow rate, the shorter the interaction between the Cd ions in the solution and

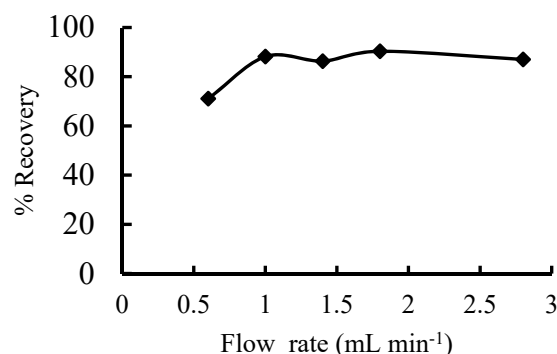the resin, so that the number of Cd^{2+} ions adsorbed by the resin is not optimal.

Figure 2. Effect flow rate on the recoveries of Cd (n=3)

The optimum flow rate as shown in Figure 2 is 1 ml min⁻¹.A flow rate of more than 1 ml min⁻¹ does not give higher adsorption of Cd^{2+} ions because the adsorption has taken place optimally. So that a flow rate of 1 ml min⁻¹was used for the next testing process.

Effect of Eluent Volume

The effect of eluent volume greatly affects the release of Cd^{2+} ions which have been adsorbed by Dowex 50WX2 resin.
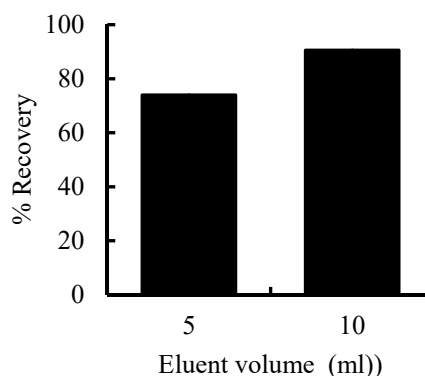

Figure 3. Effect of eluent volume on the recoveries of Cd (n=3)

Insufficient eluent volume to elute Cd^{2+} ions will cause Cd^{2+} ions to remain in the resin, which will affect the final result. In this study, the volume of 1 N HNO₃ eluent was obtained to elute optimal Cd^{2+} at a volume of 10 ml with a recovery value of 91% ± 5% (n=2).

Effect of Sample Volume

Determination of the optimum sample volume was carried out at pH 5 and flow rate of 1 ml min⁻¹using 10 ml of HNO₃ eluent volume 1 N, the optimum sample volume was obtained as shown in
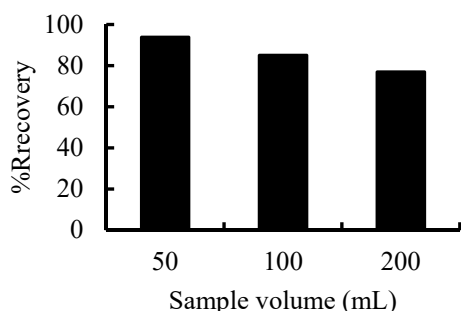
Figure 4, it was 50 ml with a recovery of 94% ± 8% (n=3).

Figure 4. Effect of sample volume on the recoveries of Cd

Characteristics of combined method with SPE and Flame-AAS

The calibration curve is the relationship between the absorption value and the Cd level in the solution. Thecalibration curve is made in the concentration range 0.01 - 0.5 mg L^{-1} in Figure 6.
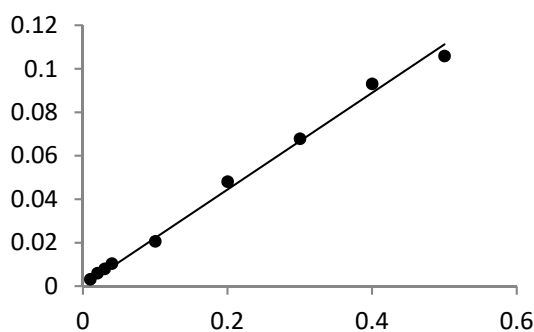

Figure 4. Calibration curve of Cd

The correlation coefficient (R^2) was 0.9977 with the linear line equation Y = 0.22246X + 0.00000.

Table 1. Detection limit of Cd

No	Concentration (mgL^{-1})		%R
	Initial Conc	Result	
1	0.001	0.0007	72
2	0.001	0.0008	81
3	0.001	0.0008	81
4	0.001	0.0005	54
5	0.001	0.0007	72
6	0.001	0.0007	72
7	0.001	0.0007	72
AV (X)		0.00072	72
SD		0.0001	
%RSD = SD/x		12.5	
S/N= X/SD		8	
MDL = 3 SD		0.0003	
LoQ= 10SD		0.0009	

The detection limit (3sd) was determined used model solution.The 500 ml of ultra pure water was spiked with 5 ml of CRM Cd 0.102 ± 0.003 mg L^{-1}.

This solution equal with Cd concentration in the solution was 0.001 mg L-1. The measurements under optimum conditions with 7 replicates[14].

Table 2 Acceptance criteria for LoD of Cd

No	Requirement	Result	Conclusion
1	%RSD = 21.44	5.89	accept
2	%R = 70% -	74	accept
3	S/N = 2.5 - 10	16.98	accept
4	MDL<spike	0.0003<0.001	accept
5	Spike conc< 10	0.001<0.003	accept
6	MDL < BML	0.0003<0.01	accept
7	If MDL accept,	0.0003	accept

In Table 1, the detection limit with an SPE is 0.0003 mg L^{-1} with an acceptance criteria fulfill the requirements (Table 2). This value is much smaller than the detection limit without SPE is 0.0077 mg L^{-1} [15]

Table 3. Accuracy of Cd

No	Concentration(mg/L)		%R
	InitialConc	Result	
1	0.0100	0.0084	84
2	0.0100	0.0095	95
3	0.0100	0.0089	89
4	0.0100	0.0093	93
5	0.0100	0.0092	92
6	0.0100	0.0100	100
7	0.0100	0.0098	98
AV (X)		0.00929	93
SD		0.0005	
%RSD = SD/X		6	

Evaluation of the results in Table 4 was carried out by comparing the test results with the acceptance criteria for accuracy (%R) in the range 75-120% [14] and% RSD < 21.7% [15].

Table 4. Acceptance criteria of Cd

No	Requierement	Result	Conclusion
1	%RSD = 21.7	6	Accept
2	%R = 70% - 125%	93	Accept

Determination of the accuracy was carried out as the detection limit determination, with a concentration of solution Cd 0.01 mg L^{-1}preparing from dilution of 0.102 ± 0.003 mg L^{-1}CRM Cd solution. The results in Table 3 showed that the concentration of Cd was 0.0093 ± 0.0005 (n=7) with recovery of 93 ± 6%.

Based on the evaluation of the accuracy of the SPE-AAS-flame method, this method is acceptable because this method give good accuration and low limit detection.

CONCLUSION

The optimum conditions for determination of Cd with SPE-AAS-flame method using Dowex 50WX2 resin as adsorbent are solution pH 5, 1 ml min^{-1} of flow rate, 10 ml of HNO$_3$ as eluent and 50 ml sample volume.The SPE-AAS-flame method with Dowex resin as a Cd metal adsorbent can be used as a new method as the development of the AAS-flame method for metal contamination analysis in clean water because it can detect Cd metal up to 0.2697 µg L^{-1} and with good accuration.

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