การตรวจสอบความสมเหตุสมผลของวิธีการวิเคราะห์หาปริมาณตะกั่วและแคดเมียมในน้ำธรรมชาติโดยเทคนิคเฟรมอะตอมมิคแอบซอร์พชั่นสเปคโตรเมทรี

Method validation for determination of lead and cadmium in natural water using flame atomic absorption spectrometry (FAAS)

อังค์วรา พูลเกษม[1]* , นีระนาถ แจ้งทอง**
Angwara Poolkasem[1]*, Neeranart changthong**

บทคัดย่อ

การตรวจสอบความสมเหตุสมผลของวิธีวิเคราะห์หาปริมาณตะกั่วและแคดเมียมในน้ำธรรมชาติ 3 ชนิด ได้แก่ น้ำบาดาล น้ำฝน น้ำแม่น้ำ ดำเนินการตามวิธีที่ปรับจากวิธีมาตรฐาน AWWA 21stEd.(2005) โดยใช้เทคนิค เฟรมอะตอมมิคแอบซอร์พชั่นสเปคโตรเมทตรี เพื่อนำมาใช้ในการทดสอบตัวอย่างน้ำต่อไป จากการศึกษา ช่วงความเป็นเส้นตรงของวิธีวิเคราะห์ตะกั่ว พบว่ามีความเป็นเส้นตรงอยู่ในช่วง 1.5-0.1 มิลลิกรัมต่อลิตร ส่วนแคดเมียม อยู่ในช่วง 0.5-0.02 มิลลิกรัมต่อลิตร และค่าขีดจำกัดการตรวจวัดเท่ากับ 0.02 มิลลิกรัมต่อลิตร และ 0.005 มิลลิกรัม ต่อลิตร ตามลำดับ ส่วนค่าขีดจำกัดการตรวจหาปริมาณสำหรับตะกั่วและแคดเมียมเท่ากับ 0.1มิลลิกรัมต่อลิตร และ 0.02 มิลลิกรัมต่อลิตร ตามลำดับ ในการศึกษาความลำเอียงและความเที่ยงของวิธีสำหรับตะกั่วและแคดเมียม โดยใช้ตัวอย่างที่เติมสารละลายมาตรฐาน 3 ระดับความเข้มข้น พบว่ามีค่าคืนกลับอยู่ในช่วงร้อยละ 110-91 และ 105-98 และมีค่าความเบี่ยงเบนมาตรฐานสัมพัทธ์อยู่ระหว่าง 3.2-0.8 ตามลำดับ ค่าคืนกลับและค่าความเบี่ยงเบน มาตรฐานสัมพัทธ์ที่ได้มีค่าอยู่ในเกณฑ์การยอมรับ และเมื่อคำนวณค่าความไม่แน่นอนของการวัดที่ระดับความเชื่อมั่นร้อยละ 95 ของตะกั่วและแคดเมียม พบว่า มีค่าน้อยกว่าร้อยละ 15 ซึ่งเป็นค่าเป้าหมายที่กำหนดไว้ ดังนั้น จึงสรุปได้ว่าวิธีการวิเคราะห์นี้เหมาะกับการใช้งานตามวัตถุประสงค์

Abstract

The method validation for determination of lead and cadmium in natural water, i.e. deep well water, rain and river water was investigated by flame atomic absorption spectrometry using the modified method based on AWWA 21st Ed., 2005 prior to the use in routine work. The characteristics of the method showed that the linear range of lead (Pb) and cadmium (Cd) were 0.1 – 1.5 mgL^{-1} and 0.02 – 0.5 mgL^{-1}, the detection limits were 0.02 and 0.005 mgL^{-1}, and the limits of quantitation were 0.1 mgL^{-1} and 0.02 mgL^{-1}, respectively. Percentage recovery of lead and cadmium were 91-110% and 98-105% respectively. Relative standard deviations for both elements were between 0.8-3.2. The percentage recovery and relative standard deviation were within acceptance limit. In addition, the percentage measurement uncertainties at 95% confidence level of cadmium and lead were less than 15% throughout concentrations of working range that subjected to the target uncertainty. Therefore, this validated method was fit for the intended use.

คำสำคัญ : แคดเมี่ยม , ตะกั่ว , น้ำธรรมชาติ ,

Keywords : Cadmium, Flame atomic absorption spectrometry, Lead, Natural water

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[1] Chemistry Program, Department of Science Service
*E-mail address: angwara@dss.go.th
** E-mail address: Neeranart@dss.go.th

1. Introduction

Although water has the simple formula H_2O, it is a complex chemical solution. “Pure” water essentially is nonexistent in the natural environment. Natural water, whether in the atmosphere, on the ground surface, or under the ground, always contains dissolved minerals and gases as a result of its interaction with the atmosphere, minerals in rocks, organic matter, and living organisms. One of the most importance problems in water is contamination of heavy metals such as lead and cadmium. Lead and cadmium are known to be toxic agents that accumulate in the living organisms and present high-toxic potential over a lifetime [1, 2]. They may enter the organism via the alimentary and/or respiratory tract, and the main non-occupational sources of these metals are foodstuffs, drinking water, and air [3]. Other important lead and cadmium sources in foodstuff and environment are the intense industrial activities leading to a pronounced increase in the concentrations of several heavy metals in natural water, soils, and plants [4]. Biological interest in lead and cadmium has centered mainly on their properties as highly toxic cumulative poison in humans and animals [5]. As a consequence, efforts towards the development of more effective, cheaper, faster, preciser, and more accurate approaches for the determination of these metals in biological and environmental materials have been increasing. The most popular instrument which is used for determination of these metals is flame atomic absorption spectrometry (FAAS). The validation of the analytical methods has become a basic prerequisite for laboratories that work in official biomonitoring control and risk assessment. However the validated methods in a laboratory should be checked and revalidated whenever they are adopted by another laboratory. The aim of this study is to validate a method of analysis of lead and cadmium in three types of natural water, (including deep well water, rain, and river water) using flame atomic absorption spectrometer, which is the modified method based on the method described in AWWA Edition 21st,2005,[7].

2. Experimental

2.1 Apparatus and reagent

2.1.1. A Varian (Mulgrave, Vic., Australia) Model Spectra AA 220 flame atomic absorption spectrometer was used for the analysis. The operation parameters of instruments for lead and cadmium were set according to the manufacturer recommendation.

2.1.2. All chemicals were of analytical-reagent grade (Merck). Distilled-deionized water (Milli-Q Millipore 18.2 $M\Omega cm^{-1}$ resistivity) was used throughout the experimental work.

2.1.3. Laboratory glassware was kept overnight in a 10% v/v nitric acid solution and then rinsed with distilled-deionized water.

2.1.4. Working standard solutions were prepared fresh daily by appropriately stepwise dilution of stock standard solution of lead and cadmium (1000 mgL^{-1} in 0.5 $molL^{-1}$ nitric acid) with 1% (v/v) nitric acid. Stock solutions of lead and cadmium used for checking accuracy of the proposed method were prepared from cadmium standard reference material NIST SRM 3108 and lead standard reference material NIST SRM 3128, respectively.

2.2 Sample handling and preparation

Natural water samples (deep well water, river water and rain) were collected and immediately filtered through 0.45 micrometer precleaned membrane immediately after sampling, and were acidified to pH 2.0 with nitric acid and stored in polyethylene bottles prior to analysis. The bottles were previously washed with the 10% v/v nitric acid afterward with distilled-deionized water and sample respectively.

2.3 Analytical procedures

2.3.1. Digestion procedures

A 100 mL well-mixed, acid-preserved sample was transferred to flask. In fume hood, the sample solution was added with 1 mL conc. nitric acid before slowly boiled and evaporated to the lowest volume possible before precipitation occurs (about 10 to 20 mL). The flask was left cool then it was washed down with distilled-deionized water and filtered through filter paper. The filtrate was transferred to a 100 mL volumetric flask, adjusted with distilled-deionized water to mark, and mixed thoroughly. Portions of this solution were aspirated to FAAS.

2.3.2. Flame atomic absorption spectrometry analysis.

The instrumental parameters with operational conditions for lead and cadmium were summarized in Table 1. A blank consisting of deionized water containing the same concentration of acid in standards and samples was aspirated to the FAAS for zero setting. Mixed standard of lead and cadmium for calibration curve were measured for absorbance. the sample solution was measured and the concentration was read directly from the instrument and as the sample has been pre-concentration, the sample was multiplied by the appropriate pre-concentration factor.

Table 1 Instrumental condition for flame atomic absorption spectrometer

Element	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Air flow (Lmin^{-1})	Acetylene flow (Lmin^{-1})	Aspiration flow (mLmin^{-1})
Lead	228.8	1.0	10.0	13.50	2.00	4.0
Cadmium	217.0	0.5	4.0	13.50	2.00	4.0

2.3.3. Validation of analytical method

The characteristic parameters of the analytical methods, following the recommendations of EURACHEM guide [6], included the limit of detection (LOD), limit of quantification (LOQ), linear range, precision, accuracy, recovery, matrix effect and uncertainty were determined for each metal by using fortified sample and reagent blank.

The limits of detection and limits of quantitation were studied by measurement of 7 independent sample blanks. LOD was mean of sample blank values plus three standard deviation while estimated LOQ was mean of sample blank values plus ten standard deviation.

The range of linearity was evaluated by checking the correlation coefficient (r) of the calibration curve that was considered acceptable when r 0.995.

The accuracy and precision were done by analyses samples which spiked with the right amount of standard solutions of lead and cadmium in three different levels of concentration (mgL^{-1}) in a single batch according to Table 2 and concentration of level 1 was LOQ.

Table 2 Concentration of fortified samples for accuracy and precision study (mgL^{-1})

Element	Level 1	Level 2	Level 3
Cadmium (Cd)	0.02	0.10	0.20
Lead (Pb)	0.10	0.50	1.00

The analytical repeatability was calculated using the relative standard deviation for 7 independent samples. The recovery was calculated as 100 C/spiked concentration where C is the element concentration found. An acceptance limit between 90 and 110% was considered as valid according to the criteria described in AWWA Edition 21st, 2005 [7].

Moreover, the matrix effect was studied by plotting a curve between absorbance (y axis) and concentration (x axis) of fortified samples in three different levels of concentration then compared the slope with slope of calibration curve.

To demonstrate the quality of the results produced and its fitness for the purpose measurement uncertainty was estimated. All possible sources of uncertainty were identified which is shown in figure 1. Uncertainty values in Table 3 are expanded uncertainty, at 95% confidence level with coverage factor, k, of 2. Combined standard uncertainties on the final results were obtained by propagating together individual uncertainty components according to the ISO/GUM [8].

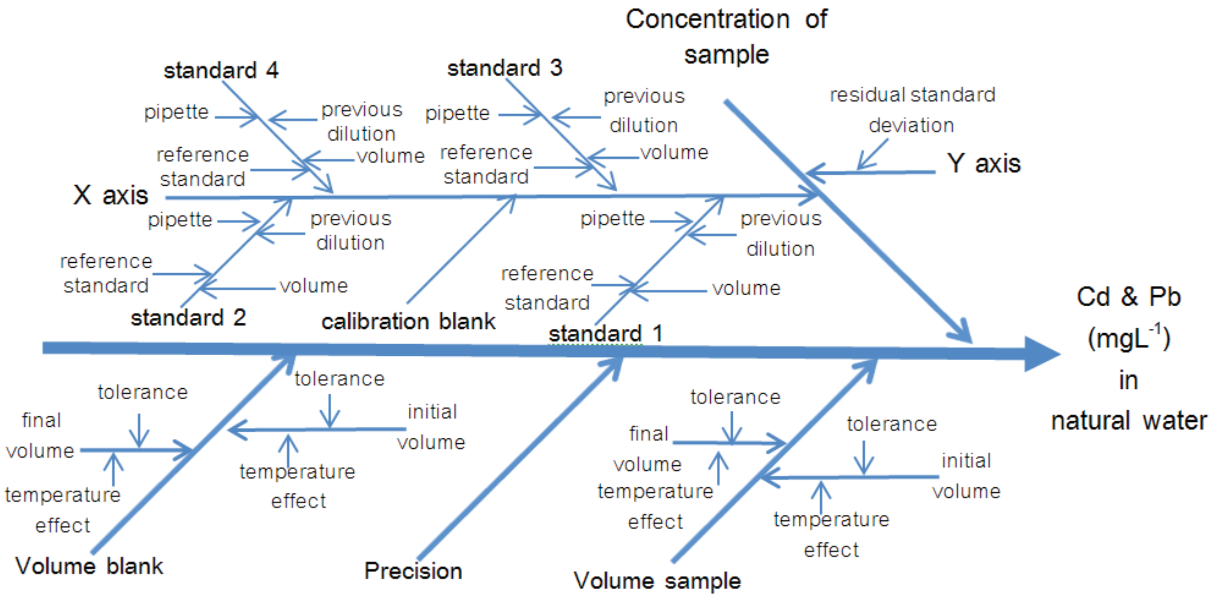


Figure 1 Cause and effect diagram for the determination of lead and cadmium in natural water

3. Results and discussion

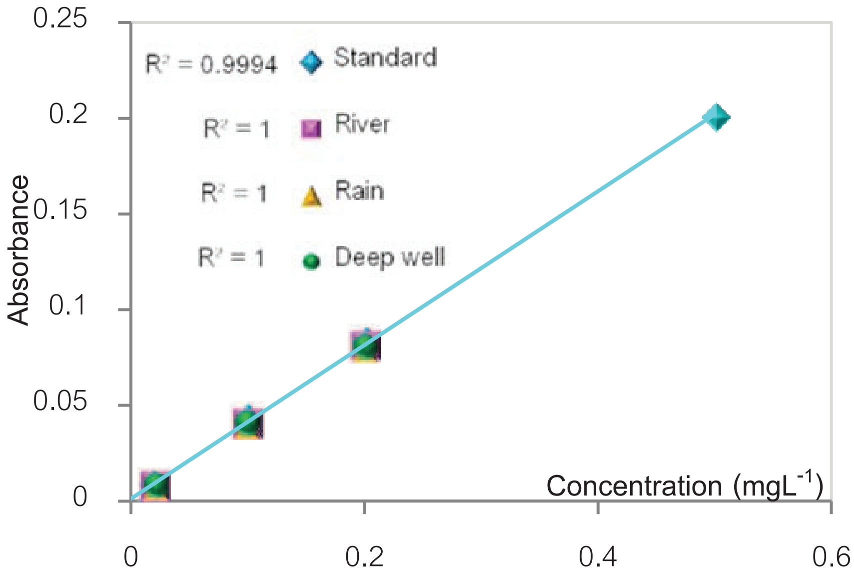
The overall performance characteristic of the method proposed is summarized in Table 3 and 4. Correlation coefficients of lead and cadmium calibration curves were better than 0.995. The validation results of present method were evaluated; the recoveries of analytes spiked into water samples were within the acceptance of 90-110 % as shown in Table 4. Good agreement was obtained between the added and analyte recovered content using the experimental procedure, thus confirming the accuracy of the procedure. For both elements analyses, percentage of relative standard deviation for repeatability (%RSD) did not exceed the limit of 8% and the expanded standard measurement uncertainties were subject to the target measurement uncertainty of 15%. The matrix effects shown in Figure 2 which showed that the slopes of fortified samples were not different from calibration curves for both elements indicated that there were no matrix effects.

Table 3 Analytical characteristics of the proposed method

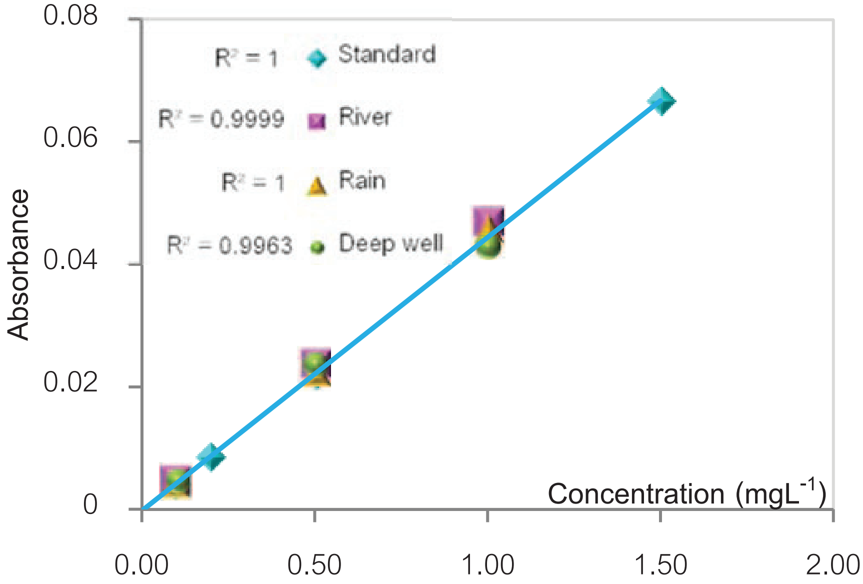
Parameter	Cadmium (n=7)	Lead (n=7)
Limit of detection (LOD), mgL^{-1}	0.005	0.02
Limit of quantitation (LOQ), mgL^{-1}	0.02	0.1
Linear range, mgL^{-1}	0.02 - 0.50	0.10 - 1.50
Precision as %RSD (max)	3.2	3.2
% Measurement uncertainty	12.5	4.84

Table 4 Determination of lead and cadmium in natural water samples (n=7)

Concentration of metals (mgL^{-1})	Deep well water		River water		Rain	
	Found (mgL^{-1})	Recovery (%)	Found (mgL^{-1})	Recovery (%)	Found (mgL^{-1})	Recovery (%)
Cd						
0	0.00	-	0.00	-	0.00	-
0.02	0.02	105	0.02	100	0.02	98
0.10	0.10	101	0.10	101	0.10	99
0.20	0.20	100	0.20	100	0.20	99
Pb						
0.00	-0.10	-	-0.01	-	-0.01	-
0.10	0.11	110	0.11	110	0.10	95
0.50	0.53	106	0.54	107	0.48	95
1.00	1.02	101	1.03	103	0.98	98



(a) Cadmium



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(b) Lead

Figure 2 Comparison of matrix fortified samples versus standard curve of cadmium and lead analysis in natural water.

4. Conclusion

The validated method presented in this paper is fit for the intended use. Therefore the test method can be used for routine work and monitoring natural water quality in any places which will improve the quality of life of people. In addition, the content of lead and cadmium in the natural collected in Ang Thong Province, Thailand were determined using this method and it was found that the concentrations of both metals were lower than the limits specified by Thailand standard of water [9].

5. Acknowledgment

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