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Verification of the Determination Method of Dissolved Metal Content using ICP-OES and Its Application for River Water in Bandar Lampung City

Ni Luh Gede Ratna Juliasih [a,1], Diky Hidayat [b,2], Purna Pirdaus [a,3], Rinawati [a,b,4,*]

[a] Chemistry Department, Faculty of Mathematics and Natural Science, Lampung University, Bandar Lampung, Indonesia
[b] Integrated Laboratory and Centra Innovation Technology, Lampung University, Bandar Lampung, Indonesia

Corresponding author: (4,) rinawati@fmipa.unila.ac.id; (1) niluhratna.juliasih@fmipa.unila.ac.id; (2) dikyhidayat93@gmail.com; (3) purnawalur@gmail.com

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Abstract

Method verification for metal analysis (Cd, Cr, Cu, Ni, Co, and Mn) in surface water using Inductively Coupled Plasma (ICP) was carried out to evaluate the method's performance in the laboratory-based on US Method EPA 200.7. The verified method is used to determine the metal content in river water flowing in Bandar Lampung. The results showed that the method used had good linearity with a regression coefficient of more than 0.995. This method's accuracy is expressed by the %RSD (relative standard deviation), which is in the range of 3.145 to 4.345% and meets the acceptance requirements with a %RSD value less than ⅔ CV Horwitz. The method accuracy obtained from the spiking analysis gives a range of 80-110% for the analysis of 1 mg/L and meets the acceptability required by AOAC. Overall, the performance of the method used is suitable for the analysis of metals in surface water. This method was applied for metal analysis in river water samples in several places in Bandar Lampung, which were the Palang Besi river (A1), the Way Balau Kedamaian river (B1), the Way Balau Kedaton river (C1), the Way Kuala river (D1), the Sumur Batu Kahuripan river (E1), Sumur Putri river (F1), and Muara Kahuripan river (G1). The concentrations of Cd, Cr, Cu, Ni, and Co metals were under the LoD method, while the Mn concentration was above the LoD method in river water samples.

1. Introduction

The river is one of the essential components for the continuity of human life and other living things, including maintaining the environmental ecosystem's balance. However, an increasing population, accompanied by an increase in human activities, causes the potential for river pollution to be even higher. Heavy metals have received attention because of their persistence, bioaccumulation, and biomagnification in the food chain, which are toxic and endanger human health and aquatic organisms [1, 2]. Heavy metals such as Pb, Cd, Cr, Cu, Ni, Co, and Mn are known to affect health significantly. Some of the diseases caused by heavy metal poisoning are anemia, various organ disorders, and decreased intelligence. Children are a group at high risk of heavy metal poisoning [3]. High metal content can also cause significant negative effects on the life of invertebrates, fish, and humans [4]. The presence of heavy metals with high concentrations in the river water environment has been reported in several areas [1, 5, 6, 7, 8, 9, 10, 11]. Considering the negative impacts caused by heavy metals, it is crucial to monitor heavy metals in waters using a method that provides valid results.

The factors that influence the laboratory test results are competent personnel, calibrated equipment, supportive laboratory resources, and valid analysis methods. Guarantee of valid analysis results is carried out through validation of the method used. Method validation is carried out by providing objective performance evidence to show that the laboratory can conduct tests with valid results. Several standard methods are available, such as methods from AOAC (Association of

Official Analytical Chemist), ASTM (American Standard Testing and Materials), SNI (Indonesian National Standard), and others. However, if this method is being used for the first time in a laboratory, limited validation or verification is required. The method verification stage is almost the same as validation. It is just that the parameters performed are not as complete as the validation [12]. The verification parameters of a method include linearity, test precision, accuracy, and detection limits.

Linearity is the ability of an analytical method to respond directly to an analyte's concentration in the sample. Linearity is a measure of how well the calibration curve relates the response (y) to concentration (x). Linearity can be measured by taking a single measurement at different concentrations, then analyzed using the correlation coefficient value [13].

Precision is a measure that shows the degree of closeness of the value between the results of repeated tests [14]. Precision can be done using repeatability techniques using repetitive procedures, tools, analysts, and periods. Precision is usually expressed as the Relative Standard Deviation (RSD).

Accuracy is a measure that shows the closeness of the test results obtained to the actual value. Accuracy can be done in 3 ways, using Certified Reference Material (CRM), comparing with other methods, and adding several standards (spiking). [15] determined the HPLC method's accuracy for determining vitamin B1. Determination of accuracy by adding spiking and expressed as a percentage of recovery has also been carried out to determine arsenic contamination in food [16].

Limit of detection (LoD) is the lowest limit of analyte concentration that can still be detected and can be significantly distinguished from blanks. Limit of Quantification (LoQ) is the lowest limit of analyte concentration detected with an acceptable level of accuracy and precision [13].

Testing of metal levels in water can be carried out by several methods, including chromatographic methods such as ion chromatography [17, 18] and spectrophotometric methods using UV vis spectrophotometer [19], using atomic absorption spectrophotometer (AAS) [10], and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) [20]. ICP-OES is an instrument that can be used for measuring metal content in water. The excitation source on the ICP is in the form of plasma generated from the electromagnetic waves of a radio frequency generator through an induction coil. This excitation source produces a flame with a higher temperature, which is higher than AAS, thereby minimizing the possibility of chemical disturbance and increasing the method's sensitivity. This tool can simultaneously measure analytes with high sensitivity and provide a low analyte detection limit to ppb units. ICP is widely used for metal analysis in soil, sediment, and water [20, 21, 22].

Considering the need for a valid method to determine the levels of heavy metals in the aquatic environment, verification was carried out on the heavy metal testing method using the ICP-OES published by the EPA, which was used in the Integrated Laboratory and Technology Innovation Center (LTSIT), University of Lampung, before the method was used for routine metal analysis. This study verifies the analysis method for metal content in river water with ICP-OES, including linearity, accuracy in %recovery, precision testing, LoD and LoQ tests, and using these methods to determine metal content in Bandar Lampung city rivers.

2. Methodology

2.1. Equipment and Materials

The tools used are the Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) Varian 715-ES, Kern ABJ-220-4NM analytical balance with an accuracy of up to 0.1 mg, sample containers, and glass tools such as the Erlenmeyer, beaker glass, volumetric flask, filter funnel, and volume pipette. The chemicals used include a standard solution of ICP multi-element 1000 mg/L (containing heavy metals analyzed: Pb, Cd, Cu, Ni, Co), paint. 1.09498.0001 Merck, Germany; Nitric acid (HNO3) 65% Merck; Aqua pure (Ultrapure water) ASTM type 1, filter paper Whatman No. 41 (size 0.45 µm).

2.2. Surface water sample preparation

Samples were taken from surface water in several places in the rivers around Bandar Lampung, namely the Palang Besi river, the Way Balau Kedamaian river, the Way Balau Kedaton river, the Way Kuala river, the Sumur Batu Kahuripan river, the Sumur Putri river, and the Muara Kahuripan river. The sampling locations are presented in Figure 1 and Table 1.

The surface water sample was filtered with Whatman No. 41. Then the filtrate was pipette ± 20 mL. The filtrate was put into a 50 mL polypropylene bottle, added HNO_3 (1: 1) to make the acid concentration at the aliquot approaching 1% (v/v) HNO_3 solution. The mixture was then closed and homogenized and ready to be measured using the ICP-OES [23].

Figure 1. Location for River Water Sampling in Bandar Lampung City

Table 1. Code and coordinates of sampling locations

Lokasi Sampling	Kode Sampel	Koordinat
Palang Besi	A1	5°40’13’’ SL 105°21’22’EL
Way Balau Kedamaian	B1	5°24’21’’ SL 105°28’64’EL
Way Balau Kedaton	C1	5°38’27’’ SL 105°26’40’EL
Way Kuala	D1	5°44’79’’ SL 105°30’16’EL
Sumur Batu Kahuripan	E1	5°43’39’’ SL 105°25’61’EL
Sumur Putri	F1	5°43’91’’ SL 105°24’58’EL
Muara Kahuripan	G1	5°45’36’’ SL 105°26’29’EL

2.3. Preparation of Standard Working Solution

A standard working solution was prepared by a multilevel dilution technique of a multi-element standard solution of 1000 mg/L diluted with 1% HNO_3. The concentration of the standard working solution used is 0.01; 0.05; 0.10; 0.50; 1.00; 2.50 and 5.00 mg/L.

2.4. Verifying Method

2.4.1. Linearity Testing

The prepared standards were sorted from lowest concentration to the highest concentration. Standards were measured in the following order: blank, standard 1, standard 2, standard 3, standard 4, standard 5, standard 6, standard 7. A calibration curve was created, and the linearity value was determined based on the correlation coefficient.

2.4.2. Accuracy

Accuracy was determined as a percentage of recovery (%R). The sample solution was prepared in 12 containers, and each included 20 mL of sample. Each of the seven prepared samples was then added with 0.2 mL of analyte derived from a standard solution of 100 mg/L mixed metal. The sample to which the analyte had been added was further added with HNO_3 (1 + 1) to make the acid concentration in the aliquots closer to the 1% (v/v) HNO_3 solution. The solution was then made into pairs consisting of the sample solution and the sample solution that had been spiked so that seven pairs of solutions were obtained. The solution was homogenized and ready to be analyzed. The measurement results were compared with the theoretical analyte concentration, which was added and calculated by equation (1).

$$\%\, Recovery = \frac{(C1-C2)}{C3} \times 100 \qquad (1)$$

where: %R = percentage of recovery

C1 = the concentration of the sample analysis results added to the analyte target standard

C2 = concentration of sample analysis result

C3 = the target standard concentration of the analyte added to the sample

2.4.3. Precision

The precision parameter is calculated using the repeatability technique. A total of 8 sample solutions were prepared, and each solution was then measured. The repeated analysis results then calculated the value of Relative Standard Deviation (% RSD) or the Coefficient of Variation (CV), then compared with 2/3 x CV Horwitz’s value. The standard deviation (SD) value is calculated using the formula in equation 2:

$$SD = \sqrt{\frac{\sum_i^n (x_i-\bar{x})^2}{n-1}} \qquad (2)$$

Note: SD = standard deviation
$\bar{x}$ = the average of the test values
x_i = nth test iteration
n = number of test repetitions

Furthermore, the value of %RSD, also known as %CV (Coefficient of Variance), was calculated using the equation (3).

$$\%RSD = \frac{SD}{\bar{x}} \times 100\% \qquad (3)$$

2.4.4. Detection Limit (LoD) and Quantification Limit (LoQ)

A blank sample was used to determine the detection limit (LoD) and limit of quantification (LoQ). A blank sample solution was prepared from a solution containing no analyte but with the same matrix as the sample solution. Six blank sample solutions were prepared and measured as the smallest concentration that the instrument could still detect. If the sample was not detected, then add a little bit of analyte as the smallest concentration. The standard deviation of the measurement results was calculated. The detection limit was counted three times the SD, and the quantification limit was calculated as ten times the SD.

3. Results and Discussion

3.1. ICP-OES optimization

ICP-OES optimization, including plasma flow rate, nebulizer pressure, pump speed, and other operational standards, needs to be done before measurement, as shown in Table 2. This equipment’s optimum conditions were also used to determine the optimum wavelength, which was the wavelength that gave the optimum emission intensity and was not disturbed by the intensity of other elements [24].

The results of wavelength selection can be seen in Table 3. Based on Table 3, it can be seen that the wavelength for each metal is different. The maximum wavelength indicates each metal’s optimum emission intensity resulting from emitting electrons of the excited metal element to a higher energy level and returning to the ground level by emitting each metallic element’s emission characteristic. This causes ICP to have high selectivity and less spectral disturbances like AAS [2]. Botes [25] stated that the ICP instrument could differentiate each element’s wavelength up to 0.1 nm.

Table 2. ICP-OES operating conditions

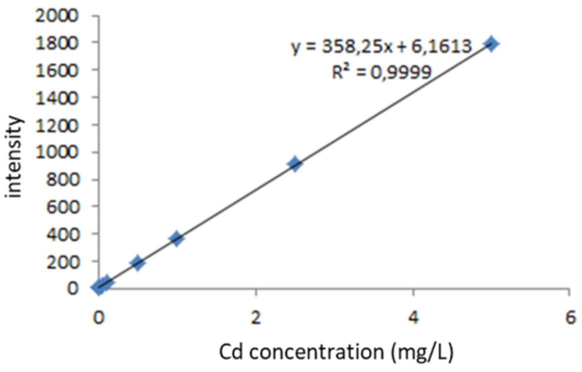
Instrument condition	Optimum conditions
Power (kW)	1.20
Plasma flow (L/minutes)	15.0
Auxiliary Flow	1.50
Nebulizer Pressure (kPa)	200
Viewing Height (mm)	8
Replicate Read Time (s)	5
Sample Uptake delay (s)	25
Instrument Stabilization delay (s)	15
Pump rate (rpm)	12
Rinse Time (s)	30
View	Radial View
Detector	Solid-State Detector (CCD Camera)
Nebulizer	V-groove Nebulizer
Spray Chamber	Sturman-Master Spray chamber
Torch	Quartz Torch ICP-OES Radial

Table 3. Wavelength selection

Element	Wavelength (nm)
Ni	231.604
Cu	327.395
Mn	257.610
Cd	214.439
Co	238.892
Cr	267.716

3.2. Linearity

Linearity describes the analytical method's ability to provide a proportional response to analytes' concentration in the sample. Linearity is determined from the correlation coefficient's value on the regression curve measured by the standard solution. Correlation coefficient values for verification of analytical methods are determined for each metal so that each metal has a calibration curve. Good linearity will give a correlation coefficient value close to number 1—the US.EPA 200.7 requires an acceptability value greater than 0.995 [23]. Metal-metal calibration curves (Cd, Cr, Cu, Ni, Co, Mn) can be seen in Figure 2. Figure 2 shows that the method's linearity is excellent, with a correlation coefficient of more than 0.995, which means it meets the USEPA 200.7 acceptance value requirements.



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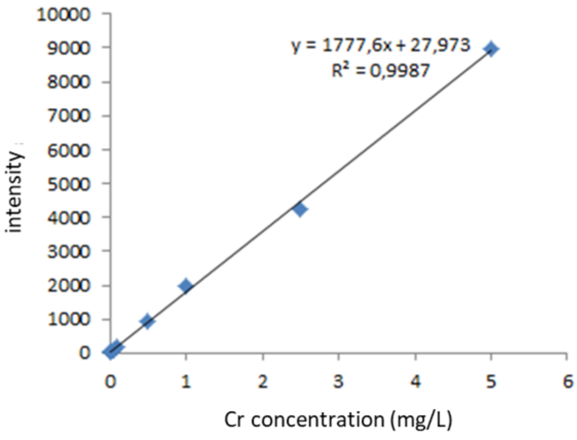

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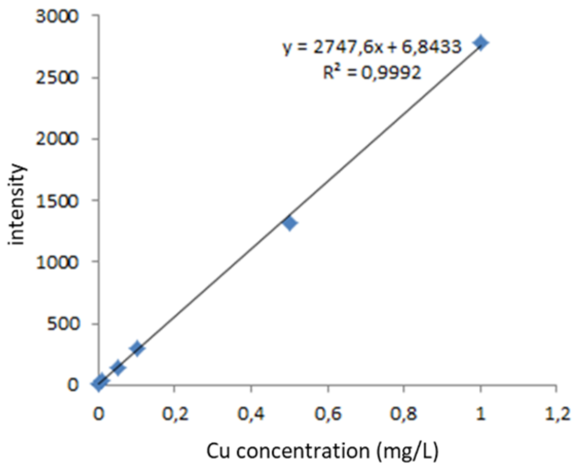

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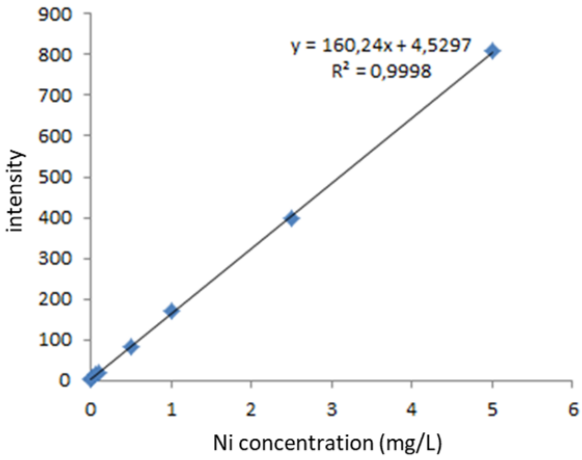

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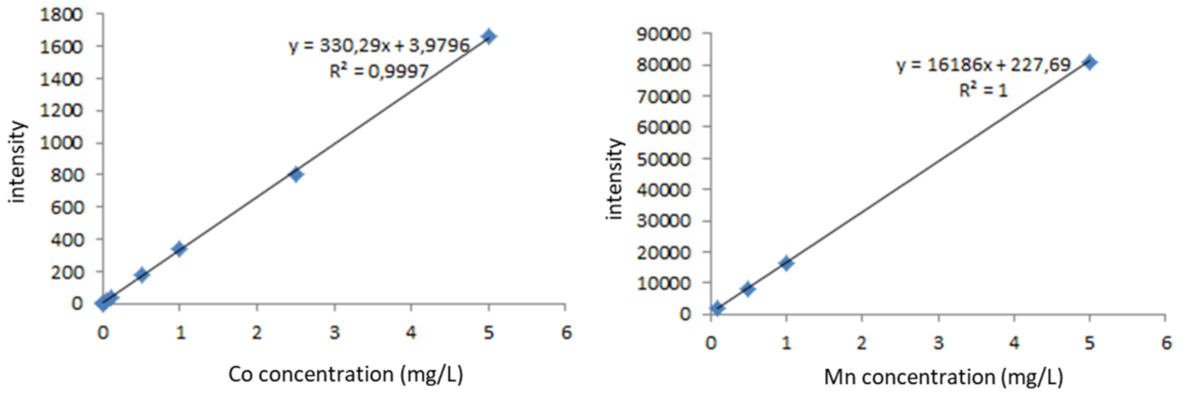

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Figure 2. Calibration curves for each metal: a) Cd, b) Cr, c) Cu, d) Ni, e) Co, f) Mn

Table 4. Equations and correlation coefficient values for metals Cd, Cr, Cu, Ni, Co, and Mn

No	Metal	Correlation coefficient equation	Correlation coefficient
1	Cd	y = 358.25x + 6.1613	0.9999
2	Cr	y = 1777.6x + 27.973	0.9987
3	Cu	y = 2747.6x + 6.8433	0.9992
4	Ni	y = 160.24x + 4.5297	0.9998
5	Co	y = 330.29x + 3.9796	0.9997
6	Mn	y = 16186x + 227.69	1.0000

3.3. Accuracy

Accuracy is expressed as the percentage of recovery (%recovery) of the standard solution added to the sample matrix. The %recovery value is obtained from comparing the difference in the analyte concentration in the sample after and before being spiked with the standard concentration spiked into the sample as in the previous equation 1. According to the AOAC Official Methods of Analysis (2012) Appendix F, the maximum range value of %recovery for analyte levels of 1 mg/L is 80-110% [26]. The accuracy of the verification results of this method can be seen in Table 5.

Table 5 shows that this method shows the percentage of recovery in the range of 87.10% to 94.93%, which means that the% recovery method for the target metal meets the acceptance requirements. The% Recovery value obtained is then carried out by the t-test with the following formula:

$$t_{calc} = \frac{1-\%_{recovery}}{SD_{recovery}} \quad (4)$$

If $t_{cal} < t_{table}$, then the measurement result does not need to be corrected with the %Recovery value obtained, and vice versa. The calculation results show that the value of $t_{cal} < t_{table}$, at the level of P = 0.05, so that the measurement results do not need to be corrected.

Table 5. Percentage of recovery values for Cd, Cr, Cu, Ni, Co, and Mn metals

Metals	C2 (mg/L)	C1 (mg/L)	C3 (mg/L)	Recovery (%)	Average Recovery (%)
Cd	0.636	1.506	1.00	87.09	87.10
	0.616	1.531	1.00	91.52	
	0.643	1.479	1.00	83.63	
	0.660	1.546	1.00	88.57	
	0.642	1.491	1.00	84.85	
	0.614	1.458	1.00	84.41	
	0.659	1.555	1.00	89.61	
Cr	0.349	1.165	1.00	81.63	87.72
	0.352	1.186	1.00	83.44	
	0.356	1.226	1.00	86.96	
	0.333	1.205	1.00	87.10	
	0.369	1.291	1.00	92.16	
	0.348	1.292	1.00	94.43	
	0.355	1.239	1.00	88.35	
Cu	0.416	1.324	1.00	90.82	88.81
	0.396	1.226	1.00	82.95	
	0.402	1.334	1.00	93.18	
	0.395	1.321	1.00	92.67	
	0.426	1.321	1.00	89.47	
	0.407	1.264	1.00	85.71	
	0.421	1.290	1.00	86.89	
Ni	0.207	1.063	1.00	85.54	91.68
	0.206	1.110	1.00	90.39	
	0.208	1.118	1.00	91.02	
	0.222	1.230	1.00	100.77	
	0.205	1.194	1.00	98.96	
	0.200	1.069	1.00	86.92	
	0.205	1.086	1.00	88.13	
Co	0.251	1.280	1.00	102.94	87.92
	0.259	1.075	1.00	81.58	
	0.241	1.042	1.00	80.14	
	0.266	1.137	1.00	87.16	
	0.248	1.090	1.00	84.20	
	0.243	1.063	1.00	81.95	
	0.268	1.242	1.00	97.45	
Mn	1.041	1.972	1.00	93.17	94.93
	0.991	1.829	1.00	83.82	
	1.051	2.011	1.00	96.00	
	1.016	2.072	1.00	105.62	
	1.068	2.109	1.00	104.13	
	0.989	1.892	1.00	90.32	
	1.053	1.967	1.00	91.42	

3.4. Precision

Precision indicates the closeness of the measurement results from multiple repetitions in a homogeneous sample. One of the techniques used to determine the value of precision is repeatability. This technique is done by performing several repeated measurements of one sample on the same day, analyst and conditions. The acceptance test for the precision value in this method compares the percentage of the standard (% RSD) with ⅔ CV Horwitz.

The precision of the verification of this method is presented in Table 6. Table 6 shows that the% RSD for all metals is less than ⅔ CV Horwitz, indicating that this method meets the acceptability requirements for precision.

Table 6. Value of method precision for Cd, Cr, Cu, Ni, Co, and Mn metals

No	metals	% RSD	⅔ CV Horwitz
1	Cd	3.196	9.000
2	Cr	3.582	8.847
3	Cu	3.629	8.831
4	Ni	3.410	8.912
5	Co	3.145	8.719
6	Mn	4.345	8.593

3.5. Detection Limit of the Method

The detection limit (LoD) and the limit of quantification (LoQ) were determined using a sample with a small concentration measured six times. Next, the standard deviation (SD) of the measurement results is calculated. The detection limit is calculated as three times the SD, and the quantification limit is calculated as ten times the SD. The LoD and LoQ values for the method are presented in Table 7.

Table 7. The LoD and LoQ values of this method for Cd, Cr, Cu, Ni, Co, and Mn

No	Metals	LoD (mg/L)	LoQ (mg/L)
1	Cd	0.008	0.026
2	Cr	0.005	0.017
3	Cu	0.007	0.022
4	Ni	0.020	0.065
5	Co	0.050	0.167
6	Mn	0.002	0.006

The results obtained from Cd, Cr, Cu, Ni, Co, and Mn metals show that the method detection limits of all types of metals analyzed are below the metal quality standard in surface water, referring to Government Regulation No. 82 of 2001 concerning Water Quality Management. and Water Pollution Control [27]. This shows the acceptability of MDL in these metals to be used for monitoring metals in waters.

3.6. Determination of Metal Content in River Water in Bandar Lampung City

The city of Bandar Lampung is flowed by 23 small rivers and two large rivers: the Way Kuala River and the Way Kahuripan River. In this study, the levels of heavy metals in river water were carried out in several places, namely the Palang Besi river (A1), the Way Balau Kedamaian (B1) river, the Way Balau Kedaton river (C1), and the Way Kuala river (D1). Locations A1, B1, and C1 are the upstream part of the tributary locations, which then join the Way Kuala River (D1). The results of monitoring metal content with a verified method can be seen in Table 8. These results indicate that the metals Cd, Cr, Cu, Co, and Ni are still below LoD. This also shows that heavy metals are still below the metal quality standard in surface water according to Government Regulation No. 82 of 2001 concerning Water Quality Management and Water Pollution Control, while Mn has been detected above LoD and LoQ. The distribution of Mn metal can be seen in Figure 3. Location B1, namely the Way Balau Kedamaian river, shows the highest concentration and is slightly above the government's quality standard.

Table 8. Results of river water analysis using verified methods

Sample codes	Metals	Metal intensity	Regression equation	Metal Content (mg/L)
A1	Cd	4.367	y = 879.18x + 6.0722	n.d.
B1		3.659		n.d.
C1		5.787		n.d.
D1		5.054		n.d.
E1		3.535		n.d.
F1		4.879		n.d.
G1		5.485		n.d.
A1	Cr	23.707	y = 2930.2x + 14.447	n.d.
B1		28.980		n.d.
C1		12.626		n.d.
D1		20.198		n.d.
E1		23.409		n.d
F1		26.690		n.d.
G1		12.173		n.d.
A1	Cu	20.408	y = 3058.1x + 21.713	n.d.
B1		18.143		n.d.
C1		10.969		n.d.
D1		9.739		n.d.
E1		31.558		n.d.
F1		17.778		n.d.
G1		14.683		n.d.
A1	Ni	6.569	y = 366.93x + 7.9223	n.d.
B1		5.704		n.d.
C1		8.573		n.d.
D1		12.017		n.d.
E1		12.883		n.d.
F1		8.416		n.d.
G1		12.840		n.d.
A1	Co	7.278	y = 821.83x + 8.3253	n.d.
B1		7.107		n.d.
C1		7.683		n.d.
D1		10.346		n.d.
E1		9.234		n.d.
F1		5.892		n.d.
G1		8.638		n.d.
A1	Mn	490.889	y = 17808x + 32.867	0.026
B1		17999.900		1.009
C1		707.277		0.038
D1		1286.030		0.070
E1		5567.860		0.311
F1		2590.100		0.144
G1		3090.990		0.172

Note: n.d. = not detected

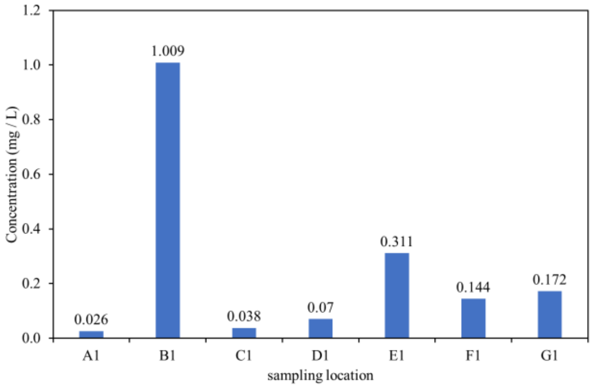

Figure 3. Dissolved Mn content

Other sampling locations are the Sumur Batu Kahuripan river (E1), the Sumur Putri river (F1), and the Muara Kahuripan river (G1). The E1 and F1 rivers' locations are part of the tributaries in the upstream and middle of the city from the Kahuripan River. As in the Way Balau River's sampling location, in the Way Kuripan river, the concentration of Cd, Cr, Cu, Ni, and Co was still below the LoD and LoQ methods, but Mn was above LoD and LoQ with the highest levels at location E1.

Based on the results obtained, it can be concluded that the metal content of Cd, Cr, Cu, Co, and Ni in the tributaries of the Way Balau and Way Kahuripan rivers is still below the established quality standards. Only Mn was detected in the two river flows, which could be related to the accumulation from excavating the hills for reclamation in the watercourse's vicinity. Periodic monitoring needs to be carried out so that the quality of river waters and their sustainable function are maintained because of the increasing activity and increasing population in Bandar Lampung. Metals also have bioaccumulative abilities, so that monitoring also needs to be done on bioindicators and sediments in the river.

Apart from metal content, pH and dissolved oxygen (DO) values in river water in Bandar Lampung City were also observed. The pH value ranges from 7.3 to 7.7, which means that it still meets the water criteria with good quality because the pH range for class I water is 6-9. The minimum DO value for class I water is six. In contrast, in Bandar Lampung City, river water has an average DO value below 4 for all samples, indicating that the surface water has been polluted by organic matter.

4. Conclusion

Verification of the analysis method for Cd, Cr, Cu, Ni, Co, and Mn in surface water using ICP-OES shows that the US.EPA.200.7 method is verified for its purpose. The method verification results show that the test parameters for linearity, precision, accuracy, detection limit (LoD), and limit of quantification (LoQ) meet the method acceptability limits. This method is applied to analyze metals in surface water from several places, namely water from the Palang Besi river (A1), the Way Balau Kedamaian river (B1), the Way Balau Kedaton river (C1), the Way Kuala river (D1), the Batu Kahuripan river Sumur. (E1), Sumur Putri river (F1), and Muara Kahuripan river (G1). Cd, Cr, Cu, and Co concentrations in the river water samples were still below the government's quality standard. However, Mn metal was detected at all sampling locations, and one location showed slightly above the established quality standard.

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References

[1] Mir Mohammad Ali, Mohammad Lokman Ali, Md. Saiful Islam, Md. Zillur Rahman, Assessment of toxic metals in water and sediment of Pasur River in Bangladesh, *Water Science and Technology*, 77, 5, (2018), 1418-1430 https://doi.org/10.2166/wst.2018.016

[2] B. Wilson, F. B. Pyatt, Heavy metal dispersion, persistance, and bioccumulation around an ancient copper mine situated in Anglesey, UK, *Ecotoxicology and Environmental Safety*, 66, 2, (2007), 224-231 https://doi.org/10.1016/j.ecoenv.2006.02.015

[3] Ababu T. Tiruneh, Amos O. Fadiran, Joseph S. Mtshali, Evaluation of the risk of heavy metals in sewage sludge intended for agricultural application in Swaziland, *International Journal of Environmental Sciences*, 5, 1, (2014), 197-216 http://dx.doi.org/10.6088/ijes.2014050100017

[4] Yujun Yi, Zhifeng Yang, Shanghong Zhang, Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin, *Environmental Pollution*, 159, 10, (2011), 2575-2585 https://doi.org/10.1016/j.envpol.2011.06.011

[5] Wike Ayu Eka Putri, Dietriech G. Bengen, Tri Prartono, Etty Riani, Konsentrasi logam berat (Cu dan Pb) di Sungai Musi Bagian Hilir, *Jurnal Ilmu dan Teknologi Kelautan Tropis*, 7, 2, (2015), 453-463

[6] Ita Emilia, Suheryanto Suheryanto, Zazili Hanafiah, Distribusi logam kadmium dalam air dan sedimen di Sungai Musi Kota Palembang, *Jurnal Penelitian Sains*, 16, 2, (2013), 59-64

[7] Dwiki Irvan Mahardika, Indah Rachmatiah S. Salami, Profil Distribusi Pencemaran Logam Berat pada Air dan Sedimen Aliran Sungai dari Air Lindi TPA Sari Mukti, *Jurnal Tehnik Lingkungan*, 18, 1, (2012), 30-42 https://doi.org/10.5614/jtl.2012.18.1.4

[8] Ni Putu Diantariani, K. G. Dharma Putra, Penentuan Kandungan Logam Pb dan Cr pada Air dan Sedimen di Sungai Ao Desa Sam Sam Kabupaten Tabanan, *Ecotrophic: Jurnal Ilmu Lingkungan (Journal of Environmental Science)*, 1, 2, (2006), 1-5

[9] Suratni Afrianti, Julaili Irni, Analisa Tingkat Pencemaran Logam Berat Timbal (Pb) di Daerah Aliran Sungai Deli Sumatera Utara, *Biolink (Jurnal Biologi Lingkungan Industri Kesehatan)*, 6, 2, (2020), 153-161 https://doi.org/10.31289/biolink.v6i2.2964

[10] Md Simul Bhuyan, Muhammad Abu Bakar, Aysha Akhtar, M. Belal Hossain, Mir Mohammad Ali, Md Shafiqul Islam, Heavy metal contamination in surface water and sediment of the Meghna River,

Bangladesh, *Environmental Nanotechnology, Monitoring & Management*, 8, (2017), 273-279 https://doi.org/10.1016/j.enmm.2017.10.003

[11] Satmoko Yudo, Nusa Idaman Said, Status Kualitas Air Sungai Ciliwung di Wilayah DKI Jakarta Studi Kasus: Pemasangan Stasiun Online Monitoring Kualitas Air di Segmen Kelapa Dua Masjid Istiqlal, *Jurnal Teknologi Lingkungan*, 19, 1, (2018), 13-22 https://doi.org/10.29122/jtl.v19i1.2243

[12] Anwar Hadi, *Persyaratan Umum Kompetensi Laboratorium Pengujian & Laboratorium Kalibrasi ISO/IEC 17025: 2017*, Gramedia Pustaka Utama, Jakarta, 2018

[13] Harmita Harmita, Petunjuk pelaksanaan validasi metode dan Cara Perhitungannya, *Pharmaceutical Sciences and Research (PSR)*, 1, 3, (2012), 117-135 http://dx.doi.org/10.7454/psr.v1i3.3375

[14] Riyanto, *Validasi & Verifikasi Metode Uji:: Sesuai dengan ISO/IEC 17025, Laboratorium Pengujian dan Kalibrasi*, Deepublish, Yogyakarta, 2015

[15] Supriyono Supriyono, Mudhiah Fitrillah, Arie Pratama Putra, Validation of High-Performance Liquid Chromatography Method for Determination of Vitamin B1 in Powder Milk, *Jurnal Kimia Sains dan Aplikasi*, 23, 5, (2020), 177-182 https://doi.org/10.14710/jksa.23.5.177-182

[16] Sri Maryati, Verifikasi dan Evaluasi Penerapan Cara Uji Cemaran Arsen dalam makanan Metode Spektrofotometri Biru Molybdenum, *Jurnal Standardisasi*, 14, 3, (2012), 228-236 http://dx.doi.org/10.31153/js.v14i3.87

[17] E. Santoyo, S. Santoyo-Gutiérrez, Surendra P. Verma, Trace analysis of heavy metals in groundwater samples by ion chromatography with post-column reaction and ultraviolet–visible detection, *Journal of Chromatography A*, 884, 1, (2000), 229-241 https://doi.org/10.1016/S0021-9673(00)00358-7

[18] Rajmund Michalski, Ion chromatography applications in wastewater analysis, *Separations*, 5, 1, (2018), 16 https://doi.org/10.3390/separations5010016

[19] Elham Ghasemi, Massoud Kaykhaii, Determination of zinc, copper, and mercury in water samples by using novel micro cloud point extraction and UV-Vis spectrophotometry, *Eurasian Journal of Analytical Chemistry*, 12, 4, (2017), 313-324 https://doi.org/10.12973/ejac.2017.00172a

[20] M. Zahir Duz, Mehmet Sagirdag, Kadir Serdar Celik, Mahmood A. Hasan, Ersin Kilinc, Geochemical multi-element ICP-OES analysis of borehole waters from SE Anatolia, *Atomic Spectroscopy*, 37, 2, (2016), 43-49 http://dx.doi.org/10.46770/AS.2016.02.002

[21] Darya Ilieva, Andriana Surleva, Manuela Murariu, Gabi Drochioiu, Mohd Mustafa Al Bakri Abdullah, Evaluation of ICP-OES method for heavy metal and metalloids determination in sterile dump material, *Solid State Phenomena*, 2018 https://doi.org/10.4028/www.scientific.net/SSP.273.159

[22] Cezara Voica, Melinda Haydee Kovacs, Adriana Dehelean, Dumitru Ristoiu, Andreea Maria Iordache, ICP-MS determinations of heavy metals in surface waters from Transylvania, *Romanian Journal of Physics*, 57, 7-8, (2012), 1184-1193

[23] United States Environmental Protection Agency (US EPA), *Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry*, Cincinnati, Ohio, 1994

[24] Xiandeng Hou, Renata S. Amais, Bradley T. Jones, George L. Donati, Inductively Coupled Plasma Optical Emission Spectrometry, in: R.A. Meyers (Ed.) *Encyclopedia of Analytical Chemistry*, https://doi.org/10.1002/9780470027318.a5110.pub3

[25] Paul Johannes Botes, Investigation of mobility of trace elements in river sediments using ICP-OES, *Master thesis*, Faculty of Natural and Agricultural Science, University of Pretoria, Pretoria, South Africa, 2003

[26] AOAC International, *Appendix F: Guidelines for Standard Method Performance Requirements*, Rockville, Maryland, 2016

[27] Peraturan Pemerintah Republik Indonesia, in: P.R. Indonesia (Ed.) 82/2001, Jakarta, 2001