DETERMINATION OF TRACE METAL CONCENTRATION IN WASTEWATER HO CHI MINH CITY USING THE INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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TÓM TẮT

XÁC ĐỊNH HÀM LƯỢNG VẾT CÁC KIM LOẠI TRONG NƯỚC THẢI Ở THÀNH PHỐ HỒ CHÍ MINH SỬ DỤNG PLASMA CAO TẦN CẢM ỨNG GHÉP KHỐI PHỔ

Trong nghiên cứu này, lần đầu tiên hàm lượng 19 ion kim loại trong 23 mẫu nước thải ở Thành phố Hồ Chí Minh được xác định sử dụng plasma cao tần cảm ứng ghép khối phổ (ICP-MS). Khoảng tuyến tính, giới hạn phát hiện, giới hạn định lượng, độ đúng, độ không đảm bảo đo, độ chính xác trong ngày và giữa các ngày đã được khảo sát. Kết quả cho thấy thiết bị ICP-MS thích hợp để phân tích hàm lượng kim loại trong nước thải. Nồng độ kim loại trong nước thải xác định được giảm dần theo thứ tự Mg > Na > Ca > Ba > Pb > Fe > Al > Zn > Mn > K > Cd > Cu > As > Cr > Tl > Ni. Ngoài ra, nghiên cứu này cũng tìm ra mối tương quan giữa các ion kim loại trong nước thải, các cặp ion sau có mối tương quan mạnh ở mức ý nghĩa 0,05%: Ca – K, Ca – Mg, Ca – Na, Cd – Cu, Cr – Pb, và Mg - Na.

***Từ khóa:** khảo sát, kim loại, ICP-MS, nước thải.*

1. INTRODUCTION

Industries play an important role in the economic growth of any country. However, most of these industries have contributed significantly to the pollution level of surface aquifers. The pollutions were various acids, alkalis, heavy metals, chlorinated hydrocarbons, petroleum hydrocarbons, dyes, and many other chemicals which greatly change the physicochemical properties of water. High concentrations of pollution compounds discharged into the water that was harmful to the aquatic environment. Pollution compounds are slowly-biodegradable and can bio-accumulate in organisms through food chains. A human can exposure to pollution compounds through the consumption of foods [1-5]. These pollution compounds, especially heavy metals are quite harmful or even seriously toxic to the aquatic ecosystem [6]. So, many aquatic organisms have disappeared due to the presence of pollution contaminants [7]. Heavy metal levels in the aquatic environment were monitored through the determination of their concentrations in lotic and lentic water systems or wastewater discharge [3, 5, 8, 9].

Many different techniques have been applied to determine metal in different samples. Many metals were determined by using flame atomic absorption spectrometry [10-11], hydride generation atomic absorption spectrometry, cold vapor-atomic absorption spectrometry [12,], fluorescence spectrometry [13,], inductively coupled plasma-mass spectrometry [14].

Compare to other documents, our study was for the first time validated the quality criteria of ICP-MS for analyzing nineteen metal levels in wastewater samples. The application of this method was then tested by analyzing nineteen metal levels in twenty-three wastewater samples in the Tham Luong Canal in Ho Chi Minh City. Based on these results, the correlation of the concentration of these metals in wastewater samples was determined.

2. MATERIALS AND METHODS

2.1. Chemicals

Analytical grade nitric acid (65%), chlorohydric acid (36%), and nineteen metals stock standard solution (1000 mg/L) were acquired from Merck (Darmstadt, Germany). The working standard solutions were prepared by diluting an appropriate aliquot of the standard stock solutions. All glassware was soaked in 20% (v/v) nitric acid for 24 h and then the glassware was rinsed three times with deionized water and dried.

2.2. Sample collection

Figure 1. Description of location of wastewater sampling

500 mL of wastewater samples were collected by random method from different sampling locations along Tham Luong Canal in Ho Chi Minh City during March 2021 which was the dry season in Ho Chi Minh City. The Tham Luong Canal is located between 10°50'45.4" and 10°47'0.7" North latitude and 106°38'08.8" and 106°35'36.3" East longitude. Sample preservation is performed by the sampler immediately upon sample collection using HNO_3 ($pH < 2$) and then samples are contained in high-density polyethylene. The location of all wastewater samples in this study is provided in figure 1.

2.3. Apparatus

ICP-MS NexION 300 X, Perkin Elmer Instruments, including: NexION 300X; autosampler ASX 520, CETAC; roughing pump; water re-circulator; the internal standards are blended by a mixing tee that is before the nebulizer and after the peristaltic pump.

2.4. Trace heavy metal analyses

Sample digestion using a block digester in dilute mineral acids is required to determine total metals in unfiltered aqueous samples.

- As soon as arrived in the laboratory, the sample was shaken well to homogenize before sub-sampling for digestion.
- Pipet a 5.0 ± 0.1 mL sub-sample and dispense the sample into a digestion tube, with each batch of samples.
- Add 2.0 ± 0.1 mL 65% HNO_3 and 1.00 ± 0.05 mL 36% HCl to each sample.
- Cap sample tubes and digest for 2.5 hours at 95 ± 5 °C (excluding the time required to warm the samples up to 95 °C).
- After 2.5 hours at 95 ± 5 °C, remove the samples from the heat source and let them cool for at least 10 minutes.
- Remove the caps and reconstitute samples back to 10 ± 0.1 mL with de-ionized water. Shake samples to mix.
- Filter the samples using the 0.45 µm filter disk.
- The filtrate is diluted at the appropriate factor and ready for ICP-MS analysis.
- The blank sample was repaired by using 5.0 ± 0.1 mL of de-ionized water in a digestion tube. Add 2.0 ± 0.1 mL of HNO_3 and 1.0 ± 0.05 mL HCl to the water and treat it as the real same sample.

The quantification of heavy metal was performed with Inductively Couple Plasma-Mass Spectrophotometry (ICP-MS 7700, Agilent, USA)

3. RESULTS AND DISCUSSION

3.1. Inductively Couple Plasma-Mass Spectrophotometry conditions

After some trials with mass, analysis mode, and internal standards of element metals using Inductively Couple Plasma-Mass Spectrophotometry (ICP-MS 7700, Agilent, USA) at a different value, these parameters were optimized to determine trace metal concentration.

Ions consisting of more than one atom cause isobaric molecular interferences. Common examples are potential interferences from $^{40}Ar^{35}Cl$ or $^{40}Ca^{35}Cl$ on ^{75}As, ^{40}Ar on ^{40}Ca, $^{40}Ar^{12}C$ on ^{52}Cr, $^{16}O^{12}C^{35}Cl$ on ^{63}Cu, $^{40}Ar^{16}O$ on ^{56}Fe, $^{12}C^{12}C$ on ^{24}Mg, $^{37}Cl^{18}O$, $^{38}Ar^{17}O$ on ^{55}Mn, $^{44}Ca^{16}O$, $^{23}Na^{37}Cl$ on ^{60}Ni, $^{34}S^{16}O_2$ on ^{66}Zn. Using the collision cell utilizing He gases decrease these molecular interferences. A list of the corrections used is given in the listing of the isotopes monitored in the NexION 300X ICP-MS software Chapter 8, Interference Correction [15]. The transport and nebulization sample solution process are caused by physical interferences. These physical interferences and matrix effects are decreased using internal standards.

3.2. Quality control criteria for the method

Linearity

Linearity was evaluated by repeated five times using different concentrations in the range in table 1 with a determination coefficient (r) from 0.9980 to 1.000. The instrument detection limit was studied using a calibration blank signal at the selected analytical masses. The method detection limit was studied using a synthetic matrix at the selected analytical masses.

These results were given in table 1. The method detection limit in this research was lower than other published methods, for which LOD was arranged from 0.1 to 17 µg/L [16-18].

Table 1. Linear dynamic range, instrument detection limit, method detection limit of some metals

Elements	Linearity (µg/L)	R^2	The instrument detection limit (µg/L)	The method detection limit (µg/L)
^{27}Al	0.20-500	0.9999	0.169	0.623
^{75}As	0.02-500	1.0000	0.022	0.059
^{137}Ba	0.02-500	1.0000	0.004	0.085
^{9}Be	0.02-500	0.9980	0.004	0.007
^{44}Ca	2.00-50000	1.0000	2.737	8.051
^{111}Cd	0.02-500	0.9999	0.005	0.007
^{52}Cr	0.02-500	0.9999	0.014	0.024
^{63}Cu	0.20-500	0.9987	0.143	0.073
^{56}Fe	1.00-500	1.0000	0.122	0.885
^{202}Hg	0.01-5	0.9997	0.004	0.003
^{39}K	2.00-10000	1.0000	0.986	0.948
^{24}Mg	2.00-50000	0.9987	0.313	2.102
^{55}Mn	0.02-500	1.0000	0.019	0.493
^{23}Na	2.00-50000	0.9996	0.992	3.234
^{60}Ni	0.02-500	0.9996	0.034	0.047
^{208}Pb	0.20-500	0.9998	0.263	0.818
^{121}Sb	0.02-500	1.0000	0.005	0.006
^{205}Tl	0.02-500	0.9997	0.003	0.006
^{66}Zn	1.00-500	0.9992	0.599	0.975

Short-term precision, long-term stability, accuracy, and uncertainty values

Intra-day precision was studied by six replicate measurements at two concentration levels which were 20 µg/L, and 50 µg/L of each element (Be, B, Al, Zn, Cr, Mn, Fe, Ni, Cu, As, Mo, Cd, Pb, Sb, Tl), 2000 µg/L, 3000 µg/L for major elements (Ca, Mg, K, Na), and 0.2 µg/L, 0.5 µg/L for Hg. Interday precision was conducted during the routine operation of the system. The RSD values were collected to evaluate the precision of this method. Statistical evaluation revealed that the relative standard deviation of metal for six replicate measurements was less than 1%. The trueness of the method within-day was between 95.2% and 108.8%. Measurement uncertainty can be expressed as an expanded uncertainty. The parameters obtained were shown in table 2. These results were shown that there are appropriately integrated modes for each element.

Table 2. Repeatability evaluates, the trueness, uncertainty, and recovery values of some metals

Element	Repeatability evaluates (%RSD)		% Uncertainty values	Recovery (%) for sample ID				
	Short-term precision	Long-term stability		1	3	8	19	20
^{27}Al	1.3	2.7	5.6	95.6	102.8	102.9	114.0	106.6
^{75}As	3.6	5.9	6.9	102.2	106.1	99.7	107.9	93.5
^{137}Ba	1.9	2.4	4.8	86.5	89.5	96.7	99.6	98.0
^{9}Be	3.8	5.5	12.5	99.4	98.2	98.5	105.4	97.9
^{44}Ca	1.7	1.5	6.4	105.4	104.5	90.9	99.5	97.7
^{111}Cd	2.7	3.1	6.8	108.3	102.0	101.7	100.2	96.6
^{52}Cr	2.5	3.2	6.3	98.1	94.9	102.1	96.8	94.6
^{63}Cu	3.0	3.8	6.9	93.3	95.3	105.4	100.6	100.9
^{56}Fe	3.0	3.5	6.7	95.4	97.9	98.9	101.1	93.9
^{202}Hg	2.0	4.9	9.9	103.9	93.9	92.5	100.5	71.5
^{39}K	1.3	2.7	5.8	100.3	103.7	103.2	100.6	96.0
^{24}Mg	2.4	2.8	5.9	102.0	114.0	88.8	100.4	90.2
^{55}Mn	1.6	2.9	6.0	99.6	92.1	105.0	94.1	91.5
^{23}Na	2.2	2.9	5.9	101.1	105.5	91.7	97.1	90.3
^{60}Ni	2.5	3.5	6.3	92.9	94.4	100.6	98.7	96.9
^{208}Pb	5.6	7.3	14.0	101.7	96.3	94.0	98.2	99.3
^{121}Sb	1.6	2.5	6.5	111.3	103.0	99.0	100.5	87.1
^{205}Tl	0.7	1.7	10.4	104.3	100.3	98.1	99.6	99.9
^{66}Zn	2.7	5.9	11.7	97.5	96.1	110.6	97.1	104.1

Spike Recovery

20 µg/L of each element (Be, B, Al, Zn, Cr, Mn, Fe, Ni, Cu, As, Mo, Cd, Pb, Sb, Tl), 2000 µg/L for major elements (Ca, Mg, K, Na) and 0.2 µg/L for Hg were spiked to the sample. The recoveries for all elements fluctuate around 100% except for Hg. It demonstrated that this method is suitable for this type of sample with high accuracy. From the analysis results, it is shown that the recovery of these metals in the wastewater sample was within the acceptable range of 80 - 110% of AOAC - app F [19].

3.3. Application of the proposed method

The distribution of metals (Al, As, Ba, Be, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Tl, and Zn) in wastewater samples from Tham Luong canal in Ho Chi Minh City has been evaluated. As shown in table 3, the results obtained revealed that the concentration of the metals was found to be in the order of Mg > Na > Ca > Ba > Pb > Fe > Al > Zn > Mn > K. In most samples, the concentration of heavy metals such as Cd, Cr, Cu, Hg, As, and Ni was low level or not detected, except Pb. Moreover, the concentration of Pb was higher than the permissible limit set by WHO (2006) which could pose a huge threat to human health and the natural environment [20].

Table 3. Level of heavy metals in wastewater samples

Sample ID	^{27}Al (µg/L)	^{75}As (µg/L)	^{138}Ba (µg/L)	^{9}Be (µg/L)	^{44}Ca (mg/L)	^{111}Cd (µg/L)	^{52}Cr (µg/L)	^{63}Cu (µg/L)	^{56}Fe (µg/L)	^{202}Hg (µg/L)
1	ND	2.3	28.7	ND	99.2	1.2	0.4	4.6	2.1	ND
2	ND	4.1	48.9	ND	543.0	1.7	0.4	3.7	7.8	ND
3	3.2	ND	45.3	ND	331.0	0.2	0.7	6.1	16.4	ND
4	ND	ND	90.1	ND	110.0	0.7	0.8	2.5	119.1	ND
5	6.7	ND	83.6	ND	183.0	2.3	1.2	3.2	90.9	ND
6	4.5	7.5	26.2	ND	413.0	2.7	3.3	2.6	2.4	ND
7	3.6	1.1	83.4	ND	180.0	2.1	7.1	5.1	91.5	ND
8	6.6	10.1	35.3	ND	314.0	1.6	8.5	3.4	6.6	ND
9	6.5	3.3	19.2	ND	434.0	5.0	3.6	3.8	8.9	ND
10	ND	2.6	452.0	ND	38.8	ND	5.1	2.9	16.1	ND
11	21.4	2.2	104.0	ND	142.0	1.1	6.3	5.7	80.0	ND
12	37.8	25.9	36.0	ND	83.1	0.8	5.8	6.2	34.1	ND
13	45.1	ND	ND	ND	ND	1.5	5.9	6.5	50.2	ND
14	34.3	2.8	46.2	ND	131.0	2.5	6.3	5.6	34.6	ND
15	14.8	13.6	41.3	ND	362.0	4.2	6.7	5.1	54.5	ND
16	50.8	14.7	39.8	ND	366.0	0.8	7.2	2.6	61.6	ND
17	73.3	3.1	44.9	ND	132.0	0.5	2.1	3.3	51.6	ND
18	44.7	25.3	35.0	ND	86.3	1.4	1.5	2.1	43.0	ND
19	182.0	ND	19.7	ND	4.94	1.8	1.4	7.8	55.7	ND
20	51.8	14.6	36.5	ND	5.95	2.7	0.8	18.4	46.8	ND
21	50.9	2.5	36.6	ND	67.6	15.1	0.7	62.9	22.5	ND
22	ND	ND	49.4	ND	51.3	6.4	0.9	15.6	32.1	ND
23	ND	5.2	55.9	ND	552.0	2.4	1.1	5.9	4.8	ND
Average	25.5	6.1	63.4	0.0	201.3	2.6	3.4	8.1	40.6	ND

Sample ID	^{39}K (mg/L)	^{24}Mg (mg/L)	^{55}Mn (µg/L)	^{23}Na (mg/L)	^{60}Ni (µg/L)	^{208}Pb (µg/L)	^{121}Sb (µg/L)	^{205}Tl (µg/L)	^{66}Zn (µg/L)
1	11.9	161.3	6.3	75.8	ND	15.2	ND	1.6	11.0
2	50.8	353.9	7.9	335.0	6.3	24.6	4.8	2.4	25.6
3	7.6	453.7	18.2	394.0	ND	30.4	ND	ND	9.5
4	9.1	184.8	24.0	185.0	ND	36.5	ND	0.6	5.0
5	9.2	235.1	35.2	256.0	ND	47.2	ND	2.5	8.3
6	25.8	450.4	ND	272.0	ND	57.4	ND	1.4	31.6
7	9.3	236.7	35.5	256.0	ND	63.1	ND	2.5	8.7
8	52.2	431.3	8.1	419.0	ND	71.3	1.1	5.2	35.3
9	11.4	623.8	10.2	284.0	3.5	40.2	1.7	9.2	21.7
10	9.2	80.8	13.2	38.5	ND	52.1	0.6	ND	ND
11	10.9	209.4	40.0	217.0	ND	49.4	0.6	1.3	ND
12	12.9	167.2	ND	98.3	ND	60.3	1.2	2.3	7.4
13	ND	120.5	ND	321.0	ND	57.3	ND	ND	ND
14	12.6	148.0	31.4	74.7	ND	66.8	0.7	1.9	43.8
15	67.6	517.0	22.6	456.0	ND	72.4	2.1	4.5	ND
16	67.5	489.0	84.2	414.0	ND	71.6	2.0	4.4	ND
17	12.0	145.0	20.3	69.3	ND	58.3	0.7	1.8	42.9
18	12.6	164.0	2.91	91.9	ND	45.9	1.3	2.2	11.9
19	0.8	2.6	20.1	1.9	ND	3.2	ND	0.8	55.4
20	2.5	3.9	26.9	1.8	ND	6.3	0.6	3.4	93.8
21	8.8	103.0	10.4	11.9	6.8	14.3	ND	3.8	63.3
22	10.2	72.1	71.9	7.2	5.9	14.9	ND	1.4	23.8
23	78.6	560.0	15.0	373.0	ND	10.7	1.9	4.8	81.1
Average	21.5	257.1	21.9	202.3	1.0	42.1	0.8	2.5	25.2

ND: Not detected.

3.4. Pearson's correlation between metals

The relationships between the contents of different elements in wastewater were analyzed by Pearson's correlation coefficient. The result showed that at a significant level of 0.05% level, the concentration of Ca – K, Ca – Mg, Ca – Na, Cd – Cu, Cr – Pb, and Mg - Na were strongly correlated; the concentration of Ca – Sb, Ca – Tl, Cd – Ni, Cu – Ni, K – Na, K – Sb, Mg – Tl were moderate correlation. Other metals were no relationship between them.

4. CONCLUSION

The method for the determination of trace metals in the wastewater sample in this paper was validated. These results showed that this method has good accuracy, precision, and linearity and is suitable for the quantitative determination of trace metals in a wastewater sample. The value for all validation parameters falls under the acceptable criteria regarding AOAC Official Methods of Analysis, Guidelines for Standard Method Performance Requirements, Appendix F. Thus, the test method in this research was suitable and ready to analyze 19 metals in the wastewater sample. Besides, the analysis of wastewater for metal contamination is important to ensure environmental health.

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