

## **DETERMINATION OF HEAVY METALS IN WATER SAMPLES USING SODIUM SULFIDE PRECIPITATION AND INORGANIC COAGULATION FOLLOWED BY FAAS DETECTION**

### **ABSTRACT**

Studies on determination of five heavy metals, i.e. copper (Cu), cadmium (Cd), chromium (Cr), lead (Pb) and nickel (Ni) in water samples collected from drains located outside five factories using sodium sulfide precipitation and aluminium sulphate inorganic coagulation followed by FAAS detection were carried out. The amount of coagulant added, effect of centrifugation time and analysis methods have been developed and optimized. Samples was analysed by FAAS after undergone digestion with 1:1 nitric acid according to EPA Method 200.7. The recoveries of analytes were in the range of 68 to 99.2.% The relative standard deviations of the studied five elements were found in the range of 0.1-12.5%. The method detection limit of Cu, Cd, Cr, Pb and Ni were 0.043, 0.012, 0.011, 0.020 and 0.008 mg/L. The presented coprecipitation procedure was successfully applied to determine five free elements in the environmental samples collected from the drains surrounding the factories. The concentration of the heavy metals in the collected water samples were not exceeded the maximum contamination levels which stipulated under Environmental Quality Act 1974.

**KEYWORDS:** Sodium Sulfide Precipitation, Aluminium Sulphate Coagulation, FAAS Analysis, Nitric Acid

### **INTRODUCTION**

Wastewater is used water that has been adversely affected in quality by anthropogenic influence. Suspended solids, biodegradable dissolved organic compounds, inorganic solids, nutrient, heavy metals and pathogenic microorganisms are the contaminants in wastewater<sup>1</sup>.

Industrial wastewater treatment is commonly performed in order to prevent environmental pollution. It involves the mechanisms and processes used to treat water that has been contaminated in some ways by anthropogenic industrial activities prior to its release into the environment or its re-use. Most of the industries produce some wet waste which is a recent trend to reduce waste production or recycle such waste within the production process by precipitating and removing the waste matter which will cause pollution to environment.

As mentioned above, heavy metals are one of the contaminants present in wastewater. Heavy metals are highly toxic and this can pose serious health risks to human beings. Types of the highly toxic heavy metals that can be found in trace amounts in wastewater are cadmium, copper, zinc, iron, lead and nickel which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries as mentioned by Wan Ngah and Hanafiah<sup>2</sup>. Although these trace metals are necessary for the human body to perform their basic metabolic functions; however, if they are consumed in high concentrations, they would cause hazard to human health. The adverse health effects of excessive amount of heavy metals in human body are high blood pressure, kidney failure, cardiovascular disease, damage to human's respiratory system, nervous system and liver<sup>3,4</sup>. Although the heavy metals are usually found in trace amount where it might not seem to cause any major harm to human being, but due to the fact that heavy metals

usually have a longer half lives, they will remain and accumulate in animal or human body, thus causing a greater concern in its health hazards<sup>5</sup>. Thus, the monitoring on the level of trace metals in wastewater must be performed by obeying Environmental Quality (Sewage and Industrial Effluents) Regulations, 1974<sup>6</sup> in order to control the level of trace metals in wastewater before it is being discharged from factories to the environment and subsequently the environmental pollution that may affect human health could be minimized.

Similar studies had been carried out by other researchers by using different analytical methods, sample preparation methods and types of samples tested. The most commonly used analytical methods in heavy metal determination are atomic absorption methods which are simple yet affordable methods, followed by the chromatographic methods. In the determination of heavy metals, pre-concentration and separation methods have been routinely used to cope with low metal levels. Different pre-concentration techniques for heavy metals such as cloud point extraction<sup>7</sup>, solid phase extraction<sup>8</sup> and chelating agent preconcentration<sup>9</sup> were performed by researchers before the samples being analyzed by flame atomic absorption spectroscopy. Types of sample that are often tested by researchers for heavy metal determination are environmental samples<sup>10</sup>, food samples<sup>11-15</sup>, biological samples<sup>16,17</sup>, as well as plastic materials<sup>18-21</sup>. Most of the methods and procedures used by the researchers are able to give reliable results on determination of heavy metals, but they require either extensive and complicated procedures or the utilized methods are too time-consuming.

Therefore, the main purpose of this project is to develop a simple yet reliable analytical method using flame atomic absorption spectroscopy to determine the heavy metal contents in water samples from five different industrial companies located in Selangor state of Malaysia. This work would be focusing on the determination of five types of heavy metals that are copper, cadmium, chromium, lead and nickel in the collected water samples. Before the developed method was applied to analyze the real collected water samples, the workable range, recovery test, limit of detection, the effect of the centrifugation time and amount of the coagulant added were performed properly in order to evaluate whether the developed method is feasible to be used to analyze real environmental samples.

## **MATERIALS AND METHODS**

### **Materials**

Copper (II) sulphate ( $\text{CuSO}_4$ ) 99.5%, sodium sulfide ( $\text{Na}_2\text{S}$ ) 98% and nitric acid ( $\text{HNO}_3$ ) 65% were purchased from SYSTERM@ChemAR, Malaysia. Aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ) 98% were purchased from R&M Chemical, Malaysia and distilled water were used to prepare all the aqueous solutions throughout the study. 1000 ppm of ASS stock standard solutions for cadmium and chromium elements both purchased from Merck, Germany; whereas, lead and nickel elements stock standard solution at the same concentration was purchased from Fischer Scientific, USA.

### **Instruments**

A iCE 3000 flame atomic absorption spectrometer (FASS) (Thermo Scientific, USA) with double beam optics, aberration-corrected Ebert monochromator with holographic grating, deuterium-lamp background correction, equipped with chromium, lead, copper, nickel and cadmium hollow cathode lamp were used throughout this work to determine the free heavy metals in the water samples. The nebulizer uptake rate was adjusted to give the optimum response of the effect of the coagulant and centrifugation time on samples. All analyses were carried out in an

air/acetylene flame with the ratio of 4:1. Centrifuge 5804R model (Eppendorf, Germany) with fixed angle rotor and six boreholes, which is able to spin up to 15000 rpm was used to precipitate the heavy metal particles formed in the water samples after added with coagulant.

### **Reagents and Solutions**

Analytical reagent grade chemicals were used in this study. The glassware used were rigorously cleaned and kept in 1 M nitric acid for overnight before rinsed three times with distilled water. Plastic bottles were used to store water samples prior to analysis. 1000 ppm Cd, Cr, Ni and Pb AAS stock standard solutions were used to prepare a series of standard solutions with the concentrations in the range of 0.1 ppm to 5 ppm in a diluted 0.5 M HNO<sub>3</sub>. This series of low concentration standard solution was used to determine the limit of detection as well as plotting the standard calibration curve for Cd, Cr, Ni and Pb. 100 ppm Cu stock standard solution was prepared by dissolving a suitable amount of copper(II) sulfate solid salt with 0.5 M nitric acid solution and lower concentration of the standard solutions are prepared from this stock standard solution for determination of limit of detection as well as plotting the standard calibration curve. 1% sodium sulfide solution was prepared by dissolving 2.5g of sodium sulfide salt in 250 mL distilled water. 30% of aluminium sulfate solution was prepared by dissolving 30g of aluminium sulfate salt 100 mL distilled water.

### **Recovery Test**

A series of spiked solutions with the concentrations ranging from 0.1 to 0.5 ppm were prepared by diluting from the stock standard solution containing mixture of Cu, Cd, Cr, Ni and Pb in the free ion form. 40 mL of each of the spiked solution were transferred to a 50 mL centrifuge tube before 2 mL of 1% sodium sulfide and 30% of aluminium sulfate solutions were added into each of the spiked solution, respectively. The mixture was shaken and left in room temperature for 5 minutes before centrifugated at 15000 rpm for 20 minutes. The supernatant was discarded slowly and gently from the centrifuge tube. 4 mL of 1 M nitric acid solution was added into the few micro litres remaining in the tube before heated in a water bath at 50°C for 5 minutes. Heated solution was left to cool down to room temperature before analysed using flame atomic absorption spectroscopy to determine the concentrations of the Cu, Cd, Cr, Ni and Pb free ions in the solution. Obtained concentrations were compared to the spiked concentrations and the recoveries were calculated in percentage.

### **Optimization**

Centrifugation duration was optimized by centrifugating six 40 mL spiked solutions with the concentration of 0.5 ppm at six different durations from 2 to 25 minutes after added with 2 mL of 1% sodium sulfide and 30% of aluminium sulfate solutions each and heated at 50 °C for 5 minutes in the water bath. Effect of the aluminium sulfate on the recoveries of the five metals was studied by repeating a similar recovery test as mentioned above except omitting the addition of the 2 mL 30% of the aluminium sulfate solution into the spiked solutions. The limit of detection (LOD) of each of the metal element was determined by analyzing a series of low concentration standard solutions from 0.1 to 2 ppm using flame atomic absorption spectrometer. LOD for each element was calculated by multiplying the standard estimate of error with three over the slope of the linear line obtained from each series of the standard solutions. Method detection limit (MDL) for each element was calculated by dividing the obtained LOD with 10 because each element was pre-concentrated to 10 times before analyzed using FASS.

### **Application of the Developed Method**

Five 100 mL of water samples were collected from the drains around five industrial factories located in Selangor state industrial area. These five factories operates businesses related to pewter, chemicals and metal can. Collected water samples were digested with 1:1 nitric acid according to EPA Method 200.7<sup>22</sup>. The digested water samples were transferred to centrifuge tube before added with 2 mL of 1% sodium sulfide and 30% of aluminiums sulfate solutions. After leaving the treated water samples for 5 minutes in room temperature, the treated water samples were centrifugated at 1500 rpm for 20 minutes and the supernatant was discarded slowly and gently. The remaining for each sample was treated with 4 mL of 1 M nitric acid at 50 °C before analysed using FAAS.

## RESULTS AND DISCUSSION

### Effect of Coagulant

The effect of aluminium sulfate which acts as a coagulant in the water sample was studied. Aluminium sulfate coagulates the sulfide heavy metal particles formed in the water sample to enhance the precipitation of the particles during the centrifugation. Similar treatment steps in the recovery test were carried out by omitting the addition of the aluminium sulfate solution into the spiked solution after sodium sulfide had been added. Treated spiked solutions were analyzed using the same conditions that had been used to analyze spiked solutions for the recovery test. The obtained results were shown in Table 1. By comparing between added coagulant and without coagulant, it is very obvious that by adding aluminium sulfate as a coagulant to enhance the precipitation of the heavy metal sulfide particles formed in the spiked solution gives higher recovery percentages. It shows a very significant different in 0.1 ppm spiked solution.

Table 1: The effect of coagulant on the recovery of heavy metals.

Metals	Recovery Percentage (%)									
	0.1 ppm		0.2 ppm		0.3 ppm		0.4 ppm		0.5 ppm	
	Coag. added	Without Coag.	Coag. added	Without Coag.	Coag. added	Without Coag.	Coag. added	Without Coag.	Coag. added	Without Coag.
Cu	89.0	75.0	98.4	86.3	97.7	91.0	96.8	90.0	99.4	87.4
Cd	75.0	45.0	96.6	80.5	99.0	91.0	99.3	94.8	93.0	84.0
Cr	97.0	22.0	88.0	45.0	97.1	63.7	90.8	72.8	97.2	77.0
Pb	99.0	72.0	91.0	65.6	94.0	78.9	97.7	83.3	95.2	83.2
Ni	78.0	34.0	93.4	68.5	91.0	70.0	94.0	72.0	88.0	70.8

Note: Coag. = coagulant

### Effect of Centrifugation Duration

The effect of the centrifugation duration on the recovery of the heavy metal elements was studied. Centrifugation duration is important because it ensures that the heavy metals particles formed in the treated water samples to be settled down and deposited at the tip of the centrifuge tube. Each treated spiked solutions with sodium sulfide and aluminium sulfate was spun in the centrifuge at 15000 rpm for 2, 5, 10, 15, 20, 25 minutes, respectively. The obtained result in figure 1 shows that spinning for longer duration increases the recovery percentages for all five heavy metals. All five heavy metal elements are able to be recovered to more than 80% after spun for 20 minutes.

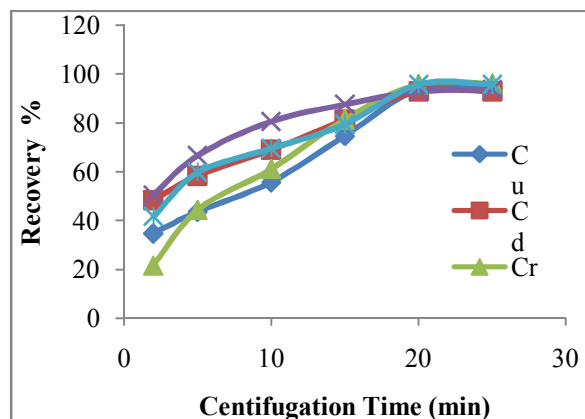


Figure 1: Effect of the centrifugation time on the recoveries of metal ions.

### Recovery Test

Accuracy of a developed method is demonstrated with recovery percentages. Closer the recovery percentage to 100% demonstrates that higher accuracy of the developed method. Spiked solution containing known amount of free heavy metal ions was used in this study to determine the accuracy of the developed method. Spiked solutions containing five types of heavy metal at the concentration range from 0.1 to 0.5 ppm were used this study. Spiked solutions were treated with excess sodium sulfide and aluminium sulfate solution before centrifugated at 15000 rpm and the deposits obtained were redissolved using nitric acid before analyzed using FAAS. As shown in Table 2, all of the obtained recovery percentages for all five heavy metal elements are fallen within 68.0-99.2% with R.S.D. values between 0.1 and 12.5%. This shows that by carrying out the treatment processes properly, there is only small amount of heavy metal ions loses in the pre-concentration process.

Table 2: Average recovery and relative standard deviation for each metal ion.

Metals	0.1 ppm		0.2ppm		0.3ppm		0.4ppm		0.5ppm		Aver. Rec.	RSDp
	Rec.	RSD	Rec.	RSD	Rec.	RSD	Rec.	RSD	Rec.	RSD		
Cu	95.1	2.8	98	2.6	94.7	3.6	96.8	1.6	98.5	1.8	96.1	3.4
Cd	68	6.7	97.3	2	93.6	6.2	99.2	0.5	92.2	2.1	90	5.5
Cr	87.6	8	86.6	6.6	93.7	2.8	94.5	2.7	96.3	0.7	91.8	6.4
Pb	96.9	2.1	88.4	2.9	94.5	3.1	97.3	0.1	93.5	4.2	94.1	3.7
Ni	83.5	12.5	91.6	5.1	95.6	3.4	98	0.8	90.1	1.3	91.8	8.1

Note: Rec. = Recovery, RSD = relative standard deviation, RSDp = relative standard deviation pooled. Aver. Rec. = the Average Recovery. All recoveries and RSDs are calculated in %.

### Real Samples Analysis

The developed method was used to determine content of the five heavy metal elements in five real water samples collected in the drain surrounding five industrial factories in Selangor state industrial area. These five factories operate businesses related to pewter, chemicals, metal can and rubber. Therefore, water discharged from these factories may contain certain amount of the heavy metals if these factories do not treat their wastewater properly. All five collected water samples were treated with necessary reagents on the next day of the sample collection day. Treated water samples were analyzed by FAAS on the third day after the sample collection day. Before the water samples were pre-concentrated using the sodium sulfide and aluminium followed by centrifugation and redissolution in acid solution, collected water samples were digested with 1:1 nitric acid according to EPA Method 200.7<sup>22</sup> to remove all the possible presence organic compounds that may hold the heavy metal elements in the complex form. Based on the obtained results shown in Table 3, water samples collected from the five industrial factories were free from copper and cadmium. Chromium was detected in water samples collected from Metal Can Factory and Rubber Factory which have the concentration of 0.04 ppm for both factories, respectively. The presence of chromium in the water sample collected near the Metal Can Factory is quite common because chromium is used in the manufacturing of metal containers especially used to be coated on steel electrolytically<sup>23</sup>, whereas detection of chromium in water sample collected near the Rubber Factory maybe due to the usage of chromium type of catalyst in the manufacturing processes such as polymerization. Water samples collected near Chemical Factory A, Metal Can Factory and Rubber Factory shows detection of lead with the concentration up to 0.08, 0.11 and 0.13 ppm, respectively. Nickel was detected in the water sample collected near Chemical Factory A, which is a cleaning chemicals production company, at the concentration of 0.2 ppm. This detection most probably is due to the usage of nickel as a hydrogenation catalyst in the production of cleaning agent such as detergent<sup>24</sup>. The concentrations of all the five heavy metal elements in the samples are lower than the maximum contamination levels, which are stipulated by the Malaysia Government as stated in the Environmental Quality Act 1974<sup>22</sup> except nickel, which was detected in water sample collected near chemical Factory A has a same concentration as the stipulated maximum contamination level. These results show that these five factories had treated their wastewater properly before discharged to the environment.

**Table 3: Comparison of heavy metals present in five wastewater samples.**

Metals	Concentration of Metals (ppm)					MDLs	MCL (ppm)
	Pewter Factory	Chemical Factory A	Chemical Factory B	Metal Can Factory	Rubber Factory		
Cu	ND	ND	ND	ND	ND	0.043	0.20
Cd	ND	ND	ND	ND	ND	0.012	0.01
Cr	ND	ND	ND	0.04	0.04	0.011	0.05
Pb	ND	0.08	ND	0.11	0.13	0.020	0.10
Ni	ND	0.20	ND	ND	ND	0.008	0.20

Note: ND = not detected. MDL = method detection limit of the developed method. MCL = maximum contamination level.

## CONCLUSION

In conclusion, the pre-concentration technique using sodium sulfide and aluminium sulfate followed by centrifugation that has been developed in this study are suitable to be used in the determination of heavy metal elements in wastewater samples. This technique is quite efficient, effective and simple in the determination of trace amount of heavy metals in the wastewater sample as the method detection limits for each heavy metal element are below the maximum contamination levels as stipulated and the overall high recovery percentages with low relative standard deviation can be obtained from the recovery test. There is no detection of copper and cadmium in all five water samples. Chromium was detected only in water samples collected from Metal Can Factory and Rubber Factory which have the concentrations of 0.04 ppm for both factories, respectively. Only the water samples collected from Chemical Company A, Metal Can Factory and Rubber Factory show detection of lead with the concentration at 0.08, 0.11 and 0.13 ppm respectively. The highest concentration detected among all the samples collected is nickel element, which is 0.20 ppm in the water sample collected from Chemical Factory A. The concentrations of all five heavy metals in the collected water samples are below the maximum contamination level stipulated in the Environmental Quality Act 1974. This result shows that these five factories had a proper wastewater treatment to treat their wastewater before discharged to the environment.

## ACKNOWLEDGEMENT

The authors would like to thank Tunku Abdul Rahman University College for supporting this research.

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