




**FACULTY OF ENGINEERING
UNIVERSITI PUTRA MALAYSIA**

**DETERMINATION OF ELEMENTS (COPPER, NICKEL AND ZINC) IN
SURFACE WATER USING FLAME ATOMIC ABSORPTION
SPECTROMETER (APHA 3111B)**

UPM/FK/MCL/TMD 1

Issue No.: 07	Effective Date: 22/04/2016
Reviewed by: Deputy Technical Manager	Approved by: Technical Manager

	FACULTY OF ENGINEERING	
	DETERMINATION OF ELEMENTS (COPPER, NICKEL AND ZINC) IN SURFACE WATER USING FLAME ATOMIC ABSORPTION SPECTROMETER (APHA 3111B) UPM/FK/MCL/TMD 1	Page : 2 of 7
		Issue No.: 07
		Effective Date: 22/04/2016

1.0 OBJECTIVE

To determine concentration of Ni, Zn and Cu elements in surface water.

2.0 SCOPE

This test method describes determination of Ni, Zn and Cu concentration in surface water using Flame Atomic Absorption Spectrometry (AAS) at ppm level.

3.0 REFERENCES

Reference Documents	Documents Title
R-20	Rice, E.W., Baird, R. B., Eaton, A.D. and Clesceri, L.S., 2012. Standard Methods for the Examination of Water & Wastewater. 22 nd Ed., APHA publisher (3111B. Direct Air-Acetylene Flame Method, 3030E. Nitric Acid Digestion;).
S-3	SOLAAR AA Software, SOLAAR Data Station (v 11.02), Spectrometer Software (v 1.3)
UPM/FK/WI/E1	Operation And Maintenance Of Flame Atomic Absorption Spectrometer (AAS)


4.0 TERMINOLOGY, GLOSSARY AND DEFINITIONS

AAS	: Atomic Absorption Spectrometry
Ni	: Nickel
Zn	: Zinc
Cu	: Copper
ppm	: Part per million
SRM	: Standard Reference Materials
CRM	: Certified Reference Materials

5.0 MATERIALS AND EQUIPMENT

5.1 Chemicals, Gas and Solvent

- 5.1.1 Nitric Acid (HNO₃, purity:65%)*(AR)
- 5.1.2 Acetylene Gas, standard commercial grade
- 5.1.3 Deionized water
- 5.1.4 Compressed air
- 5.1.5 Ni²⁺ SRM (1000 ppm)
- 5.1.6 Zn²⁺ SRM (1000 ppm)
- 5.1.7 Cu²⁺ SRM (1000 ppm)

	FACULTY OF ENGINEERING	
	DETERMINATION OF ELEMENTS (COPPER, NICKEL AND ZINC) IN SURFACE WATER USING FLAME ATOMIC ABSORPTION SPECTROMETER (APHA 3111B) UPM/FK/MCL/TMD 1	Page : 3 of 7
		Issue No.: 07
		Effective Date: 22/04/2016

5.2 Glasswares, Consumables and Equipment

- 5.2.1 Glass pipette (1mL, 5mL, 10 mL), grade A
- 5.2.2 Volumetric flask (25mL, 100mL, 1000mL), grade A
- 5.2.3 Atomic Absorption Spectrometry (AAS)
- 5.2.4 pH Meter
- 5.2.5 Whatman no.1 filter paper
- 5.2.6 Glass beaker
- 5.2.7 Glass filter funnel
- 5.2.8 Ribbed watch glass
- 5.2.9 Hot plate


6.0 METHODS

6.1 Samples Preparation

- 6.1.1 Sample must not contain particulates or organic material.
- 6.1.2 In a fumehood, transfer 100mL sample into a beaker and add 5mL HNO₃ (purity 65%).
- 6.1.3 Check the acidity of sample (pH~2). Acidify with 1.5mL /L HNO₃ if required.
- 6.1.4 Cover the beaker with a ribbed watch glass.
- 6.1.5 Gently heat the beaker on hot plate until sample volume reduce to approximately 20mL. Make sure sample does not boil and no area of the bottom of the beaker is allowed to go dry.
- 6.1.6 Cool the sample to room temperature.
- 6.1.7 Filter the sample using Whatman filter paper no.1 placed in a filter funnel, to remove any insoluble materials.
- 6.1.8 Transfer the filtrate to a 100mL volumetric flask.
- 6.1.9 Adjust the volume with deionised water to 100mL mark and mix.
- 6.1.10 Record the readings (element, concentration range) in Material Characterization Laboratory (TMD 1) Worksheet (UPM/FK/MCL/W1).

6.2 Preparation of Calibration Standard Solutions

- 6.2.1 Prepare a blank solution (2% HNO₃) by aliquot 20mL of 65% HNO₃ in 1L volumetric flask. Add deionized water to 1000mL mark.
- 6.2.2 Prepare at least 5 calibration solutions covering the range of concentration to be determined using a standard reference material for each metal.
- 6.2.3 For Cu²⁺, SRM containing 1000ppm Cu²⁺ is used. Prepare standard calibration solution (0.2ppm, 0.4ppm, 0.6ppm, 0.8ppm and 1ppm) as follow:
 - 6.2.3.1 Pipette 10mL of SRM containing 1000ppm Cu²⁺ into 100mL volumetric flask and add deionized water to 100mL mark. This give 100ppm standard solution.
 - 6.2.3.2 Pipette 10mL of 100ppm standard solution into 100mL volumetric flask and add 2% HNO₃ to 100mL mark. This give 10ppm standard solution.
 - 6.2.3.3 Using 10ppm standard solution, pipette 2mL, 4mL, 6mL, 8mL and 10mL into 5 different volumetric flasks and mark to 100mL level with 2% HNO₃ to give

 UPM UNIVERSITI PUTRA MALAYSIA BERILMU BERBAKTI	FACULTY OF ENGINEERING	
	DETERMINATION OF ELEMENTS (COPPER, NICKEL AND ZINC) IN SURFACE WATER USING FLAME ATOMIC ABSORPTION SPECTROMETER (APHA 3111B) UPM/FK/MCL/TMD 1	Page : 4 of 7
		Issue No.: 07
		Effective Date: 22/04/2016

calibration solution of 0.2ppm, 0.4ppm, 0.6ppm, 0.8ppm and 1ppm, respectively.

6.2.4 For Ni^{2+} , SRM containing 100ppm Ni^{2+} is used. Prepare standard calibration solutions (0.1ppm, 0.15ppm, 0.2ppm, 0.25ppm and 0.3ppm) as follow:

6.2.4.1 Pipette 10mL of SRM containing 1000ppm Zn^{2+} into 100mL volumetric flask and add deionized water to 100mL mark. This give 100ppm standard solution.

6.2.4.2 Pipette 10mL of 100ppm standard solution into 100mL volumetric flask and add 2% HNO_3 to 100mL mark. This give 10ppm standard solution.

6.2.4.3 Pipette 10mL of 10ppm standard solution into 100mL volumetric flask and add 2% HNO_3 to 100mL mark. This give 1ppm standard solution.

6.2.4.4 Using 1ppm standard solution, pipette 10mL, 15mL, 20mL, 25mL and 30mL into 5 different volumetric flasks and mark to 100mL level with 2% HNO_3 to give calibration solution of 0.1ppm, 0.15ppm, 0.2ppm, 0.25ppm and 0.3ppm, respectively.

6.2.5 For Zn^{2+} , SRM containing 1000ppm Zn^{2+} is used. Prepare standard calibration solution (0.2ppm, 0.4ppm, 0.6ppm, 0.8ppm and 1.0ppm) as follow:

6.2.5.1 Pipette 10mL of SRM containing 1000ppm Zn^{2+} into 100mL volumetric flask and add deionized water to 100mL mark. This give 100ppm standard solution.

6.2.5.2 Pipette 10mL of 100ppm standard solution into 100mL volumetric flask and add 2% HNO_3 to 100mL mark. This give 10ppm standard solution.

6.2.5.3 Using 10ppm standard solution, pipette 2mL, 4mL, 6mL, 8mL and 10mL into 5 different volumetric flasks and mark to 100mL level with 2% HNO_3 to give calibration solution of 0.2ppm, 0.4ppm, 0.6ppm, 0.8ppm and 1ppm, respectively.

6.3 AAS Equipment set up and optimization


6.3.1 AAS equipment is set up and optimize according to UPM/FK/WI/E1.

6.4 Standard Calibration Plot

6.4.1 Aspirate blank and zero the instrument.

6.4.2 Aspirate 5 concentrations of standard calibration solution. The range of concentration is within a linear working range of the test method (with good precision as reported in Method validation Report for TMD1), as indicated below:

Element	Linear Working Range with good precision (ppm)
Cu	0.1 - 1.0
Ni	0.02 – 0.3
Zn	0.1 – 1.0

	FACULTY OF ENGINEERING	
	DETERMINATION OF ELEMENTS (COPPER, NICKEL AND ZINC) IN SURFACE WATER USING FLAME ATOMIC ABSORPTION SPECTROMETER (APHA 3111B) UPM/FK/MCL/TMD 1	Page : 5 of 7
		Issue No.: 07
		Effective Date: 22/04/2016

6.4.3 Generate a calibration curve, with $R^2 = >0.95$.

6.4.4 Perform QC.

6.5 Quality Control

6.5.1 QC is conduct and recorded in Material Characterization Laboratory (TMD 1) Worksheet (UPM/FK/MCL/W1).

6.5.2 QC sample is prepared using a known concentration sample in 2% HNO_3 . The concentration of QC sample should be within the range of standard calibration used in section 6.4.

6.5.3 Aspirate QC sample.

6.5.4 Read QC result (pass/fail) from the instrument.

6.5.5 QC pass: proceed step 6.6.

6.5.6 QC fail: repeat step 6.5.3 for a maximum 3 times. For subsequent QC failure, proceed with Nonconformity Procedure (UPM/FK/MRQ 7) and record in F5 form.

6.5.7 Conduct QC every 10 samples (if samples more than 10).

6.5.8 Rinse with blank in between the sequence.

6.6 Analysis of Sample

6.6.1 Rinse nebulizer by aspirating with deionized water.

6.6.2 Aspirate blank and zero instrument.

6.6.3 Aspirate sample.

6.6.4 Read concentration from instrument read out and record in Material Characterization Laboratory (TMD 1) Worksheet (UPM/FK/MCL/W1).

6.6.5 If sample concentration value is outside calibration range, proceed step 6.7 for linearity concentration range.

6.6.6 Rinse with deionized water.

6.6.7 Aspirate with blank solution.

6.6.8 Aspirate the next sample and record reading.

6.6.9 Repeat the sequence 6.6.4 to 6.6.6 for every sample.

6.6.10 Conduct QC every 10th samples.

6.6.11 Print the calculated/generated results from the instrument. This step is optional.

6.6.12 Upon analysis completion, rinse the nebuliser with deionized water and proceed with equipment standard operating procedure for shutdown.

6.7 Sample concentration value higher than the linear working range


6.7.1 Perform sample dilution in 2% HNO_3 to concentration value within the range of calibration plot.

6.7.2 Perform analysis of sample in step 6.6.

6.7.3 Record the dilution factor used in UPM/FK/MCL/W1.

6.8 Sample concentration lower than the linear working

6.8.1 For concentration close to minimum working range value (in section 6.4), perform sample spiking, step 6.9.

	FACULTY OF ENGINEERING	
	DETERMINATION OF ELEMENTS (COPPER, NICKEL AND ZINC) IN SURFACE WATER USING FLAME ATOMIC ABSORPTION SPECTROMETER (APHA 3111B) UPM/FK/MCL/TMD 1	Page : 6 of 7
		Issue No.: 07
		Effective Date: 22/04/2016

6.9 Sample Spiking Procedure

6.9.1 Prepare spike sample by pipetting 1mL of a known concentration of analyte (SRM) into 100mL sample. The concentration value of spiked sample should be within standard calibration plot range.

$$\text{Spiked concentration desired} = \frac{1\text{mL of SRM} \times \text{concentration of SRM}}{100\text{mL sample}}$$

6.9.2 Prepare spike blank by repeat step 6.8.5 by pipetting the same amount of SRM into blank (2% HNO₃).

6.9.3 Perform AAS analysis for spiked samples and spiked blank using step 6.6.

6.9.4 Record reading in UPM/FK/MCL/W1 and calculate the % recovery for spiking using formula:

$$\% \text{ Recovery} = \frac{\text{measured concentration in spiked sample}}{\text{measured concentration in spiked blank}} \times 100$$

6.9.5 Spike recoveries value between 85%-115% are good precision and proceed with analysis.

6.9.6 For recoveries value outside 85%-115% range, repeat step 6.8.5 by using analyte concentration within precision level.


6.10 Data Analysis

6.10.1 Data is analysed using software SOLAAR Series Data Station Software (v 11.2).

6.10.2 Sample concentration is calculated based on 3 replicate measurements.

6.10.3 For spiked sample, result is calculated as the following formula:

$$\text{Sample concentration (ppm)} = \frac{\text{Absorbance of sample}}{\text{Absorbance of spike}} \times \text{Spike concentration}$$

	FACULTY OF ENGINEERING	
	DETERMINATION OF ELEMENTS (COPPER, NICKEL AND ZINC) IN SURFACE WATER USING FLAME ATOMIC ABSORPTION SPECTROMETER (APHA 3111B) UPM/FK/MCL/TMD 1	Page : 7 of 7
		Issue No.: 07
		Effective Date: 22/04/2016

7.0 RECORDS

No.	File/Documents	Location and Duration	Responsibility	Authority and Method of Disposal
1.	UPM/FK/TR/FL-15 Test Report <ul style="list-style-type: none"> • Application for Testing Services Form (UPM/FK/F 3-A) • Material Characterization Laboratory (TMD 1) Worksheet (UPM/FK/MCL/W1) • Amendment to Test Report or Calibration Certificate Form (UPM/FK/F 10) • Nonconformity Form (UPM/FK/F5) 	Laboratory 6 years	TM/DTM	QM/DCO Shred