CHEMICAL ANALYSIS OF WATER, SEDIMENT AND SOIL SAMPLES

Cooperation beyond borders.
Interreg-IPA Cross-border Cooperation Romania-Serbia Programme is financed by the European Union under the Instrument for Pre-accession Assistance (IPA II) and co-financed by the partner states in the Programme.
Project RoRS 337- ROmania Serbia NETwork for assessing and disseminating the impact of copper mining activities on water quality in the cross-border area (RoS-NET2)

TABLE OF CONTENT

OBJECTIVES OF PROCEDURE FOR CHEMICAL ANALYSIS

This procedure describes the method for determination of the selected chemical elements presented in the soil and water samples in various concentration ranges using the atomic emission spectrometry with inductively coupled plasma (hereinafter referred to as ICPOES). Prior to ICPOES analysis the samples is preceded by dissolution of the previously prepared soil samples with a mixture of acids.

The content of the analyte has been determined by the method of calibration curve. The chemical elements which will be analyzed in the water (surface and underground) samples are the following: total Fe, Fe^{2+}, Fe^{3+} (calculated), Mn, Cu, Mo, Zn, As, Ni, Pb, Cd, Cr, Hg, S, and Se. In addition, pH, T and dissolved oxygen will be measured in the water samples.

Soil samples will be analyzed on the following chemical elements: Cd, Cr, Cu, Ni, Pb, Zn, Hg, As, Mo and Se. The choice of given chemical elements was carried out according to the results of previous analysis of samples from the same or the surrounding area, as well as on the basis of statutory legislation of the Republic of Serbia.

The analysis of the soil samples on the elements present in the larger and smaller concentrations, as well as those present in trace amounts, using ICPOES technique is very useful for a variety of geochemical exploration, evaluation study, study of human health risk assessment, taking appropriate preventive measures, etc.

ICP OES OPERATING AND MEASURING CONDITIONS FOR WATER, SEDIMENT AND SOIL SAMPLES

The chemical analysis of water, sediment and soil samples will be performed using ICPOES device. Below is provided the apparatus, reagents and standards which are required for the preparation of chemical analysis of water, soil and sediment samples. A detailed description of the process of chemical analysis, chosen operating parameters, quality control of chemical analysis etc. is given bellow.

Devices and apparatuses

- atomic emission spectrometer with inductively coupled plasma, ICPAES
- Automatic system for dissolution of samples, Vulkan, Horiba
- 30 mL Teflon vessel with a stopper (Savillex)
- hot plate

Reagents

- Bidistilled water, conductivity of 0.05 μS/cm
- Hydrochloric acid (HCl), conc. (37%)
- Nitric acid (HNO3), conc. (63%)
- The solution for the optic reprofiling

The calibration standards

The two sets of primary calibration solution, each of 10 mg/L, are used for the preparation of secondary calibration solutions of different concentrations.

1. **Set I** - LGC Ultra Scientific CRM IMS-102 - mix in a 2% HNO_3 containing 10 mg/L of the following elements: As, Cd, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se and Zn.

2. **Set II** - LGC Ultra Scientific CRM IMS-103 - mix in H_2O containing 10 mg/L of the following elements: Mo and S.

The final concentrations of the prepared calibrations standards are in the range 0-100 mg/L.

Safety precautions

All personnel in the laboratory must wear a gown, goggles and appropriate protective equipment during operation (details provided in Annex II).

Description of the procedure for chemical analysis

Analysis of the sediment and soil samples by atomic emission spectrometry with inductively coupled plasma (ICPOES) comprises the following steps:

- measurement of the prepared samples,

-acid dissolution of the samples,

- running the samples with ICPOES and interpretation of the results.

Prior to the analysis, the plasma need to be stabilizes and optic reprofiled according to the manufacturer recommendation. The device is calibrated by using the above calibration solution. The recommended operating conditions for water, sediment and soils samples using ICPOES are given in Table 1.

Table 1 - ICPOES operating conditions

Parametri	
Forward power (W)	1450
Coolant flow (L/min)	13
Nebulizer flow (L/min)	0.75
Auxiliary flow (L/min)	1
Plasma torch	Quartz, demountable, 2.0 mm injector tube
Spray chamber	Scott
Nebulizer	Cross-flow
Sample aspiration rate	2 mL/min

Samples of water are measured directly without prior preparation.

Measurement of the sediment and soil samples

Previously prepared soil sample is measured on an analytical balance to four decimal places. The total amount of the sample amounts to 0.5000 g (or 0.2500g). After the dissolution of the

sample, the sample transferred quantitatively into volumetric flask of 50 mL (or 25 mL) and diluted to the nominal value. The final dilution factor is DF-100. If the analyte is present in a sample at a concentration > 10% from the highest point of the calibration curve it is necessary to further dilute the sample.

Dissolution of sediment and soil samples

Several procedures for dissolution of sediment and soil samples have been used. Depending on the needs, intentions, and the demands of users, two procedures for the dissolution of the sediment and soil sample are most often used: The dissolution method with aqua regia (HCl: HNO_3 = 3: 1) and the dissolution process with a mixture of 4 acid (HNO_3 / HCl / HF / $HClO_4$).

The dissolution of the sediment and soil samples using a multi-acid ("almost complete dissolution") is suitable for dissolving certain types of a soil and sediments. However, there are exceptions, ie. some samples is impossible to dissolve completely by using the procedure with four acid. The procedure with four acid is not applicable for completely resistant or resistant minerals, refractory oxides, as well as by a secondary minerals. Examples of the incomplete dissolution of the Ba and barite, and Cr in the chromate, Ti in rutile, cassiterite in Sn, Al in a corundum, rare earth elements in monazite et al.

The samples can be dissolved on a hot plate, in an automatic system for dissolving (Vulcan), as well as to microwave digestion. Selection of dissolution depends primarily on the needs and number of samples.

In laboratories of Mining and metallurgy Institute Bor (MMI), sediments and soil samples have been dissolved in an automatic system for the dissolution (Vulcan) using aqua regia. The Vulcan system posses a cabacility to dissolve for a few hours the 84 samples at once. Also, the consumption of acid is smaller than in the conventional dissolution process on a hot plate. In addition, the environmental aspect is important, dissolution is carried out in a closed system of steam through the scrubber are rinsed before going into the atmosphere.

All the samples (analyzed sediment and soil samples, the blank samples, duplicates, replicates, certified reference materials, reference materials, control samples, etc.) will be dissolved in an identical manner.

Running the samples with ICPOES and interpretation of the results

All measurements will be performed with ICPAES device. Due to its multi-element capability, high dynamic linear range and sensitivity, ICPAES has been widely used for the analysis of water, sediment and soil samples. The wavelength range between 165 and 770 nm can be analyzed.

For each analyzed element with ICPOES technique it is possible to choose multiple wavelengths. Table 2 presents the recommended wavelengths for the analysis the elements of interest from water, sediment and soil samples.

Table 2 – Recommended wavelength for selected elements

Hemijski element	Talasna dužina (nm)
As	189.042
Cd	214.438, 226.502
Cr	205.618, 267.716
Cu	324.754
Hg	184.950, 194.227
Fe	259.941
Mn	257.611
Mo	202.095
Ni	231.604
Pb	220.351
S	180.731
Se	196.090
Zn	213.856, 206.191

Quality control of ICPAES analysis

Quality control of chemical analysis is carried out in the laboratory by running CRM.

THE FRAMEWORK OF CHEMICAL TESTING

This procedure shall apply throughout the implementation of the project (09.10.2019-09.09.2021). Summary of the activities to be carried out according to the procedure is given in Table 1.

Table 1 – Summary of physico-chemical analysis of samples per quarter

QUARTER	ACTIVITY
I	1. Literature review of the applicable standards and regulations for chemical analysis of water and soil samples. 2. Development of the method (selection of operating parameters, elimination of spectral interference, the selection of wavelength, etc.,) for determinations of chosen elements in water, sediment and soil samples using ICPAES technique. 3. Entering the results of chemical analyzes in the database of chemical analysis in an Excel document. 4. Preparation of tender documentation. 5. Issuing chemical orders (Annex I).
II	1. Chemical analysis of water samples from the 1st selected location in order to select the acidic mine water for the neutralization with $Ca(OH)_2$. 2. Chemical analysis of the sludge samples after acid leaching. 3. Chemical analysis of the solution after LP and TCLP tests. 4. Chemical analysis of the sediment and soil samples. 5. Entering the results of chemical analyzes in the database of chemical analysis in an Excel document. 6. Issuing chemical orders (Annex I).
III	1. Chemical analysis of water samples from the 1st selected location in order to select the acidic mine water for the neutralization with $CaCO_3$. 2. Chemical analysis of the sludge samples after acid leaching. 3. Chemical analysis of the solution after LP and TCLP tests. 4. Chemical analysis of the sediment and soil samples. 5. Entering the results of chemical analyzes in the database of chemical analysis in an Excel document. 6. Issuing chemical orders (Annex I).
IV	1. Chemical analysis of the solution after the neutralization process of the water selected from 1st location on the pilot plant facility. 2. Chemical analysis of the sludge samples after acid leaching. 3. Chemical analysis of the solution after LP and TCLP tests. 4. Chemical analysis of the sediment and soil samples. 5. Entering the results of chemical analyzes in the database of chemical

	analysis in an Excel document. 6. Issuing chemical orders (Annex I).
V	1. Chemical analysis of water samples from the 2nd selected location in order to select the acidic mine water for the neutralization with $Ca(OH)_2$. 2. Chemical analysis of the sludge samples after acid leaching. 3. Chemical analysis of the solution after LP and TCLP tests. 4. Chemical analysis of the sediment and soil samples. 5. Entering the results of chemical analyzes in the database of chemical analysis in an Excel document. 6. Issuing chemical orders (Annex I).
VI	1. Chemical analysis of water samples from the 2nd selected location in order to select the acidic mine water for the neutralization with $CaCO_3$. 2. Chemical analysis of the sludge samples after acid leaching. 3. Chemical analysis of the solution after LP and TCLP tests. 4. Chemical analysis of the sediment and soil samples. 5. Entering the results of chemical analyzes in the database of chemical analysis in an Excel document. 6. Issuing chemical orders (Annex I).
VII	1. Chemical analysis of the solution after the neutralization process of the water selected from 2nd location on the pilot plant facility. 2. Chemical analysis of the sludge samples after acid leaching. 3. Chemical analysis of the solution after LP and TCLP tests. 4. Chemical analysis of the sediment and soil samples. 5. Entering the results of chemical analyses in the database of chemical analysis in an Excel document. 6. Issuing chemical orders (Annex I).+++++++++++++++
VIII	1. The formation of the final database with the results of chemical analyzes that were performed during the project. **Deliverable** D.T1.4.1 - Report regarding the physicochemical characterization of the analyzed samples

RESOURCES AND RESPONSIBILITIES

Resources	Responsibility
Responsible persons for chemical analysis-Serbian site: 1. Renata Kovačević - Expert for ICP-OES chemical analysis 2. Jelena Petrović - Expert for XRF chemical analysis	Preparation of calibration standards and all working samples (blanks, check standards, CRM etc.) Measuring and dissolution of sediment and soil samples. Chemical analysis of water, sediment and soil samples using atomic emission spectrometer with inductively coupled plasma. Preparation of results data base. Issuing chemical orders.