Uluslararası İleri Doğa Bilimleri ve Mühendislik Araştırmaları Dergisi
Sayı 7, S. 56-61, 7, 2023
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Araştırma Makalesi

IJANSER
https://as-proceeding.com/index.php/ijanser
ISSN: 2980-0811

International Journal of Advanced Natural Sciences and Engineering Researches
Volume 7, pp. 56-61, 7, 2023
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Research Article

A comparison of methods of analysis of heavy metals in soil samples of Mitrovica environment, Republic of Kosovo

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(Received: 31 July 2023, Accepted: 09 August 2023)

(1st International Conference on Modern and Advanced Research ICMAR 2023, July 29-31, 2023)

.**ATIF/REFERENCE:** Aliu, M., Šajn, R. & Stafilov, T. (2023). A comparison of methods of analysis of heavy metals in soil samples of Mitrovica environment, Republic of Kosovo. *International Journal of Advanced Natural Sciences and Engineering Researches*, 7(7), 56-61.

Abstract – In this work, the distribution of heavy metals in surface soil samples (0-5 cm) from the Mitrovica Region, was studied. The investigated region (301.5 km^2) is covered by a sampling grid of 1.4×1.4 km. In total 156 soil samples from 149 locations were collected. Digestion methods, including Aqua Regia Digestion (mixture of HNO_3 and HCl and water at 95ºC - the 1DX1 method) and acid digestion: use of concentrated acids such as hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO_3) and perchloric acid ($HClO_4$) (ISO 14869- 1:2001(E) method), are used to prepare samples for spectroscopic analysis. High-sensitivity spectroscopy techniques such as inductively coupled plasma emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) were applied to measure the concentration of Ni and Co in soil samples. Data analysis and construction of the map were performed using the Statistica (ver. 9), AutoDesk Map (ver. 2008) and Surfer (ver. 9) software. It was found that the average content of Ni and Co in the surface soil for the entire study area is 96 mg/kg (with a range of 7.6-2600 mg/kg) and 22 mg/kg (with a range of 2.7-1600 mg/kg), respectively. The obtained average and median values obtained by ICP-MS are very similar to those obtained by ICP-AES. Namely, the correlation factor for Co and Ni between the results from both methods are 0.92 (for normal distribution), 0.93 (for logarithmic) and 0.94 (for rank), and 0.86 (for normal distribution), 0.94 (for logarithmic) and 0.96 (for rank), respectively. The obtained results show that the high concentrations of Ni and Co in the surface soil samples may originate from similar sources and their distribution follows the lithology of the study area.

Keywords – Soil, Spatial Distribution, Nickel, Cobalt, ICP-MS, ICP-AES, Mitrovica Region, Republic of Kosovo

I. INTRODUCTION

Heavy metals in the environment originate from two anthropogenic sources, one connected with human activity and the other concerned with the natural circulation of the metals throughout nature. There are many different sources of heavy metal contaminants including chemical and metallurgical industries [1,2]. Elements such as Fe, Zn, Mn, Cu, Co and Ni play a crucial role in the normal growth and some vital functions of living organisms if present in trace amount as micronutrients, however, becomes a matter of concern if exceed their permissible levels [3]. There are many analytical methods to determine the concentrations of major elements and trace elements in soils, either directly in solid samples or indirectly, in liquids after acid digestion. Various digestion methods are used to determine the mass concentration of trace metals in soils, including different combinations of concentrated acids [4].

This paper presents the origins of nickel and cobalt, methods of determining the given elements, and means of preparing samples for environmental analysis.

II. MATERIALS AND METHOD

A. *Study area*

The current study was conducted in Mitrovica city and the surrounding region, Republic of Kosovo (Fig.1). The study area is large (24 NNW-SSE km x 18 WWS-EEN km) and is located in the northern part of Kosovo, which is limited by the coordinates (WGS 84) longitude 20.74528°-20.99235° (E) and latitude 42.78522°-42.99330° (N). The study area contains significant polymetallic deposits (Pb, Zn, Mn and Cr) and important deposits of lead and zinc.

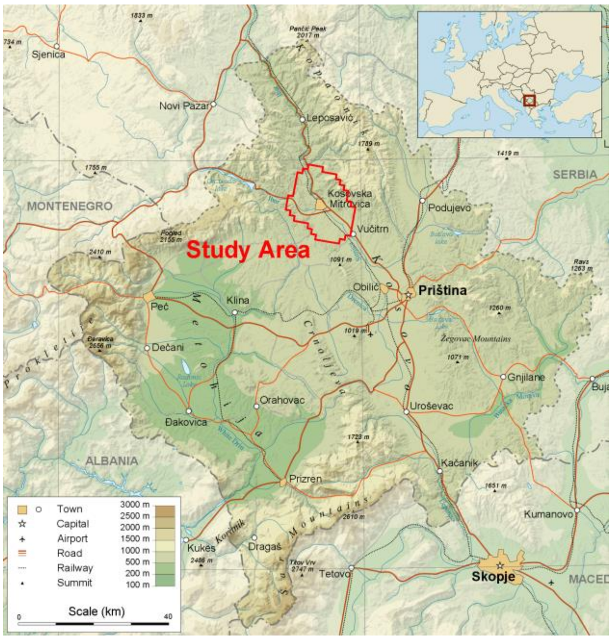

Fig. 1 Location of the study area

B. *Collection of soil samples and chemical analysis*

Out of 156 soil samples were taken at a depth of 0-5 cm over an area of 301.5 km^2 where the soil had not been recently disturbed and away from the waste locations. The complete investigated region was covered by a basic sampling grid of 1.4x1.4 km, but in the diagonal cross-section of each entire grid cell, one more sample was added (Fig. 2). The samples were located using Global Positioning System (GPS) and topographic maps at a scale of 1:25,000. One sample represents the composite material collected at the central sample point itself and at least four points with a radius of 50 m around it towards N, E, S and W.

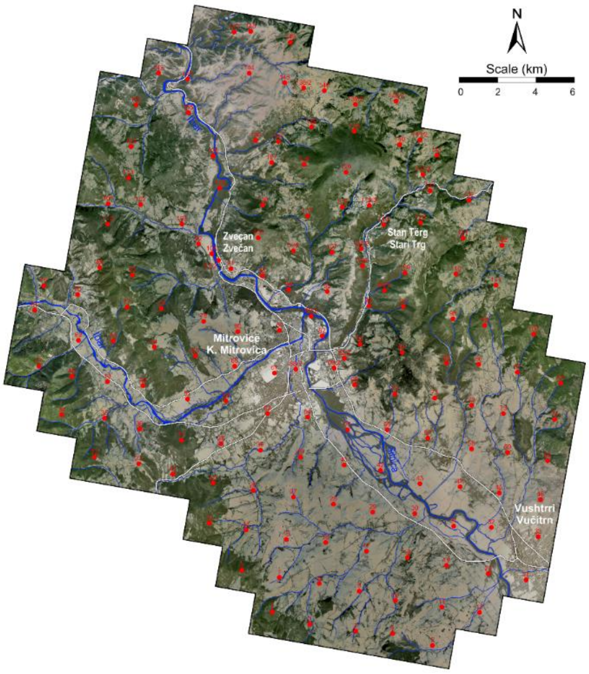

Fig. 2 Soil sample locations in the study area

Soil samples were air-dried, crushed, cleaned from extraneous material, and sieved through a plastic sieve with 2 mm mesh. The sieved mass was quartered and milled in an agate mill. The digestion process used 0.5 g of soil samples, digested with HNO_3 (Tracepur, 69% m/V, Merck), HF (Tracepur, 48% m/V, Fluka), $HClO_4$ (*p.a.*, 70% m/V, Alkaloid) and HCl (Tracepur, 36% m/V, Merck) according to ISO 14869-1:2001(E) method.

Procedure: Weigh precisely 0.500 g of the milled soil sample and placed it in a Teflon digestion vessel and add 10 mL of nitric acid. Place the dish on the asbestos net plate at ring at 100 ˚C and evaporate until approximately 1 mL of nitric acid remains. Note that several successive additions of nitric acid may be necessary until the emission of nitrous vapors ceases to remove all organic matter. After the last addition of nitric acid, remove the dish from the hot plate and cool it to room temperature before undertaking the digestion. After cooling add 10 mL of hydrofluoric acid and 3 mL of perchloric acid to the pretreated portion. Heat this mixture on the hot plate until the dense fumes of perchloric acid and silicon tetrafluoride cease. Do not allow the mixture to evaporate to complete dryness. Remove the vessel from the hot plate and allow cooling, adding 2 mL of hydrochloric acid or 2 mL of nitric acid and approximately 5 mL of water to dissolve the residue. Transfer this solution quantitatively to the 50 mL volumetric flask, fill to the mark and mix well.

Stock standard Ni and Co solution (1000 mg/L) supplied by Merck was used for calibration. Working standards were prepared by appropriate diluting of stock solution. During the preparation and measurements, great care was taken to prevent contaminating any of the solutions. Deionized water was always used for the dilutions and for the final rinsing of glassware. The concentrations of standard solutions for calibration are 1 µg/ml, 10 µg/ml and 200 µg/ml. All the chemicals used were of analytical reagent grade. An optical emission spectrometer with inductively coupled plasma, ICP-OES, (Varian 715-ES) was employed to determine Ni and Co concentration using argon plasma. The instrumentation and operating conditions for this ICP-AES system are given in Table 1.

Table 1. Instrumentation and operating conditions for ICP-AES system

<table>
<tr><th colspan="4">RF Generator</th></tr>
<tr><td colspan="2">Operating frequency</td><td colspan="2">40.68 MHz free-running, air-cooled RF generator</td></tr>
<tr><td colspan="2">Power output of RF generator</td><td colspan="2">700–1700 W in 50 W increments</td></tr>
<tr><td colspan="2">Power output stability</td><td colspan="2">Better than 0.1%</td></tr>
<tr><th colspan="4">Introduction Area</th></tr>
<tr><td colspan="2">Sample Nebulizer</td><td colspan="2">V- groove</td></tr>
<tr><td colspan="2">Spray Chamber</td><td colspan="2">Double-pass cyclone</td></tr>
<tr><td colspan="2">Peristaltic pump</td><td colspan="2">0-50 rpm</td></tr>
<tr><td colspan="2">Plasma configuration</td><td colspan="2">Radially viewed</td></tr>
<tr><th colspan="4">Spectrometer</th></tr>
<tr><td colspan="2">Optical Arrangement</td><td colspan="2">Echelle optical design</td></tr>
<tr><td colspan="2">Polychromator</td><td colspan="2">400 mm focal length</td></tr>
<tr><td colspan="2">Echelle grating</td><td colspan="2">94.74 lines/mm</td></tr>
<tr><td colspan="2">Polychromator purge</td><td colspan="2">0.5 L min^{-1}</td></tr>
<tr><td colspan="2">Megapixel CCD detector</td><td colspan="2">1.12 million pixels</td></tr>
<tr><td colspan="2">Wavelength coverage</td><td colspan="2">177 nm to 785 nm</td></tr>
<tr><td colspan="2">Wavelength for Ni, Co measurement</td><td colspan="2">231.604 nm, 238.892 nm</td></tr>
<tr><th colspan="4">Conditions for program</th></tr>
<tr><td>RFG Power</td><td>1.0 kW</td><td>Pump speed</td><td>25 rpm</td></tr>
<tr><td>Plasma Ar flow rate</td><td>15 L min^{-1}</td><td>Stabilization time</td><td>30 s</td></tr>
<tr><td>Auxiliary Ar flow rate</td><td>1.5 L min^{-1}</td><td>Rinse time</td><td>30 s</td></tr>
<tr><td>Nebulizer Ar flow rate</td><td>0.75 L min^{-1}</td><td>Sample delay</td><td>30 s</td></tr>
<tr><td>Background correction</td><td>Fitted</td><td>No of replicates</td><td>3</td></tr>
</table>

All soil samples were also analysed for Ni and Co with ICP-MS at the ACME laboratory, Ltd. in Vancouver, Canada (ACME, 2010; http://acmelab.com), after aqua regia digestion (mixture of HCl, HNO_3, and water at 95°C - 1DX method). For this study, both certified reference materials (NIST-SRM 2711a, Montana II Soil, National Institute of Standards & Technologies, Gaithersburg, MD, USA) and spiked intra-laboratory samples were analyzed at a combined frequency of 20% of the samples.

Universal kriging with the linear variogram interpolation method [5] was applied to construct the maps of areal distributions of Ni and Co values in the surface soil.

III. RESULTS

Data from the descriptive statistics of measurements of nickel and cobalt by both techniques (ICP-MS and ICP-AES) in the soil samples collected from the investigated region (N=156) are presented in Table 2 and their spatial distributions with the results obtained by ICP-MS and ICP-AES are presented on Figs. 3-6, respectively. In Figs. 7 and 8 the logarithmic correlation between both data sets is given.

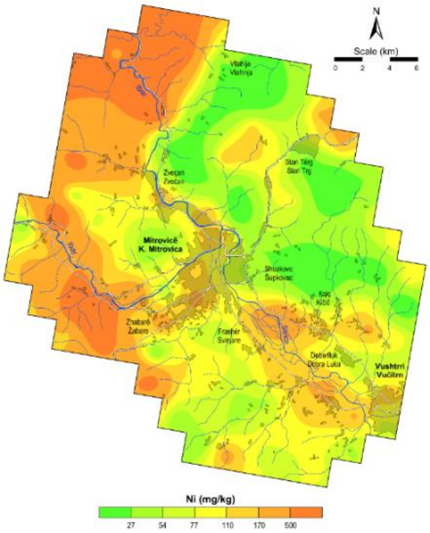

Fig. 3 Spatial distribution of nickel in Mitrovica area from the results obtained by ICP-MS

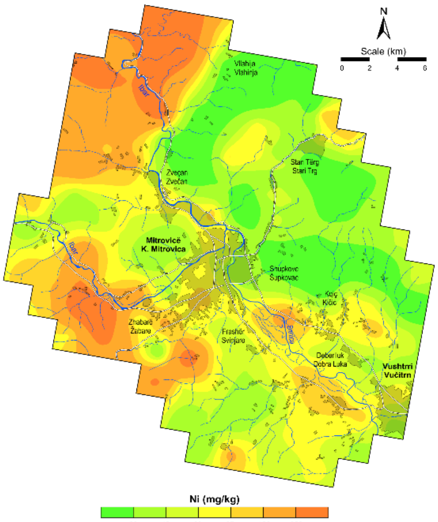

Fig. 4 Spatial distribution of nickel in Mitrovica area from the results obtained by ICP-AES

Table 2. Descriptive statistics of measurements for nickel and cobalt in soil, N=156 (values given in mg/kg)

El.	Technique	X	Xg	Md	P_{10}	P_{90}	Min	Max
Ni	ICP-MS	96	239	87	23	421	7.6	2600
	ICP-AES	226	94	86	20	421	7.6	2568
Co	ICP-MS	22	174	22	10	43	2.7	1600
	ICP-AES	28	22	21	9.7	43	2.7	1560

N – number of observations; *Md* – median; *X* – arithmetical mean, *Xg* – geometrical mean; *Min* – minimum; *Max* – maximum; P_{10} – 10 percentiles; P_{90} – 90 percentiles.

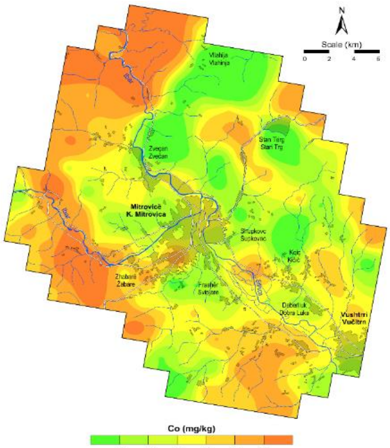

Fig. 5 Spatial distribution of cobalt in Mitrovica area from the results obtained by ICP-MS

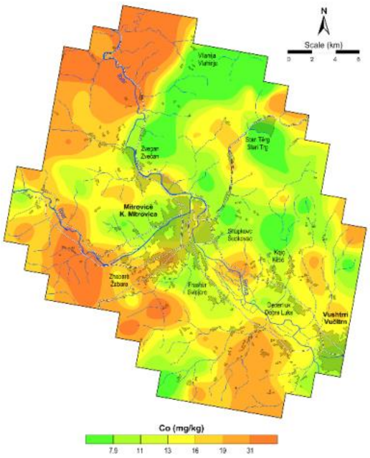

Fig. 6 Spatial distribution of cobalt in Mitrovica area from the results obtained by ICP-AES

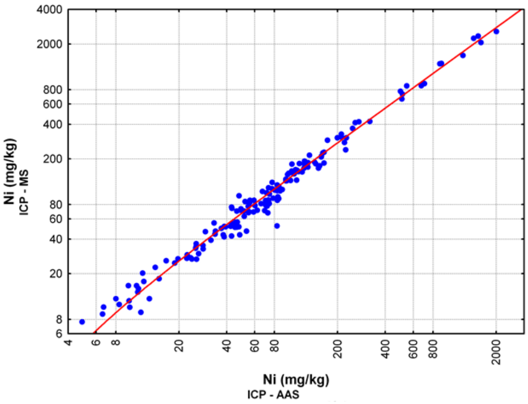

Fig. 7 Scatterplot diagram between data obtained for Ni by ICP-MS and ICP-AES

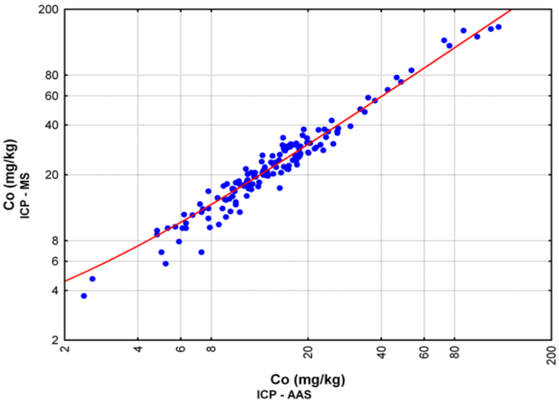

Fig. 8 Scatterplot diagram between data obtained for Co by ICP-MS and ICP-AES

IV. DISCUSSION

Nickel and Co are commonly associated with primary and secondary phyllosilicates, especially serpentine, talc, and chlorite and sometimes Fe-rich silicates, e.g., olivine, pyroxene, and hornblende [6]. Cobalt is siderophilic and found in S-bearing rocks as sulfidic minerals such as cobaltite (CoAsS). Nickel can be both siderophilic or chalcophilic, substituting for Fe in minerals such as pentlandite $(Ni,Fe)_9S_8$ or millerite (NiS) [7]. Nickel is required for several essential enzymes in plants and animals, but overexposure can be toxic.

Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals with properties similar to iron and nickel. Cobalt occurs as the biochemically important vitamin B12 and is essential for good health in animals and humans [8]. Cobalt is dispersed in the environment in low concentrations. The primary anthropogenic sources of cobalt in the environment are the burning of fossil fuels, application of cobalt-containing phosphate fertilizers, mining, and smelting of cobalt-containing ores, processing of cobalt-containing alloys, and industries that use or process cobalt compounds [8].

Cobalt has both beneficial and harmful effects on human health. It is present in vitamin B12 which is essential to maintain human health and has been used as a treatment for anemia. Excessive exposure and uptake of cobalt in industrial exposure are known to cause health effects, although it is not known to cause cancer.

Humans add cobalt by releasing small amounts into the atmosphere from coal combustion and mining, processing of cobalt-containing ores, and the production and use of cobalt chemicals.

Cobalt cannot be destroyed once it has entered the environment. It may react with other particles or adsorb on soil particles or water sediments. Cobalt will only mobilize under acidic conditions, but ultimately most cobalt will end up in soils and sediments. On the other hand, soils near mining and melting facilities may contain very high amounts of cobalt, so the uptake by animals through eating plants can cause health effects.

In this study, the average content of Co in the surface soil for the entire study area is 22 mg/kg (with a range of 2.7-1600 mg/kg). From descriptive statistics (Table 2), it can be seen that the obtained average and median values for Co obtained by ICP-MS are very similar to those obtained by ICP-AES. Namely, the correlation factor for Co between the results from both methods is 0.92 (for normal distribution), 0.93 (for logarithmic), and 0.94 (for rank).

In the present study, the average Co content in the topsoil for the entire study area is higher than the corresponding European average value of 9 mg/kg in European topsoil [9], and the average content value (8 mg/kg) of Co in soils worldwide [6].

Igneous rocks are the primary source of Ni found in soils. In soils, the total concentration of a trace element such as Ni is related directly to the concentration in the parent material and to the weathering processes [10]. The losses of Ni from soil occur in solution either by leaching or in the runoff, in eroded material, and in harvested goods. Gain of Ni to soil occurs naturally through the accession of soil eroded from elsewhere and the addition of agricultural chemicals.

Nickel is present in all soil and is a very abundant natural element that can be combined with other metals, such as iron, copper, chromium, and zinc, to form alloys. These alloys are used to make coins, jewelry, and items such as valves and heat exchangers. Nickel compounds are used for nickel plating, to color ceramics, to make some batteries, and as substances known as catalysts that increase the rate of chemical reactions. Most nickel is used to make stainless steel [11].

The major source of nickel exposure to the general population is food. Some foods are naturally high in nickel including chocolate, soybeans, nuts, and oatmeal. Higher levels of exposure can occur in industries that use nickel. The most common harmful health effect of nickel in humans is an allergic reaction. Industrial exposures to higher concentrations in the air are known to cause serious health effects.

In this study was found that the average content of Ni in the surface soil for the entire study area is 96 mg/kg (with a range of 7.6-2600 mg/kg). Similarly to Co the obtained average and median values obtained by ICP-MS are very similar to those obtained by ICP-AES. Namely, the correlation factor for Ni between the results from both methods is 0.86 (for normal distribution), 0.94 (for logarithmic), and 0.96 (for rank).

The average Ni content in European topsoil is 9 mg/kg [9] and in soils worldwide is 18 mg/kg [6]. The average amount of Ni in the topsoil for the entire study area (96 mg/kg) exceeds the estimated

European Ni average [10] of topsoil by a factor of 10.6 and the average content value of Ni in soils worldwide [6] by a factor of 5.3.

The geochemical maps (Figs. 3-6) of the spatial distribution of Co and Ni in soils of the investigated area with the results obtained by ICP-MS and ICP-AES show that Cobalt and nickel content in soil increase gradually to the western and southern part of the investigated area, as the distance to the industrial zone increases makes us believe that the Co and Ni input must be associated with natural phenomena, such as a rock weathering and chemical processes in soil. This also means that the Pb-Zn mining and smelting activity had little effect on the spatial distribution of Co and Ni.

Spatial distribution maps of Co and Ni show their predominance in the area of Triassic serpentinites in the northeastern and western parts of the study area. The lowest contents are found on the outcropping of Miocene latites, quartz-latites and pyroclastites. Reference [12] has also found high contents of Co (>100 mg/kg) and Ni (>1000 mg/kg) in soils formed on ultrabasic migmatites of the northern and western sectors of the study area.

V. CONCLUSION

This study has shown that the data of Ni and Co in the surface soil of the Mitrovica region, the Republic of Kosovo obtained by ICP-AES and ICP-MS are very similar. The high concentrations of Ni and Co in the surface soil samples may originate from similar sources and their distribution follows the lithology of the study area. Spatial distribution maps of Co and Ni show their predominance in the area of Triassic serpentinites on the northeastern and western parts of the study area. The lowest contents are found on the outcropping of Miocene latites, quartz-latites and pyroclastites.

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