

## APPLICATION OF $k_0$ -INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS FOR DETERMINATION OF MAJOR AND TRACE ELEMENTS IN SOME MANGANESE MINERALS

Radojko Jaćimović<sup>\*1</sup>, Milena Taseska-Gjorgijevski<sup>2</sup>, Trajče Stafilov<sup>3</sup>,  
Gligor Jovanovski<sup>4</sup>, Petre Makreski<sup>\*3</sup>

<sup>1</sup>*Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*

<sup>2</sup>*Institute of Agriculture, Ss. Cyril and Methodius University,  
Blvd. Aleksandar Makedonski b.b., MK-1000, Skopje, R. Macedonia*

<sup>3</sup>*Institute of Chemistry, Faculty of Natural Sciences and Mathematics,  
Ss Cyril and Methodius University, Arhimedova 5, Skopje, R. Macedonia*

<sup>4</sup>*Research Center for Environment and Materials, Macedonian Academy of Sciences and Arts,  
Blvd. Krste Misirkov 2, 1000 Skopje, R. Macedonia  
radojko.jacimovic@ijs.si // petremak@pmf.ukim.mk*

**Abstract:** The content of major, minor and various trace elements in three manganese minerals from the Republic of Macedonia was determined. The studied minerals belong to the carbonate group [kutnohorite,  $\text{Ca}(\text{Mn}^{2+}, \text{Mg}, \text{Fe}^{2+})(\text{CO}_3)_2$ , from Sasa mine] and to the inosilicate subgroup [carpholite,  $\text{Mn}^{2+}\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4$ , from Vrbsko locality; rhodonite ( $\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})\text{SiO}_3$ , from Sasa mine]. Carousel facility of the 250 kW TRIGA reactor and multielement technique  $k_0$ -instrumental neutron activation analysis ( $k_0$ -INAA) were used for irradiation and for the determination of the elements content. Using intermediate/medium and long half-life radionuclides, in total, thirty-eight elements in the investigated minerals were determined. The content of As, Co, Ga, K, Na, Sc and Zn in carpholite, of As, K, Na, Ta, W and Zn in rhodonite and of Hg, Sr, Ta and REEs in kutnohorite was found to be higher compared to the other investigated trace elements. It was also found that kutnohorite contains lower amounts of trace elements compared with their content in carpholite and rhodonite.

**Key words:** carpholite; rhodonite; kutnohorite; Macedonia;  $k_0$ -INAA

### INTRODUCTION

Minerals are naturally occurring, inorganic, solid substances with a definite (not necessarily fixed) chemical composition. Their inner structure exhibit regular three-dimensional arrangement of the building units (atoms, ions, molecules). Due to the natural process of mineral formation, traces of other elements that are not constituents of the chemical formula could be frequently incorporated, causing thereby changes in mineral physical characteristics. In addition, varieties of minerals are quite easily interchangeable, enabling one mineral to grade into another and build a solid-solution series.

One of the most important reasons to analyze the content of traces in various minerals is related to the potential economic value of the trace elements that justify the mineral excavations. It could later lead to eventual opening of new mining facilities. This finding could also provide very important information on the geology of the mineral locality

and the wider area (Stafilov, 2000; Brugger & Gieré, 2000).

Manganese is an alkaline earth element that occurs in various oxidation numbers from  $-3$  to  $+7$  with only one naturally occurring isotope. Manganese does not occur in the environment as a native element. However, it is an abundant naturally occurring element in more than 100 minerals, including sulfides, oxides, carbonates, silicates, phosphates and borates. Of more commercial importance are the secondary deposits of oxides and carbonates, including the minerals: pyrolusite ( $\text{MnO}_2$ ), which is the most common, hausmannite ( $\text{Mn}_3\text{O}_4$ ) and rhodochrosite ( $\text{MnCO}_3$ ). Large quantities of manganese nodules found on the bottom of the oceans may also become a significant source of manganese (Chukhrov et al., 1980). The most significant application of manganese minerals comprises the production of ferromanganese alloy or

improvement of hardness, stiffness and strength of steel. Due to the use of manganese minerals of relatively pure grade as a basic material for alloys with special electrical and thermal characteristics (Olsen et al., 2007), in general, they must contain impurities in the range of ppm levels or less. Therefore, the determination of microimpurities in manganese minerals is valuable and important analytical task. Widely used method for manganese tracking in either high or low-level concentration is direct electrothermal atomic absorption spectrometry (ETAAS), which permits determination of some microelements with high accuracy (Stafilov, 2000). However, matrix interferences from one side and the strong contamination of the graphite furnace with manganese as a matrix element hamper application of direct ETAAS in the trace elements evaluation in minerals. In such cases, preliminary separation and preconcentration of trace elements is appropriate and useful method (Minczewski et al., 1982; Mizuike, 1983; Zolotov & Kuzmin, 1990). The liquid-liquid extraction of  $\text{Mn}(\text{DTC})_2$  complex in different organic solvents is used for manganese separation before FAAS or ETAAS measurement of trace elements is carried out (Boucher et al., 1990; Marczenko & Balcerzak, 2000; Taseska et al., 2008).

Different separation and preconcentration methods have been suggested including solvent extraction, column solid phase extraction and cloud point extraction (Pawliszyn, 1997; Dulski, 1999). Methods for the removal of manganese(II) from aqueous solutions are based mainly on coprecipitation of manganese(II) as sulfide with iron(III) or lanthanum(III) or liquid/liquid extraction of dithiocarbamate, oxinate, or thiooxinate complexes using various anion-exchangers (Rane, 1971; Claassen et al., 1977; Zendelovska et al., 2000; Stafilov & Zendelovska, 2002; Filiz, 2007).

Instrumental methods (INAA, XRF, PIXE) are rarely used to determine trace elements due to matrix and inter-element interferences and background effects (Frantz et al., 1994; Jaćimović et al., 2002, 2008, 2015; Nečemer et al., 2003; Makreski et al., 2008; Taseska et al., 2012, 2014). In this work, a  $k_0$ -method of instrumental neutron activation analysis ( $k_0$ -INAA) was used for direct determination of major and trace elements in three manganese minerals from the Republic of Macedonia [kutnohorite,  $\text{Ca}(\text{Mn}^{2+}, \text{Mg}, \text{Fe}^{2+})(\text{CO}_3)_2$ ; carpholite,  $\text{Mn}^{2+}\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4$  and rhodonite,  $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})\text{SiO}_3$ ] without preliminary digestion of the sample. The number of elements determined simultaneously in the studied minerals was thirty eight.

## EXPERIMENTAL

### *Samples*

Kutnohorite,  $\text{Ca}(\text{Mn}^{2+}, \text{Mg}, \text{Fe}^{2+})(\text{CO}_3)_2$ , and rhodonite,  $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})\text{SiO}_3$ , minerals were collected from Sasa mine, whereas carpholite,  $\text{Mn}^{2+}\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4$ , was sampled from Vrbsko locality, Republic of Macedonia (Figure 1). Mineral single crystals were carefully hand-picked under an optical microscope from the ore sample and ground to powder.

### *$k_0$ -Instrumental neutron activation analysis*

About 100 mg of powder was sealed into a pure polyethylene ampoule. For determination of short-lived radionuclides, a sample and a standard (Al with 0.1% Au (IRMM-530R) disc of 7 mm in diameter and 0.1 mm high) were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated for 15 s in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor of the Jožef Stefan Institute with a thermal neutron flux of

$1.1 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ . For determination of intermediate/medium and long-lived radionuclides an aliquot and standard Al with 0.1% Au were prepared on the same way as above and irradiated for 12 hours in the CF of the TRIGA reactor.

After short irradiation (15 s) the aliquot was measured after 3–4 hours cooling time on an absolutely calibrated HPGe detector with 45% relative efficiency. After long irradiation (12 hours) the aliquot was measured after 2, 8 and 25 days cooling time on the same HPGe detector (Smodiš et al., 1988). Measurements were performed at such distances that the dead time was kept below 10 % with negligible random coincidences.

For peak area evaluation, the HyperLab (HyperLab 2002 System, 2002) program was used. For determination of  $f$  (thermal to epithermal flux ratio) and  $\alpha$  (parameter which measures the epithermal flux deviation from the ideal 1/E distribution), the "Cd-ratio" method for multimonitor is applied (Jaćimović et al., 2003). The  $f = 28.74$  and  $\alpha = -0.0023$  values were used to calculate the element

concentrations. For elemental concentrations and effective solid angle calculations a software

package called KayWin® User's Manual [Kayzero for Windows (KayWin®), 2011].



Fig. 1. Kutnohorite from Sasa (top), rhodonite from Sasa (middle) and carpholite from Vrbsko (bottom)

## RESULTS AND DISCUSSION

The results of the chemical composition of the investigated manganese minerals kutnohorite,  $\text{Ca}(\text{Mn}^{2+}, \text{Mg}, \text{Fe}^{2+})(\text{CO}_3)_2$ , which belongs to the carbonate group of minerals, and carpholite,  $\text{Mn}^{2+}\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4$ , and rhodonite,  $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})\text{SiO}_3$ , which belong to the inosilicate subgroup of minerals, obtained by  $k_0$ -INAA are given in Table 1, together with their combined standard uncertainty (net peak area, nuclear data for particular nuclide, neutron flux parameters, full-energy peak detection efficiency, etc.).

It was found that the major metal constituents in carpholite are manganese (11.75%) and Fe (0.7035%), whereas the second inosilicate rhodonite contains 31.71% Mn, 5.458% Ca and 0.4122% Fe (Table 1). According to the obtained major elements, the chemical formulae of the minerals should be  $(\text{Mn}, \text{Fe})\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4$  for carpholite and  $(\text{Mn}, \text{Ca}, \text{Fe})\text{SiO}_3$  for rhodonite. Unfortunately, the determination of magnesium content was not possible, because it was decayed before the measurement took place after 2.579 hours being the half-life

for  $^{56}\text{Mn}$  ( $^{27}\text{Mg}$  disintegrates very fast because its half-life is 9.462 min). The major metal constituents of kutnohorite sample were Ca (27.9543%), Mn (11.20%) and Fe (0.2205%) (Table 1), deriving the following chemical formula  $\text{Ca}(\text{Mn,Fe})(\text{CO}_3)_2$ .

The contents of As, Co, Ga, K, Na, Sc and Zn in carpholite, of As, K, Na, Ta, W and Zn in rhodonite and of Hg, Sr, Ta and rare-earth elements (REEs) in kutnohorite were found to be higher compared to the other investigated trace elements (Table 1).

The results obtained from the  $k_0$ -INAA revealed that the Mn content is very close to the averaged results obtained from the X-ray microprobe analysis conducted on three different spots (Jovanovski et al., 2012) (Table 2). The minerals are very suitable candidates for further studies aimed to method development towards elimination of the Mn and determination of the following elements due to the very strong matrix interferences (Ag, Ba, Cr, Cs, Cu, Eu, Hf, In, Nd, Rb, Sb, Se, Tb and Zr). These investigations are in progress.

Table 1

*Element content for the studied manganese minerals (mg/kg) obtained by  $k_0$ -INAA*

Element	Minerals					
	Carpholite		Rhodonite		Kutnohorite	
	Content	Uncertainty	Content	Uncertainty	Content	Uncertainty
Ag		<1.47		<0.34		<0.42
As	10.0	0.4	14.9	0.5	0.349	0.013
Au	0.00634	0.00040	0.00147	0.00013		<0.00047
Ba		<15		<8.8		<10
Br	0.919	0.037		<0.065		<0.031
Ca		<2064	54580	1964	279543	9828
Cd		<1.48		<0.75		<0.42
Ce		<0.63	0.50	0.059	1.99	0.10
Co	58.2	2.0	0.15	0.021		<0.050
Cr		<1.6		<0.47		<0.53
Cs		<0.30		<0.07		<0.086
Cu		<38		<3.1		<8
Eu		<0.21		<0.011	0.285	0.011
Fe	7035	248	4122	146	2205	79
Ga	38.7	1.4	1.84	0.07		<0.1
Hf		<0.14	1.15	0.04		<0.058
Hg		<0.17		<0.16	1.37	0.06
In		<2.1		<0.8		<1.0
K	66.0	4.2	15.1	1.9	16.3	0.8
La	0.166	0.007	0.344	0.013	0.833	0.029
Mn	117500	4117	317100	11110	112000	3923
Mo	1.97	0.11		<0.51		<0.38
Na	114	4	16.9	0.6	7.51	0.26
Nd		<1.4		<0.7		<0.99
Rb		<4.2		<1.7		<2.4
Sb		<0.050	0.629	0.023	0.0232	0.0017
Sc	40.6	1.4		<0.005		<0.007
Se		<1.0		<0.49		<0.62
Sm	0.0479	0.0018	0.0758	0.0027	0.783	0.027
Sr		<105		<27	99.5	4.7
Ta	5.37	0.19	12.6	0.4	90.0	3.2
Tb		<0.077		<0.018	0.431	0.019
Th	0.185	0.013	0.0630	0.0066		<0.043
U		<0.031	0.0601	0.0062	0.0701	0.0045
W	0.178	0.034	16.9	0.6	0.583	0.021
Yb	0.0848	0.0089	0.0526	0.0043	1.17	0.04
Zn	727	26	167	6		<3.7
Zr		<101		<21		<21

Table 2

The content of Mn (in %) obtained by X-ray microprobe analysis (XRMA) (Jovanovski et al., 2012) and  $k_0$ -INAA (this work, see Table 1)

Mineral	XRMA				$k_0$ -INAA
	Spot 1	Spot 2	Spot 3	Average	
Carpholite	9.87	10.92	10.80	10.53	11.75
Rhodonite	32.01	34.44	30.22	32.22	31.71
Kutnohorite	11.48	12.53	11.44	11.82	11.20

## CONCLUSION

The  $k_0$ -method of instrumental neutron activation analysis ( $k_0$ -INAA) was successfully applied for the determination of 38 elements in three manganese minerals (kutnohorite, carpholite and rhodonite) from the Republic of Macedonia. The contents of As, Co, Ga, K, Na, Sc and Zn in carpholite, of As, K, Na, Ta, W and Zn in rhodonite and of Hg, Sr, Ta and REEs in kutnohorite were found to be higher

compared to the other investigated trace elements. It was determined that kutnohorite contains lower amounts of trace elements.

**Acknowledgment:** The authors are grateful for financial support through 2017–2018 bilateral joint project funded by the Ministry of Education and Science of the Republic of Macedonia and the Slovenian Research Agency (ARRS).

## REFERENCES

- Boucher L. J., Kotowski M., Koeber K., Tille D. (1990): *Mn Manganese: Coordination Compounds 7 (Gmelin Handbook of Inorganic Chemistry)*, Springer-Verlag, Berlin.
- Brugger J., Gieré R. (2000): Origin and distribution of some trace elements in metamorphosed Fe–Mn deposits, Val Ferrera, eastern Swiss Alps, *The Canadian Mineralogist*, **38**, 1075–1101.
- Claassen V. P., De Jong G. J., Brinkman U. A. T. (1977): The extraction of manganese(II) from aqueous thiocyanate solutions with liquid anion-exchangers, *Fresenius' Zeitschrift für analytische Chemie*, **287**, 138–141.
- Chukhrov F. V., Gorshkov A. I., Rudnitskaya E. S., Beresovskaya V. V., Sivtsov A. V. (1980): Manganese minerals in clays: A review, *Clays and Clay Minerals*, **28**, 346–354.
- Dulski T. R. (1999): *Trace Elemental Analysis of Metals*, Marcel Dekker Inc., New York.
- Filiz M. (2007): Extraction of Mn(II) from aqueous hydrochloric acid solutions into Alamine 336–m-xylene system, *Hydrometallurgy*, **87**, 58–62.
- Frantz E., Palme H., Wolfgang T., El Goresy A., Pavičević M. (1994): Geochemistry of Ti-As minerals and host rocks at Allchar (Macedonia), *Neues Jahrbuch für Mineralogie Abhandlungen*, **167**, 359–399.
- HyperLab 2002 System (2002), Installation and quick start guide, HyperLabs Software, Budapest, Hungary.
- Jačimović R., Lazaru A., Mihajlović D., Ilić R., Stafilov T. (2002): Determination of major and trace elements in some minerals by  $k_0$ -instrumental neutron activation analysis, *Journal of Radioanalytical and Nuclear Chemistry*, **253**, 427–434.
- Jačimović R., Smodiš B., Bučar T., Stegnar P. (2003):  $k_0$ -NAA quality assessment by analysis of different certified reference materials using the KAYZERO/SOLCOI software. *Journal of Radioanalytical and Nuclear Chemistry*, **257**, 659–663.
- Jačimović R., Makreski P., Stibilj V., Stafilov T. (2008): Determination of major and trace elements in iron reference materials using  $k_0$ -NAA, *Journal of Radioanalytical and Nuclear Chemistry*, **278**, 795–799.
- Jačimović R., Stafilov T., Stibilj V., Taseska M., Makreski P. (2015): Application of  $k_0$ -method of neutron activation analysis for determination of trace elements in various mineral samples (A review), *Macedonian Journal of Chemistry and Chemical Engineering*, **34**, 169–179.
- Jovanovski G., Boev B., Makreski P. (2012): *Minerals from the Republic of Macedonia with an Introduction to Mineralogy*, Macedonian Academy of Sciences and Arts, Skopje.
- Kayzero for Windows (KayWin®) User's Manual (2011), for reactor neutron activation analysis (NAA) using the  $k_0$ -standardization method, Version 2.42.
- Makreski P., Jačimović R., Stibilj V., Stafilov T., Jovanovski G. (2008): Determination of trace elements in iron

- minerals by instrumental and radiochemical neutron activation analysis, *Radiochimica Acta*, **96**, 855–861.
- Marczenko Z., Balcerzak M. (2000): *Separation, Preconcentration and Spectrophotometry in Inorganic Analysis*, Elsevier, Amsterdam.
- Minczewski J., Chwastowska J., Dybczynski R. (1982): *Separation and Preconcentration Methods in Inorganic Trace Analysis*, John Wiley & Sons: New York.
- Mizuike A. (1983): *Enrichment Techniques of Trace Analysis*, Springer-Verlag, Berlin.
- Nečemer, M., Kump P., Rajčević M., Jaćimović R., Budič B., Ponikvar M. (2003): Determination of sulfur and chlorine in fodder by X-ray fluorescence spectral analysis and comparison with other analytical methods, *Spectrochimica Acta, Part B*, **58**, 1367–1373.
- Olsen S. E., Tangstad M., Lindstad T. (2007): *Production of Manganese Ferroalloys*, Sintef and Tapir Academic Press, Trondheim.
- Pawliszyn J. (1997): *Solid Phase Microextraction: Theory and Practice*, Wiley-VCH, Waterloo.
- Rane A. T. (1971): Synergic extraction of manganese(II) with thiocyanate and pyridine, *Journal of Radioanalytical and Nuclear Chemistry*, **8**, 117–122.
- Smodiš B., Jaćimović R., Jovanović S., Stegnar P., Vukotić P. (1988): Efficiency characterisation of HP Ge detectors for use in the  $k_0$ -method of neutron activation analysis, *Vestnik Slovenskega kemijskega društva*, **35**, 397–408.
- Stafilov T. (2000): Determination of trace elements in minerals by electrothermal atomic absorption spectrometry, *Spectrochimica Acta, Part B*, **55**, 893–906.
- Stafilov T., Zendelovska D. (2002): Determination of trace elements in iron minerals by atomic absorption spectrometry, *Turkish Journal of Chemistry*, **26**, 271–280.
- Taseska M., Jaćimović R., Stibilj V., Stafilov T., Makreski P., Jovanovski G. (2012): Determination of trace elements in some copper minerals by  $k_0$ -instrumental neutron activation analysis, *Applied Radiation and Isotopes*, **70**, 35–39.
- Taseska M., Karadjova I., Stafilov T. (2008): Determination of trace elements in manganese salts after preliminary matrix separation, *Eurasian Journal of Analytical Chemistry*, **3**, 1–9.
- Taseska M., Stafilov T., Bačeva K. (2014): Determination of trace elements in some arsenic minerals by atomic emission spectrometry with inductively coupled plasma after matrix removal, *International Journal of Pure and Applied Chemistry*, **9** (1–2) 47–55.
- Zendelovska D., Čundeva K., Stafilov T. (2000): Applicability of dithiocarbamates as colloid collectors for flotation preconcentration of manganese in traces before its ETAAS determination, *Microchimica Acta*, **135**, 55–61.
- Zolotov Y. A., Kuzmin N. M. (1990): *Preconcentration of Trace Elements*, Elsevier, Amsterdam.

## Резиме

**ПРИМЕНА НА  $k_0$ -ИНСТРУМЕНТАЛНА НЕУТРОНСКА АКТИВАЦИОНА АНАЛИЗА  
ЗА ОПРЕДЕЛУВАЊЕ НА МАТРИЧНИ ЕЛЕМЕНТИ И ЕЛЕМЕНТИ ВО ТРАГИ  
ВО НЕКОИ МИНЕРАЛИ НА МАНГАН**

**Радојко Јаќимовиќ<sup>\*1</sup>, Милена Тасеска-Ѓорѓијевски<sup>2</sup>, Трајче Стафилев<sup>3</sup>,  
Глигор Јовановски<sup>4</sup>, Петре Макрески<sup>\*3</sup>**

<sup>1</sup>Институтот „Јожеф Штифен“, Јамова цесџа 39, 1000, Љубљана, Словенија

<sup>2</sup>Земјоделски институт, Универзитетот „Св. Кирил и Методиј“ во Скопје,  
бул. Александар Македонски бб, 1000 Скопје, Р. Македонија

<sup>3</sup>Институтот за хемија, Природно-математички факултет, Универзитетот „Св. Кирил и Методиј“ во Скопје,  
Архимедова 5, 1000 Скопје, Р. Македонија

<sup>4</sup>Испражувачки центар за животно средина и материјали, Македонска академија на науките и уметностите,  
бул. Крсте Мисирков 2, 1000 Скопје, Р. Македонија  
radojko.jacimovic@ijs.si // petremak@pmf.ukim.mk

**Клучни зборови:** карфолит, родонит, кутнохорит, Македонија,  $k_0$ -ИНАА

Во три мангански минерали по потекло од Република Македонија беше определена содржината на матричните, споредните и елементите во траги. Испитуваните минерали ѝ припаѓаат на карбонатната група [кутнохорит,  $\text{Ca}(\text{Mn}^{2+}, \text{Mg}, \text{Fe}^{2+})(\text{CO}_3)_2$ , од Саса] и на иносиликатната подгрупа [карфолит,  $\text{Mn}^{2+}\text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4$ , од локалитетот Врбеко; родонит ( $\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})\text{SiO}_3$ , од Саса]. За озрачување и определување на содржината на елементите беа користени ротациониот систем на реактор TRIGA од 250 kW и мулти-елементната техника  $k_0$ -инструменталната неутронска

активациона анализа ( $k_0$ -ИНАА). Вкупно беа определени 38 елементи со користење на радионуклиди со средно и долго време на полураспад. Утврдено е дека содржината на As, Co, Ga, K, Na, Sc и Zn во карфолитот, на As, K, Na, Ta, W и Zn во родонитот, како и на Hg, Sr, Ta и REEs во кутнохоритот е повисока во споредба со содржината на другите елементи во траги. Исто така е најдено дека кај кутнохоритот содржината на елементите во траги е помала во споредба со нивната содржина во карфолитот и родонитот.