

Extraction of selected elements from commercial fertilizers

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ABSTRACT

Two commercial fertilizers preparation methods for ICP OES analysis of were used for two different fertilizers types: urea and NPK (mineral fertilizer containing nutrients N, P, and K), as organic and inorganic fertilizers, respectively. The aim of our research was the comparison of two methods for the preparation of samples, the determination of the contents of elements, and the comparison of obtained results with the maximum allowed concentrations. The first preparation method consists of digestion with 18.5% HCl, and the other method is the digestion with *aqua regia*. Regarding the extraction of some secondary nutrients and micronutrients (Ca, Mg, Fe, Mn, Cu, Zn, and B) from NPK fertilizer, better extraction was achieved using the first method for B, Ca, and Mg, while the other method was better for Fe, Mn, Cu, and Zn. On the basis of the results of the analysis, the digestion with *aqua regia* is suitable for almost all investigated 3d metals from both samples, except for NPK, for which the degree of the extraction is somewhat higher. Determined concentrations of some toxic elements (As, Cr, Cd, Ni, and Pb) do not cross the maximum allowable concentrations (MAC).

Keywords: urea, NPK fertilizer, elements, ICP OES

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Introduction

Agricultural productivity can be enhanced using fertilizers because they contain nutrients, but they can also have toxic elements responsible for soil contamination (Li et al., 2013; Lima et al., 2015; Machado et al., 2017; Viso and Zachariadis, 2018). In general, fertilizers can be divided into natural and synthetic (inorganic, *e.g.*, NPK, and organic, *e.g.*, urea). Primary nutrients are N, P, and K; secondary nutrients are Ca, Mg, Na, and S; micronutrients are B, Co, Cu, Fe, Mn, Mo, and Zn; and trace elements are As, Cd, Cr, Ba, Ni, Se, V, U, Th and Pb (Otero et al., 2005).

The optimal quantity of NPK varies with soil types and climatic conditions (Muimba-Kankolongo, 2018). Urea contains 46% N, and it is the most concentrated solid nitrogen fertilizer, which in the soil goes to ammonium carbonate, and, therefore, can change local pH (Finch et al., 2014).

Determination of toxic elements in various fertilizers was performed using a couple of techniques based either on 1) Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS), 2) The High-Resolution Continuous Source Flame Absorption Spectroscopy (HR-CS-FAAS) (Bechlin et al., 2014; Borges et al., 2011; Borges et al., 2015; De Morais et al., 2017; De Oliveira Souza et al., 2015); or 3) Cold Vapor Atomic Absorption Spectroscopy (CV-AAS) for Hg (Zhao and Wang, 2010). Regarding nutrients in fertilizers, their concentrations were determined using LIBS (Laser-Induced Breakdown Spectroscopy) (Andrade and Rodrigues Pereira-Filho, 2016; Nicolodelli et al., 2016; Nunes et al., 2014), and Total X-Ray Fluorescence (TXRF) (Resende and Nascentes, 2016). Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) is fast, and it can be used for the determination of both nutrients and toxic metals in fertilizers, with minimal interference (Bartos, 2014; Kane and Hall, 2006; Kimura, 2016; Nziguheba and Smolders, 2008; Rui et al., 2012).

This study presents the results of the determination of selected elements using ICP OES in two fertilizers: inorganic (NPK) and organic (urea), using two different methods to prepare samples.

Experimental

The determination of the concentrations of selected elements in the samples of commercial fertilizers was performed at ICP OES, series iCAP 6000 (ThermoScientific, Cambridge, United Kingdom). Parameters of the instrument used during the measurements of the concentrations of the selected elements are provided in Table 1.

Table 1. ICP OES parameters

Parameters	Values
RF generator power (W)	1150
Peristaltic pump velocity (rpm)	50
Nebulizer gas flow (L/min)	0.5
Washing time (s)	30
Number of measurements	3

The following standards were used for the calibration of the instrument: multielement standard solution IV for ICP, TraceCERT, Fluka Analytical, Switzerland (Al, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Tl, V and Zn); multielement standard solution III for ICP, TraceCERT, Fluka Analytical, Switzerland (Ca, K, Mg, and Na); standard Si, TraceCERT, Fluka Analytical, Switzerland; standard P, TraceCERT, Fluka Analytical, Switzerland and standard Hg, TraceCERT, Fluka Analytical, Switzerland.

After calibration, samples of urea and NPK were analyzed at four different wavelengths. Concentrations were read at the wavelength with the best calibration curve also satisfying criteria of no interference from the left or the right side in the spectrum and with a high Signal/Background ratio. Carefully chosen wavelengths for each element and the characteristics of calibration curves (r , LOD, and LOQ) are provided in Table 2.

Table 2. Characteristics of the calibration curves

Element and λ (nm)	R	LOD (mg/kg)	LOQ (mg/kg)
Al 396.152	0.999907	0.0711	0.2370
As 189.042	0.999979	0.0647	0.2155
B 249.773	0.999984	0.0177	0.0591
Ba 455.403	0.999949	0.0019	0.0062
Be 313.107	0.999995	0.0013	0.0043
Ca 393.366	0.999921	0.0056	0.0186
Cd 226.502	0.999996	0.0062	0.0206
Co 228.616	0.999998	0.0106	0.0354
Cr 283.563	0.999995	0.0169	0.0564
Cr 267. 716	0.999943	0.0254	0.0847
Cu 324.754	0.999993	0.0216	0.0719
Fe 238.204	0.999993	0.0191	0.0635
Mg 279.553	0.999996	0.0116	0.0386
Mn 257.610	0.999953	0.0039	0.0130
Na 588.995	0.999982	0.0012	0.0038
Ni 231.604	0.999980	0.0133	0.0442
P 213.618	0.999975	0.0930	0.3101
Pb 220.353	0.999998	0.0587	0.1958
Si 251.611	0.999938	0.0428	0.1427
V 309.311	0.999989	0.0120	0.0399
Zn 202.548	0.999996	0.0032	0.0106

Preparation of commercial fertilizers for ICP OES analysis

Samples of NPK 16:16:16 (SPECIAL, elixir Zorka) as an inorganic mineral fertilizer and urea (EK MŰTRAGYA, 46 % N) as an organic fertilizer were ground in the mortar and dried at 120°C for 5 h. Two methods were used for the dissolution of these fertilizers to determine the efficacy of the element extractions.

Method I: Dissolution of solid commercial fertilizers with 18.5 % HCl

Approximately 1 g of urea and NPK were measured in Erlenmeyer flasks (150 ml), then added 10 ml 18.5 % HCl (Sigma-Aldrich, Germany). The content was warmed at a hot plate for around 20 min, then cooled to room temperature, filtered using blue filter paper (AHLSTROM MUNKSJÖ, Germany), and the filtrates were collected in 25 ml volumetric flasks and filled up with deionized water (ThermoScientific, 2017).

Method II: Dissolution of solid commercial fertilizers with aqua regia

Approximately 1 g of urea and NPK were measured in Erlenmeyer flasks (150 ml), then added 10 ml aqua regia (the mixture conc. HCl (Sigma-Aldrich, Germany) and conc. HNO₃ (Macron, Germany) in the ratio 3:1). The content was warmed at a hot plate and evaporated to dryness. Afterward, 5 ml conc. HCl (Sigma-Aldrich, Germany) was added to both samples and warmed around 5 min until the dissolution of the dry residues. The samples were cooled, filtered through the blue filter paper (AHLSTROM MUNKSJÖ, Germany), and the filtrates were collected in 25 ml volumetric flasks and filled up with deionized water

(<https://www.ssi.shimadzu.com/sites/ssi.shimadzu.com/files/Products/literature/ICP/J092.pdf>).

Microsoft Office 2010 package was used to process and display the results, and the results are represented as mg of element per kilogram of dry fertilizer sample.

Results and Discussion

In this paper, it was investigated the extraction of selected elements from mineral NPK fertilizer and urea as an organic fertilizer using two different methods of the preparation of samples of solid fertilizers. Concentrations of determined elements are shown in Table 3. Based on the obtained results, high concentrations of the elements were observed in the samples of NPK fertilizers (independently on the preparation method) compared to the values of the concentrations of elements in the samples of urea. These results are thought-provoking, and they are telling us that NPK fertilizer was unequivocally a more significant pollutant than urea, particularly since it has been used for years and continually in agriculture. It seems that more or less increased content in NPK fertilizer compared to urea most probably leads from phosphate raw material used in the process of the production of this fertilizer (Zeremski-Škorić et al., 2010).

Regarding the efficacy of the extractions of primary nutrients from NPK fertilizer (phosphorus and potassium), better extraction results for potassium are achieved using the *method I*, while *method II* is better for determining phosphorus. The efficacy of the investigated methods for some secondary nutrients and micronutrients of NPK fertilizer (Ca, Mg, Fe, Mn, Cu, Zn, and B) is different from one element to another. The *method I* shows a higher degree of extraction to B, Ca, and Mg, while *method II* is better for the rest of the above-mentioned elements. Co and Ni are better extracted using *method II*, but the difference is negligible.

Concentrations of As, Cr, Al, and V obtained using *methods I* and *II* do not differ significantly. It means that these two methods are the same regarding the extractions of the above-mentioned elements from NPK fertilizers.

For most elements from the 3d transition series, *method II* was shown as a better method. The reactive mixture (HNO₃:HCl=1:3) of this method, besides very high oxidative character, also contains reactive chemical species, nitrosyl cation ($\ddot{N} \equiv \ddot{O}^+$) (Safarova et al., 2011). Since metals from the 3d series of the Periodic Table of Elements show high affinity towards the ligands with N-donor atom, probably nitrosyl cation from *aqua regia* contributes to the extractions of the above-mentioned metals forming with them stable complexes.

Method II is better for extracting Ba, Co, Fe, Mg, Mn, Ni, and P from the sample of urea, while for the rest of the investigated elements except Si, this method is inferior. Based on results given in Table 3, it is observed that *method II* is better than the *method I* for the extraction of transition metals from sample NPK, but for the sample of urea, it seems that the extraction capability of *aqua regia* is weakened for these metals, and it is best reflected on Cu, Cr, and Zn. It is most probably that nitric acid from *aqua regia* during heating is spent on the degradation of urea, which leads to this outcome for this type of sample.

Zeremski-Škorić et al. (2010) determined the content of toxic metals (Cd, Cr, Ni, and Pb) in NPK fertilizers and gave the range of their concentrations in NPK fertilizers (0.52-6.38 mg/kg Cd, 0.66-127.33 mg/kg Cr, 0.91-18.16 mg/kg Ni, and 0.37-6.86 mg/kg Pb). Interestingly, our average concentrations of mentioned toxic metals are in the range of the concentrations given by these researchers.

Table 3. Average concentration \pm SD (mg/kg)

Sample	Al	As	B	Ba	Be	Ca	Cd
NPK (I)	910 \pm 30	2.46 \pm 0.05	102 \pm 2	1.42 \pm 0.04	0.77 \pm 0.04	910 \pm 30	4.6 \pm 0.2
NPK (II)	920 \pm 20	2.41 \pm 0.07	96 \pm 2	1.14 \pm 0.01	0.797 \pm 0.005	650 \pm 20	4.88 \pm 0.02
Urea (I)	7.1 \pm 0.1	n.d.	5.3 \pm 0.2	0.325 \pm 0.003	n.d.	26.1 \pm 0.5	n.d.
Urea (II)	5.95 \pm 0.05	n.d.	1.86 \pm 0.03	0.352 \pm 0.005	n.d.	21.8 \pm 0.7	n.d.
Sample	Co	Cr	Cu	Fe	K	Mg	Mn
NPK (I)	1.3 \pm 0.2	69 \pm 4	7.5 \pm 0.3	3300 \pm 200	119000 \pm 10000	1120 \pm 60	194 \pm 9
NPK (II)	1.65 \pm 0.01	73.1 \pm 0.7	8.7 \pm 0.2	3560 \pm 20	87000 \pm 4000	910 \pm 20	205 \pm 2
Urea (I)	0.325 \pm 0.008	0.43 \pm 0.02	0.91 \pm 0.01	39.0 \pm 0.2	350 \pm 20	3.5 \pm 0.2	0.54 \pm 0.01
Urea (II)	0.36 \pm 0.01	0.38 \pm 0.02	0.79 \pm 0.04	45.7 \pm 0.5	132 \pm 9	3.9 \pm 0.2	0.79 \pm 0.02
Sample	Na	Ni	P	Pb	Si	V	Zn
NPK (I)	68 \pm 5	14.5 \pm 0.6	41000 \pm 3000	1.66 \pm 0.08	276 \pm 5	111 \pm 3	940 \pm 80
NPK (II)	47 \pm 2	15.218 \pm 0.005	48100 \pm 300	1.52 \pm 0.06	37.5 \pm 0.7	112 \pm 2	1070 \pm 5
Urea (I)	1.62 \pm 0.07	0.515 \pm 0.005	5.5 \pm 0.4	0.90 \pm 0.07	16.92 \pm 0.06	n.d.	7.6 \pm 0.2
Urea (II)	0.85 \pm 0.03	0.64 \pm 0.01	6.33 \pm 0.01	0.68 \pm 0.01	16.7 \pm 0.4	n.d.	6.31 \pm 0.08

(I)-Method I

(II)-Method II

n.d.-not detected

There are numerous published investigations on determining the contents of heavy (and/or toxic) metals in phosphorus fertilizers. Mortvedt et al. (1981) gave the contents of the following metals: Cd (2-153), Cu (1-18), Mn (3-73), Ni (10-156), Pb (4-8), and Zn (1-1.290) mg/kg, in diammonium phosphate (DAP) fertilizers. In our work, the average values of the concentrations are in the range of concentrations for Cd, Cu, and Ni; the concentration of manganese is higher approximately three times, lead is present in three to six times less quantities, and a significantly higher concentration of zinc is observed.

Considering that the commercial fertilizers are used without any control and for a longer time for crops and plant cultures, to increase the yield and quality of the products, they can be potential pollutants of agricultural soils. Therefore, each country gives regulations about the maximum allowed quantities of some toxic metals in commercial fertilizers. Maximum allowable concentrations (MAC) for arsenic, cadmium, chromium, nickel, lead, and mercury are given in Table 4. (Official Gazette of Serbia, No. 41/09, 2009) and Regulations for the European Union (European Union, 2019)).

Table 4. MAC (mg/kg) of some toxic elements in NPK fertilizers

Toxic element	MAC (mg/kg)
Arsenic (As)	40 ^b
Cadmium (Cd)	75 ^a 60 ^b
Chromium (Cr)	500 ^a 2 (Cr (VI)) ^b
Nickel (Ni)	100 ^{a,b}
Lead (Pb)	100 ^a 120 ^b
Mercury (Hg)	1 ^{a,b}

a – data from Gazette of Serbia, no. 41/09)

b – Maximum allowed value determined for the European Union.

Comparing the values of toxic elements from Table 3 with MAC values, it is observed that NPK and urea do not contain any value above the MAC, although at first sight NPK fertilizer looks contaminated with heavy metals.

Concentrations of chromium and nickel in the samples of NPK fertilizers are even around 7 times lower than MAC values recommended by Serbian regulations, and cadmium is found in even lower quantities.

Conclusion

This study compared the contents of 21 elements in two different fertilizers types: urea and NPK, using two different methods (the *method I* and *method II*) for preparing the samples. Based on the obtained results, we conclude that the contents of all elements are higher in NPK fertilizer than in urea. The extraction methods efficacy of the extractions is different from one element to another, except for the 3d elements for which its efficacy *method II*. From the primary nutrients in NPK fertilizer and urea K is more abundant than P. From the selected secondary nutrients and micronutrients in NPK fertilizer, the abundance of the elements is as follows: Fe, Mg, Ca, Zn, Mn, B, and Cu, while for urea is: Fe, Ca, Zn, Mg, B, Cu, and Mn. Concentrations of potentially toxic elements (As, Cd, Cr, and Pb) are lower than the maximum allowed value by Serbian regulation.

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Conflict-of-Interest Statement

None.

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