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Determination of impurities in fertilizers purchased in Almaty (Kazakhstan)

Abstract. Two solid (Double superphosphate and Phosphoric) and two liquid (Peat and Microfertilizer) fertilizers from Russia and Kazakhstan were evaluated with regard to macronutrients content (K, Ca), transition elements (Cr, Fe, Co, Zn, Hg), alkaline earth (Sr), semi-metals (As), rare earth elements (Ce, Eu, La, Nd, Sc, Sm, Tb, Yb) and Th and U. For analysis, the k0-INAA was used. For QA/QC purposes for k_0-INAA the certified reference material BCR-320R channel sediment was used and irradiated together with the samples. The highest content of REEs was obtained in Double superphosphate, while in liquid fertilizers REEs were mostly below the limit of detection of the method used. Most elements in liquid organic fertilizers (Peat and Microfertilizer) were determined in insignificant level, except iron, which belongs to the essential micronutrients. The content of iron was at least 57 times higher in case of Peat fertilizer in comparison to Microfertilizer. Content of iron was higher in case of Phosphoric fertilizer than in Double superphosphate (about five times).

Key words: fertilizers, Kazakhstan, impurities, nutrients, k_0-INAA.

Introduction

For modern society, sustainable agriculture plays essential role. Although techniques applied during the production of the target crop can have delayed consequences. One of the common techniques is the application of the different types of fertilizers. Due to the intensive cultivation, the fertility of soil decreased in many parts of the world. In order to sustain crop yields more fertilizers might be required, leading to the environmental concern [1].

Most of the fertilizers have complicated composition, which can content not only target elements-nutrients, but also contaminants, which is tending to accumulate in agricultural soils over the years, and have negative influence on the nature [2]. Radionuclides and rare earth elements (REEs) are common contaminants in fertilizers, especially in the case of P-containing mineral fertilizers [3-7]. Phosphorus-containing mineral fertilizers have high concentration of toxic elements, due to the rock phosphates, which are used as a raw material during their production [8]. The negative effect of continuous application of mineral fertilizers was demonstrated in several studies [9-11]. For instance, the combined application of mineral and organic fertilizers leads to enhance of content of trace elements in maize [10], which is evident of accumulation of trace elements in soil and following transfer to crop. Have to be mentioned that one of the main sources of REEs pollution of the soil is P-containing mineral fertilizers. Soils, which were longingly fertilized by phosphate fertilizers, received high doses of REEs [12].

In addition, REEs contamination leads to reduction in soil macro and micro fauna diversity [13]. There is scarce information about different contaminants in mineral fertilizers, which may be purchased on the local markets of Kazakhstan, or produced in the country. In Kazakhstan, there is no regulation related to permissible concentration of toxic elements, such as As, Pb or Hg in mineral fertilizers. For instance, Technical regulations "Requirements for the safety of fertilizers" [14] provides only general information about regulation of mass fraction of biuret, the specific activity of phosphorus containing fertilizers and biological safety of organic and organo-mineral fertilizers, without any specification of permissible concentration of contaminants. In addition, have to be mentioned, that there is no limitation in content of REEs in mineral fertilizers. Fertilizers, which are exported from Eurasian Economic Union countries regulates by technical regulations of the Eurasian Economic Union "Requirements for mineral fertilizers" [15], where provided general terms about radiation and chemical safety of fertilizers, without specification of limit of each toxic element, except copper in ammonium nitrate fertilizer.

It is evident that the applied fertilizers should be controlled systematically for content of toxic elements. At the same time, most of the commonly used fertilizers have complicated composition and it takes long time for the analysis of their composition. We focused on two solid and two liquid mineral fertilizers, which are available on the local market in Almaty (Kazakhstan). For determination of mass fractions of major, minor and trace elements, the k_0-instrumental neutron activation analysis (k_0-INAA) was used. The method is validated and widely used for simultaneous determination of major, minor and trace elements in various materials [16-18].

Materials and methods

Sample description. In the presented work four different fertilizers were analyzed. Double superphosphate (20% of P_2O_5, 5% of N in Garden Retail Service, Russia) and Pphosphoric (20% of P_2O_5, 8% of N in Garden Retail Service, Russia) are solids; Peat (3% of P_2O_5, 3% of K_2O, 1% of N in AgroSnabRetail, Russia) and Microfertilizer (1% of N in Scientific production and technical center "Zhalyn", Kazakhstan) are liquid organic fertilizers. All samples are commonly used in agriculture and can be purchased in specialized shops of Kazakhstan. The samples of solid fertilizers were crushed in mortar and homogenized before the analysis.

k_0-INAA analysis. For k_0-INAA an aliquot of fertilizer sample (varied from 190 mg to 240 mg) and a liquid sample (varied from 2.6 g to 2.9 g) was sealed into polyethylene ampoule. For determination of intermediate/median and long-lived radionuclides an aliquot and standard Al-0.1%Au (ERM-EB530A alloy) were stacked together, fixed in polyethylene vial and irradiated for 12 hours in the carousel facility of the TRIGA Mark II reactor (Ljubljana, Slovenia) with a thermal neutron flux of 1.1×10^{12} cm^{-2} s^{-1} [17].

After irradiation, the aliquot was measured after 4, 8 and 23 days cooling time on absolutely calibrated HPGe detectors (40 % and 45 % relative efficiency). For peak area evaluation, the HyperLab program was used [19]. The values f = 22.54 (thermal to epithermal flux ratio) and α = –0.0075 (epithermal flux deviation from the ideal 1/E distribution) in the chosen irradiation channel of the carousel facility were used to calculate mass fractions. For mass fractions and effective solid angle calculations the software package Kayzero for Windows V3 [20] was applied, where the k_0-database from the year 2020 was used [21].

For QA/QC purposes for k_0-INAA the certified reference material BCR-320R channel sediment was used and irradiated together with the samples. The data obtained by k_0-INAA are evaluated using E_n-score as defined in ISO 13528 [22] and graphically presented on Figure 1 only for certified elements.

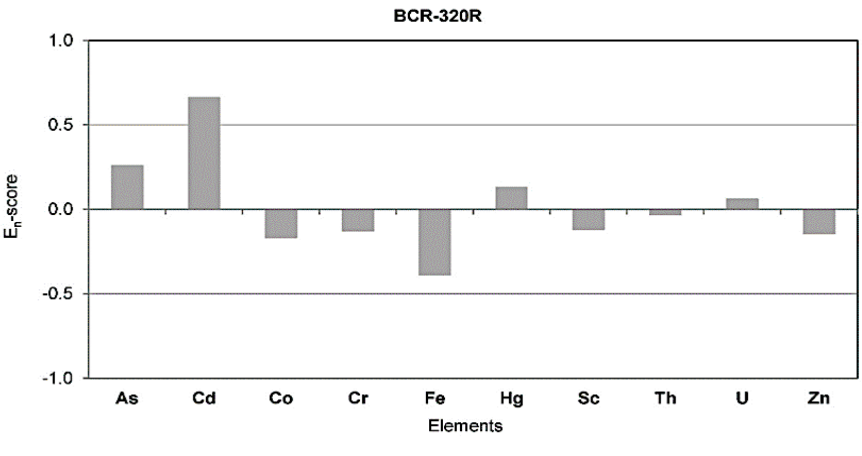

Figure 1 – Evaluation of k_0-INAA data by E_n-score for BCR-320R channel sediment

As can be seen from the Figure 1, calculated E_n-scores are within the following inequality $E_n \leq 1.0$, which indicate successful performance of the k0-INAA method.

Results and discussion

The mass fractions of elements obtained by k_0-INAA with combined standard are in Table 1, uncertainty for studied fertilizers is given in mg/kg.

The highest content of K and Ca, which belongs to the macronutrients, were obtained in Phosphoric mineral fertilizer. Comparing our data presented in the Table 1 with producers' data, it can be seen that, the content of K in Peat fertilizer is low than content provided by the producer. This finding can cause concern about the reliability of the information provided by the producer, which can lead to inappropriate fertilizer use by a farmer.

Table 1 – The content of element obtained by k_0-INAA

El.	Double superphosphate/solid form[a]	Phosphoric/solid form[a]	Peat/liquid	Microfertilizer/liquid
K	1400 ± 80	82700 ± 2900	< 12[b]	6.21 ± 0.33
Ca	184600 ± 6500	194500 ± 7000	85.8 ± 4.1	< 3.2[b]
Ba	51.2 ± 3.9	91.9 ± 5.6	0.800 ± 0.044	< 0.078[b]
Cs	0.356 ± 0.015	0.597 ± 0.022	0.00130 ± 0.00011	< 0.0005[b]
Na	1524 ± 53	4273 ± 150	430 ± 15	2.73 ± 0.10
Rb	8.86 ± 0.37	23.0 ± 0.8	0.0301 ± 0.0056	< 0.017[b]
Sr	1205 ± 43	866 ± 32	2.40 ± 0.12	< 0.20[b]
Cr	12.9 ± 0.5	19.9 ± 0.7	0.0734 ± 0.0030	< 0.0046[b]
Fe	2630 ± 100	12470 ± 440	22.6 ± 0.8	< 0.39[b]
Co	1.00 ± 0.04	17.0 ± 0.6	0.00993 ± 0.00043	< 0.0007[b]
Zn	24.4 ± 0.9	46.2 ± 1.7	0.428 ± 0.018	0.131 ± 0.007
Hg	< 0.23[b]	< 0.07[b]	< 0.0021[b]	< 0.0013[b]
As	1.57 ± 0.07	10.8 ± 0.4	0.0139 ± 0.0009	< 0.0008[b]
Sb	0.172 ± 0.008	0.325 ± 0.013	0.00401 ± 0.00016	< 0.00011[b]
Se	< 0.55[b]	< 0.39[b]	0.00380 ± 0.00054	< 0.0023[b]
Ce	194 ± 7	43.1 ± 1.5	0.0301 ± 0.0013	< 0.002[b]
Eu	4.72 ± 0.17	0.849 ± 0.036	0.000421± 0. 000088	< 0.00003[b]
La	112 ± 4	20.1 ± 0.7	0.0128 ± 0.0005	< 0.0002[b]
Nd	85.1 ± 3.0	18.7 ± 0.9	< 0.0001[b]	< 0.002[b]
Sc	0.647 ± 0.023	2.43 ± 0.09	0.00514± 0.00018	< 0.00004[b]
Sm	14.8 ± 0.5	4.00 ± 0.14	0.00254 ± 0. 00009	< 0.00006[b]
Tb	1.84 ± 0.06	0.533 ± 0.019	0.00037 ± 0.00004	<0.00016[b]
Yb	3.94 ± 0.14	1.44 ± 0.05	< 0.00067[b]	< 0.00001[b]
Th	8.76 ± 0.29	1.76 ± 0.06	0.00489 ± 0.00021	< 0.0003[b]
U	8.37 ± 0.29	12.8 ± 0.5	0.00139 ± 0.00011	0.000899 ± 0.000047

a – mass fractions are given on air dry mass basis;
b – limit of detection (LD) of the method used calculated using equation

The highest content of K and Ca, which belongs to the macronutrients, were obtained in Phosphoric mineral fertilizer. Comparing our data presented in the Table 1 with producers' data, it can be seen that, the content of K in Peat fertilizer is low than content provided by the producer. This finding can cause concern about the reliability of the information provided by the producer, which can lead to inappropriate fertilizer use by a farmer.

LD = 2.706 + 4.653 $\sqrt{B}$, where B is the background calculated in the gamma energy region where the peak in question is supposed to be present. It should be mentioned that KayWin software then calculates the mass fraction of an element taking the LD (net peak counts) as the input parameter in its basic equation of the k_0-method.

The highest concentration of Co, Cr, Zn and As among the investigated samples were determined in Phosphoric mineral fertilizer, meanwhile the lowest values were determined in liquid organic Microfertilizer. Due to lack of information about permissible concentration of toxic elements in fertilizer according to local regulations, there was no option for comparison of obtained values to standard. For all investigated samples, mercury was below the limit of detection of the used method.

Most elements in liquid organic fertilizers (Peat and Microfertilizer) were determined in insignificant level, except iron, which belongs to the essential micronutrients (see Table 1). The content of iron was at least 57 times higher in case of Peat fertilizer in comparison to Microfertilizer. Content of iron was higher in case of Phosphoric fertilizer than in Double superphosphate (about five times). Despite that fact that iron is essential components for plants, its high concentration may lead to decrease in P availability for plants due to the formation of iron-phosphate salts and it is therefore harmful to plants indirectly [8].

It should be mentioned that significant content of strontium in both solid fertilizers was determined. The content of strontium was 1.4 times higher for Double superphosphate in comparison to the Phosphoric fertilizer. Strontium can substitute calcium in biological system due to their chemical properties similarity, which can cause different illness of plant. For instance, strontium affected to photosynthesis, decreasing the level of chlorophyll in algae and higher plant, which can cause chlorosis [23].

Among the rare earth elements significant differences were determined for solid fertilizers. The content of Ce, Eu, La, Nd, Sm, Tb, Yb in Double superphosphate was 4.5, 5.6, 5.6, 4.5, 3.7, 3.5, 2.7 times higher in comparison to the Phosphoric fertilizer. Only content of Sc was 3.8 times higher in case of Phosphoric fertilizer. It is interesting to note that, both of phosphate containing fertilizers are produced by same producer, however as it can be seen from the results, there is significant difference in REEs content, which can be explained with the usage of different raw materials and different processing methods. The differences of REEs content in solid fertilizers might indicate the different origin of raw material used for production of fertilizers. In series of studies [12, 24, 25] are shown that apatite carbonate minerals are more enriched in REEs. In case of investigated Double superphosphate, raw material used for production could be apatite carbonate minerals. Among the liquid fertilizer, REEs was detected using k_0-INAA mostly in Peat sample, while in Microfertilizer sample their contents were below the limit of detection due to low induced activity of radionuclides by neutrons in the sample. In order to increase the sensitivity of the k_0-method for such kind of samples, the pre-concentration procedures should be applied before the sample irradiation or appropriate radiochemical procedures.

In comparison of two solid fertilizers, content of thorium was lower in case of Phosphoric fertilizer, nevertheless the content of uranium was vice versa, slightly lower in case of Double superphosphate. Based on our results presented in Table 1 it is evident that the producer used different processing methods and raw materials for production of phosphate containing fertilizers.

Conclusion

The highest content of K and Ca, which belongs to the macronutrients, were obtained in Phosphoric mineral fertilizer. The highest concentration of Co, Cr, Zn and As among the investigated samples were determined in Phosphoric mineral fertilizer, meanwhile the lowest values were determined in liquid organic Microfertilizer. For all investigated samples, mercury was below the limit of detection of the used method.

Most elements in liquid organic fertilizers (Peat and Microfertilizer) were determined in insignificant level, except iron, which belongs to the essential micronutrients. The content of iron was at least 57 times higher in case of Peat fertilizer in comparison to Microfertilizer. Content of iron was higher in case of Phosphoric fertilizer than in Double superphosphate (about five times).

The present study explores that high concentration of iron was determined in Phosphoric fertilizer, despite that iron mostly nontoxic for plants, it can have hidden negative side effect, which leads to reduce the availability of P in plant [8]. Our study revealed another problem, there is no regulation on the content of REEs and toxic elements in mineral fertilizers in Kazakhstan and more specific research about their effect on plants. The addition of REEs and other metals due to regularly usage of phosphate containing mineral fertilizers might lead to potential risk for agriculture and environment sustainability. Future investigation of other different mineral fertilizers which are available on local market is necessary. In addition, risk assessment study is needed for evaluation of impact of REEs to soil and plant.

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