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Assessment of minor and trace elements in mineral fertilizers purchased in Almaty city, Kazakhstan, using k_0 -INAA

Abstract. The fertilizers are essential in agriculture as they supply macro and micronutrients to growing crops. The appropriate consumption of nutrients, as well as minimized concentrations of pollutants are the basis of good health of human. The control of content of minor and trace elements in fertilizers can lead to improvement of living conditions of local population. The presenting study is aimed on the investigation of concentration of minor and trace elements, purchased in Almaty city, Kazakhstan. The concentrations were found by k_0 -INAA method after crushing and homogenization of the samples. Ljubo-zeleno mineral fertilizer contains high concentration of calcium, potassium, sodium, as well as elevated concentrations of strontium and barium. In Fertika main components are calcium and potassium, although strontium and barium are presented in lower concentrations, than in Ljubo-zeleno mineral fertilizer. In Bujskie udobreniya monopotassium phosphate and ammonium nitrate Fasko mineral fertilizers most of analyzed components (except macrocomponents) are contained in concentrations, lower than the limit of detection of the used method.

Key words: mineral fertilizers, minor and trace elements, k_0 -INAA.

Introduction

Agriculture plays a great role in modern life, as the exponentially growing population need to increase crop yields to provide food [1]. Deficiencies in essential nutrients or unavailability in soil can result in a lower quantity and quality of produced foods [2-4]. The question of accumulation of different elements by growing crops is complex and very complicated, although the presence of elements in soils is one of the most important factors, influencing on chemical composition of crops. The usage of different types of chemicals for improvement of crops quality also became “normal” for modern society. One type of these chemicals are fertilizers, which serve a source of most important macro and micronutrients for growing plants. Macronutrients include calcium, potassium, magnesium, phosphorus, and sulfur, while selected micronutrients are iron, manganese, sodium, silicon, and zinc, among others [5]. These nutrients are required by plants in various quantities and are essential for crop growth, development, and yield [6-8]. They can enter agroecosystems through both

natural (weathering of soil parent material) and anthropogenic processes (use of fertilizers, organic manures, industrial and municipal wastes, metal-based pesticides, irrigation, and atmospheric deposition) [9].

Although fertilizers can consist not only of those elements, which are essential for these crops, but also of other accompanying elements, which in some cases can be dangerous and even poisonous for animals and human. So, for example, in case of phosphate fertilizers used for agricultural purposes, the starting material for their production are phosphate rocks. Phosphate rock is a general term which refers to rock which is most commonly of the apatite group $\{Ca_5(PO_4)_3[F, OH \text{ or } Cl]\}$ [10]. Phosphate rock of sedimentary origin exists in the earth's crust in the form of calcium phosphates $Ca_3(PO_4)_2$ and the rock contains NORM (naturally occurring radioactive material) [11-12].

Hence, precise control of concentration of elements in fertilizers is one of the factors, which can improve the quality of living conditions of human in general. The presenting study is aimed on determination of minor and trace elements in several mineral

fertilizers, which were purchased in the specialized shops of Almaty city, and hence are used by locals for improvement of quality of crops.

Materials and methods

Description of fertilizers

In the study five different fertilizers were chosen for investigation, among them are “Ljubo-zeleno” (Russian Federation), organic-mineral mixture Fer-

tika (Russian Federation), superphosphate Fasko (Garden Retail Service, Russian Federation), monopotassium phosphate (Bujskie udobreniya, Russian Federation) and ammonium nitrate Fasko (Garden Retail Service, Russian Federation). Most of them are recommended for usage for vegetables, commonly grown in Kazakhstan and used by local population, including private houses and farms.

The content of some components is presented by producer and presented in Table 1.

Table 1 – Content of components, reported by producer

Fertilizer	N, %	P ₂ O ₅ , %	K ₂ O, %
Ljubo-zeleno	10	12	15
Fertika	-	5	8
Superphosphate Fasko	9	30	-
Monopotassium phosphate Bujskie udobreniya	-	50	33
Ammonium nitrate Fasko	33	-	-

All samples of fertilizers were crushed in mortar and homogenized before the analysis.

Description of k_0 -INAA

The mass of aliquot taken for k_0 -instrumental neutron activation analysis (k_0 -INAA) varied from 0.200 g to 0.210 g [13]. The sample was sealed in a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). A sample together with an Al-0.1%Au standard (IRMM-530R produced by Institute for Reference Materials and Measurements (IRMM), Belgium) were stacked together, fixed in the polyethylene vial in sandwich form and irradiated for 18 h in the carousel facility of the TRIGA Mark II reactor of Jožef Stefan Institute (JSI) [14-15] at a thermal neutron flux of $1.1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Following irradiation the aliquot was measured after 4, 8 and 22 days cooling time on absolutely calibrated high-purity germanium (HPGe) detectors (40% and 45% relative efficiency). For peak area evaluation, the HyperLab 2002 program was used [16]. The values $f = 28.43$ (thermal to epithermal flux ratio) and $\alpha = -0.0042$ (epithermal flux deviation from the ideal 1/E distribution) were used to calculate element concentrations. For elemental concentrations and effective solid angle calculations, the software package Kayzero for Windows was applied [17]. The k_0 -INAA procedure at the Department of Environmental Sciences of the JSI is accredited according to ISO/IEC 17025 by the Slovenian Accreditation Agency

(Accreditation Certificate LP-090). For QA/QC purposes for k_0 -INAA the certified reference material BCR-320R channel sediment (produced by IRMM, Belgium) was used.

In order to prove the reliability of the results the calculation of E_n -score via the following equation was used [18]:

$$E_n = \frac{X_{lab} - X_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}, \quad (1)$$

where: X_{lab} and X_{ref} are results of determination of concentration in laboratory and reference values, correspondently; U_{lab} and U_{ref} are uncertainties ($k=2$) for laboratory and reference values. The results obtained by k_0 -INAA with their associated combined standard uncertainties (u_c) are given in Table 2 and compared with certified values. Combined standard uncertainty (u_c) is calculated as follows:

$$u_c = \sqrt{u_{Np,AREA}^2 + u_{c,method}^2} \quad (2)$$

where $u_{Np,AREA}$ is uncertainty for number of counts in net peak area of gamma ray and $u_{c,method}$ is the combined standard uncertainty of the k_0 -INAA established as 3.5% with a coverage factor $k=1$. The overall combined standard uncertainty of 3.5% is obtained by quadratic summation of the individual contributions [$k_0 \sim 1\%$, $Q_0 \sim 1\%$, $\alpha \sim 1.5\%$, $f \sim 1\%$, $\varepsilon_p \sim 2\%$ and coincidence correction factors (COI) $\sim 1.5\%$] as described elsewhere [19-21].

Table 2 – Results obtained by k_0 -INAA for BCR-320R channel sediment on dry mass basis

El.	This work		IRMM		E_n
	Content (mg/kg)	u_c (mg/kg)	Certified value (mg/kg)	U (k=2) (mg/kg)	
Ag	0.517	0.073			
As	23.1	0.8	21.7	2	0.55
Au	0.0076	0.0003			
Ba	263	9			
Br	82.0	2.9			
Ca	36746	1305			
Cd	2.70	0.18	2.64	0.18	0.15
Ce	34.7	1.2			
Co	9.94	0.35	9.7	0.6	0.26
Cr	60.4	2.1	59	4	0.24
Cs	4.32	0.15			
Cu	< 909		46.3	2.9	N/A
Eu	0.695	0.037			
Fe	25746	903	25700	1300	0.02
Ga	8.41	0.75			
Hf	4.77	0.17			
Hg	0.891	0.049	0.85	0.09	0.31
K	12269	452			
La	19.9	0.7			
Mo	1.01	0.09			
Na	9325	329			
Nd	17.6	0.7			
Rb	63.5	2.2			
Sb	1.13	0.04			
Sc	5.39	0.19	5.2	0.4	0.34
Se	0.804	0.092	(0.96)	(0.18)	N/A
Sm	3.07	0.11			
Sr	191	8			
Ta	0.506	0.019			
Tb	0.429	0.015			
Th	5.27	0.19	5.3	0.4	-0.05
U	1.55	0.05	1.56	0.2	-0.04
Yb	1.51	0.05			
Zn	329	12	319	20	0.32
Zr	179	8			

Notes: u_c – combined standard uncertainty; U – expanded uncertainty (k=2); Results in brackets are informative values; N/A – not applicable; < – Limit of detection (LD) of the method used.

The calculated E_n -scores are within the following inequality $|E_n| \leq 1.0$ [18], hence the used method shows good results.

Results and discussion

The measurement of the fertilizers was done in duplicate, the obtained data are presented in Tables 3-7. Averaged value (X_{AVG}) and its associated uncertainty ($u_{X_{AVG}}$) are calculated as follows:

$$X_{AVG} = \frac{X_1 + X_2}{2} \quad (3)$$

$$u_{X_{AVG}} = \sqrt{\frac{1}{2}(X_1^2 + u_{c,1}^2 + X_2^2 + u_{c,2}^2) - X_{AVG}^2} \quad (4)$$

where X_1 , X_2 , $u_{c,1}$, $u_{c,2}$ denote the result and its associated combined standard uncertainty for each replicate, respectively, X_{AVG} is the averaged value of two replicates. For data presented as LD, the averaged value represents the higher value of the replicates if not stated otherwise.

The data of the Table 3 showed that Ljubo-zeleno mineral fertilizer contains high concentration of calcium, potassium, sodium, which were essential components of mineral fertilizers. Although elevated concentrations of strontium and less of barium, which being chemical analogue of calcium, can substitute it in biological systems, causing serious illnesses of animals and human, should be mentioned. Thorium and uranium also were detected in this mineral fertilizer.

Table 3 – The results obtained by k_0 -INAA for Ljubo-zeleno are given on air dry mass basis

El.	Replicate 1		Replicate 2		Average			n
	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	u_c (%)	
Ag	< 0.18		< 0.16		< 0.18			2
As	< 1.5		< 1.4		< 1.5			2
Au	< 0.0032		< 0.0024		< 0.0032			2
Ba	123	5	127	5	125	5	4.3	2
Br	43.4	1.5	44.1	1.5	43.7	1.6	3.6	2
Ca	145100	5200	133800	4802	139450	7548	5.4	2
Cd	< 4.8		< 3.8		< 4.8			2
Ce	238	8	244	9	241	9	3.7	2
Co	0.538	0.020	0.539	0.023	0.538	0.021	4.0	2
Cr	3.80	0.33	3.93	0.70	3.86	0.55	14.3	2
Cs	0.195	0.012	0.180	0.008	0.188	0.013	6.7	2
Cu	< 4223		< 4353		< 4353			2
Eu	5.99	0.21	5.90	0.21	5.95	0.22	3.6	2
Fe	1487	53	1462	52	1475	54	3.6	2
Ga	< 7.1		< 6.8		< 7.1			2
Gd	21.2	0.9	21.9	0.9	21.6	0.9	4.3	2
Hf	0.258	0.011	0.277	0.013	0.268	0.016	5.8	2
Hg	< 0.064		< 0.18		< 0.18			2
K	140000	4974	140200	4996	140100	4986	3.6	2
La	135	5	138	5	136	5	3.7	2
Mo	< 3.6		1.87	0.44	1.87	0.44	23.7	1
Na	27740	978	26620	941	27180	1111	4.1	2
Nd	110	4	113	4	111	4	3.9	2
Pr	< 50.7		< 39.9		< 50.7			2
Rb	47.0	1.7	45.8	1.6	46.4	1.8	3.8	2

Continuation of table 3

El.	Replicate 1		Replicate 2		Average			<i>n</i>
	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	u_c (%)	
Sb	0.102	0.006	0.074	0.006	0.088	0.015	17.6	2
Sc	0.165	0.006	0.149	0.005	0.157	0.010	6.1	2
Se	< 0.49		< 0.51		< 0.51			2
Sm	18.0	0.6	18.3	0.6	18.1	0.7	3.6	2
Sn	< 50.7		< 21.6		< 50.7			2
Sr	4726	168	4807	170	4767	174	3.6	2
Ta	0.500	0.018	0.499	0.018	0.499	0.018	3.6	2
Tb	2.14	0.07	2.19	0.08	2.16	0.08	3.7	2
Th	8.36	0.29	8.61	0.30	8.48	0.32	3.8	2
Tm	0.812	0.075	0.773	0.041	0.792	0.063	8.0	2
U	1.86	0.09	1.78	0.08	1.82	0.10	5.4	2
W	< 2.6		< 2.5		< 2.6			2
Yb	2.83	0.10	2.85	0.10	2.84	0.10	3.6	2
Zn	10.6	0.5	11.4	0.5	11.0	0.6	5.7	2
Zr	< 22.6		< 20.5		< 22.6			2

Notes: u_c – combined standard uncertainty; *n* – number of replicates; < – Limit of detection (LD) of the method used.**Table 4** – The results obtained by k_0 -INAA for Fertica are given on air dry mass basis

El.	Replicate 1		Replicate 2		Average			<i>n</i>
	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	u_c (%)	
Ag	< 0.14		< 0.14		< 0.14			2
As	0.788	0.039	0.796	0.051	0.792	0.045	5.7	2
Au	< 0.0012		< 0.0011		< 0.0012			2
Ba	43.5	2.5	41.5	2.2	42.5	2.5	6.0	2
Br	131	5	126	4	128	5	4.0	2
Ca	104800	3697	103300	3646	104050	3747	3.6	2
Cd	< 1.0		< 1.2		< 1.2			2
Ce	24.5	0.9	27.4	1.0	25.9	1.7	6.7	2
Co	2.18	0.08	2.25	0.08	2.22	0.08	3.8	2
Cr	11.3	0.4	11.5	0.5	11.4	0.5	4.1	2
Cs	0.328	0.013	0.330	0.012	0.329	0.013	3.8	2
Cu	< 575		< 604		< 604			2
Eu	0.519	0.023	0.477	0.021	0.498	0.031	6.1	2
Fe	3391	119	3495	123	3443	132	3.8	2
Ga	< 1.9		< 2.9		< 2.9			2
Gd	< 1.6		< 1.6		< 1.6			2
Hf	0.354	0.013	0.335	0.013	0.345	0.016	4.7	2
Hg	< 0.060		< 0.125		< 0.125			2

Continuation of table 4

El.	Replicate 1		Replicate 2		Average			<i>n</i>
	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	u_c (%)	
K	64580	2273	64140	2260	64360	2277	3.5	2
La	16.2	0.6	17.8	0.6	17.0	1.0	5.8	2
Mo	0.217	0.097	0.342	0.123	0.279	0.127	45.6	2
Na	1987	70	1995	70	1991	70	3.5	2
Nd	9.93	0.63	11.37	0.67	10.7	1.0	9.1	2
Pr	< 6.0		< 10.2		< 10.2			2
Rb	7.42	0.29	7.62	0.30	7.52	0.31	4.2	2
Sb	0.0867	0.0054	0.0837	0.0041	0.0852	0.0051	5.9	2
Sc	1.15	0.04	1.19	0.04	1.17	0.05	3.9	2
Se	< 0.32		< 0.25		< 0.32			2
Sm	1.55	0.06	1.65	0.06	1.60	0.08	4.8	2
Sn	< 16.0		< 16.6		< 16.6			2
Sr	289	11	303	11	296	13	4.5	2
Ta	0.365	0.013	0.370	0.014	0.367	0.014	3.7	2
Tb	0.231	0.008	0.246	0.009	0.238	0.011	4.8	2
Th	2.35	0.08	2.38	0.08	2.36	0.09	3.6	2
Tm	< 0.13		< 0.13		< 0.13			2
U	0.978	0.036	0.975	0.036	0.977	0.036	3.7	2
W	< 0.32		< 0.54		< 0.54			2
Yb	1.16	0.04	1.17	0.04	1.16	0.04	3.6	2
Zn	12.0	0.5	12.9	0.5	12.4	0.6	5.0	2
Zr	< 15.2		< 15.6		< 15.6			2

Notes: u_c – combined standard uncertainty; *n* – number of replicates; < – Limit of detection (LD) of the method used.

In Fertika (Table 4) main components were calcium and potassium, less – iron and sodium. Strontium and barium were presented in it, but in lower

concentrations, than in Ljubo-zeleno mineral fertilizer. The same situation was observed for thorium and uranium.

Table 5 – The results obtained by k_0 -INAA for superphosphate Fasko are given on air dry mass basis

El.	Replicate 1		Replicate 2		Average			<i>n</i>
	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	u_c (%)	
Ag	< 0.52		< 0.44		0.52			2
As	2.20	0.32	2.32	0.33	2.26	0.33	14.5	2
Au	< 0.0151		< 0.0195		0.0195			2
Ba	246	17	250	11	248	15	5.9	2
Br	2.81	0.18	3.04	0.25	2.92	0.24	8.3	2
Ca	91750	3803	86250	3673	89000	4641	5.2	2
Cd	< 10.8		< 10.7		10.8			2

Continuation of table 5

El.	Replicate 1		Replicate 2		Average			n
	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	u_c (%)	
Ce	1088	38	1085	38	1087	38	3.5	2
Co	1.49	0.06	1.50	0.06	1.49	0.06	3.7	2
Cr	19.5	0.8	18.5	0.8	19.0	1.0	5.0	2
Cs	0.405	0.020	0.377	0.026	0.391	0.027	6.9	2
Cu	< 6018		< 6466		6466			2
Eu	18.5	0.7	18.6	0.7	18.6	0.7	3.6	2
Fe	3775	134	3756	138	3766	136	3.6	2
Ga	< 18.3		< 19.3		19.3			2
Gd	66.4	2.7	68.3	2.6	67.4	2.8	4.2	2
Hf	0.693	0.031	0.683	0.030	0.688	0.031	4.5	2
Hg	< 0.57		< 0.49		0.57			2
K	2698	329	3672	431	3185	620	19.5	2
La	652	23	650	23	651	23	3.5	2
Mo	3.70	1.36	< 2.1		3.70	1.36	36.8	1
Na	3253	114	3283	116	3268	116	3.5	2
Nd	423	15	424	15	423	15	3.6	2
Pr	117	9	109	9	113	10	8.6	2
Rb	12.6	0.7	11.5	0.6	12.1	0.9	7.1	2
Sb	0.264	0.016	0.249	0.018	0.256	0.019	7.3	2
Sc	0.839	0.030	0.819	0.029	0.829	0.031	3.7	2
Se	< 1.8		< 1.2		1.8			2
Sm	63.1	2.2	63.2	2.2	63.1	2.2	3.5	2
Sn	< 145		< 130		145			2
Sr	6169	220	6137	216	6153	218	3.5	2
Ta	1.27	0.05	1.30	0.05	1.28	0.05	3.9	2
Tb	6.28	0.22	6.23	0.22	6.26	0.22	3.5	2
Th	17.4	0.6	17.4	0.6	17.4	0.6	3.6	2
Tm	5.16	0.31	4.46	0.33	4.81	0.47	9.8	2
U	12.0	0.5	12.1	0.5	12.0	0.5	3.9	2
W	< 3.3		< 3.4		3.4			2
Yb	7.36	0.26	7.29	0.26	7.32	0.26	3.6	2
Zn	33.1	1.6	33.1	1.4	33.1	1.5	4.6	2
Zr	52.8	19.0	< 62.2		52.8	19.0	36.1	1

Notes: u_c – combined standard uncertainty; n – number of replicates; < – Limit of detection (LD) of the method used.

In superphosphate Fasko mineral fertilizer (Table 5), calcium, iron, and potassium were the main components. Strontium and barium found in significant concentrations in Fasko mineral fertilizers, as well as uranium and thorium, are present in considerable quantities.

In monopotassium phosphate (Table 6) the dominant component was potassium, which is evident. Most of the rest components were contained in concentrations, lower than the limit of detection of the used method.

Table 6 – The results obtained by k_0 -INAA for monopotassium phosphate are given on air dry mass basis

El.	Replicate 1		Replicate 2		Average			<i>n</i>
	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	u_c (%)	
Ag	< 0.20		< 0.18		< 0.20			2
As	< 0.17		< 0.63		< 0.63			2
Au	< 0.0035		< 0.0027		< 0.0035			2
Ba	< 21		< 20		< 21			2
Br	< 0.24		< 0.23		< 0.24			2
Ca	< 894		< 897		< 897			2
Cd	< 4.5		< 3.3		< 4.5			2
Ce	< 1.5		< 1.4		< 1.5			2
Co	< 0.021		< 0.020		< 0.021			2
Cr	< 1.3		< 1.2		< 1.3			2
Cs	< 0.044		< 0.040		< 0.044			2
Cu	< 1049		< 1101		< 1101			2
Eu	< 0.0057		< 0.0030		< 0.0057			2
Fe	< 17		< 11		< 17			2
Ga	< 4.3		< 4.5		< 4.5			2
Gd	< 6.0		< 5.5		< 6.0			2
Hf	< 0.069		< 0.064		< 0.069			2
Hg	< 0.42		< 0.39		< 0.42			2
K	284900	9998	286400	10050	285650	10052	3.5	2
La	< 0.028		< 0.020		< 0.028			2
Mo	< 5.7		< 4.4		< 5.7			2
Na	1751	61	1736	61	1744	62	3.5	2
Nd	< 4.8		< 4.5		< 4.8			2
Pr	< 13.0		< 13.4		< 13.4			2
Rb	33.5	1.2	34.0	1.3	33.8	1.3	3.7	2
Sb	0.314	0.013	0.303	0.014	0.309	0.014	4.7	2
Sc	0.0105	0.0006	0.0104	0.0005	0.0105	0.0006	5.3	2
Se	< 0.99		< 0.91		< 0.99			2
Sm	< 0.081		< 0.057		< 0.081			2
Sn	< 48		< 44		< 48			2
Sr	< 30		< 28		< 30			2
Ta	< 0.016		< 0.014		< 0.016			2
Tb	< 0.018		< 0.016		< 0.018			2
Th	< 0.10		< 0.09		< 0.10			2
Tm	< 0.53		< 0.49		< 0.53			2
U	< 0.54		< 0.40		< 0.54			2
W	< 1.1		< 1.1		< 1.1			2
Yb	< 0.10		< 0.09		< 0.10			2
Zn	1.37	0.15	1.67	0.14	1.52	0.21	13.9	2
Zr	< 21.9		< 20.0		< 21.9			2

Notes: u_c – combined standard uncertainty; *n* – number of replicates; < – Limit of detection (LD) of the method used.

Table 7 – The results obtained by k_0 -INAA for ammonium nitrate Fasko are given on air dry mass basis

El.	Replicate 1		Replicate 2		Average			n
	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	Content (mg/kg)	u_c (mg/kg)	u_c (%)	
Ag	< 0.029		< 0.029		< 0.029			2
As	0.0111	0.0016	0.0141	0.0017	0.0126	0.0023	17.9	2
Au	< 0.00004		0.00042	0.00002	0.00042	0.00002	4.8	1
Ba	5.34	0.25	5.16	0.23	5.25	0.26	4.9	2
Br	0.0339	0.0021	0.0237	0.0016	0.0288	0.0055	19.0	2
Ca	< 170		121	20	121	20	16.3	1
Cd	< 0.068		< 0.051		< 0.068			2
Ce	0.0303	0.0051	0.0413	0.0051	0.0358	0.0075	21.0	2
Co	< 0.009		< 0.002		< 0.009			2
Cr	0.523	0.058	0.846	0.058	0.685	0.172	25.1	2
Cs	< 0.004		< 0.003		< 0.004			2
Cu	< 11.7		< 13.6		< 13.6			2
Eu	< 0.001		< 0.001		< 0.001			2
Fe	52.1	2.2	53.2	2.2	52.7	2.3	4.3	2
Ga	< 0.071		< 0.077		< 0.077			2
Gd	< 0.095		< 0.057		< 0.095			2
Hf	< 0.005		0.00678	0.00068	0.00678	0.00068	10.1	1
Hg	< 0.017		< 0.017		< 0.017			2
K	< 7.4		7.85	1.60	7.85	1.60	20.4	1
La	0.0138	0.0009	0.0214	0.0012	0.0176	0.0039	22.4	2
Mo	< 0.027		< 0.015		< 0.027			2
Na	14.7	0.5	15.8	0.6	15.2	0.8	5.1	2
Nd	< 0.053		< 0.051		< 0.053			2
Pr	< 0.27		< 0.28		< 0.28			2
Rb	< 0.17		< 0.16		< 0.17			2
Sb	0.00770	0.00040	0.00743	0.00036	0.00757	0.00040	5.3	2
Sc	0.00268	0.00015	0.00299	0.00013	0.00283	0.00021	7.4	2
Se	< 0.031		< 0.014		< 0.031			2
Sm	0.00354	0.00015	0.00455	0.00019	0.00404	0.00053	13.1	2
Sn	5.05	0.46	7.09	0.46	6.07	1.12	18.4	2
Sr	30.8	1.3	31.1	1.2	30.9	1.3	4.1	2
Ta	< 0.0028		< 0.0028		< 0.0028			2
Tb	< 0.0012		< 0.0009		< 0.0012			2
Th	< 0.0021		0.00420	0.00057	0.00420	0.00057	13.5	1
Tm	< 0.0078		< 0.0079		< 0.0079			2
U	0.00637	0.00045	0.00512	0.00037	0.00574	0.00075	13.1	2
W	< 0.013		< 0.016		< 0.016			2
Yb	0.00369	0.00046	0.00338	0.00035	0.00353	0.00044	12.4	2
Zn	0.245	0.062	0.200	0.040	0.223	0.057	25.6	2
Zr	< 3.6		< 1.6		< 3.6			2

Notes: u_c – combined standard uncertainty; n – number of replicates; < – Limit of detection (LD) of the method used.

In ammonium nitrate Fasko mineral fertilizer (Table 7), most of the analyzed elements were presented in very low concentrations.

Conclusion

The current investigation provided the data on minor and trace elements, presented in five fertilizers, purchased in specialized shops of Almaty city, Kazakhstan. Among them are “Ljubo-zeleno” (Russian Federation), organic-mineral mixture Fertika (Russian Federation), superphosphate Fasko (Garden Retail Service, Russian Federation), monopotassium phosphate (Bujskie udobreniya, Russian Federation) and ammonium nitrate Fasko (Garden Retail Service, Russian Federation). The fertilizers under investigation are recommended for growing of vegetables, commonly used by local population for everyday consumption.

The analysis was done by k_0 -instrumental neutron activation analysis. The quality control of the method was done, based on measurements of certified reference material BCR-320R channel sediment. The obtained values of E_n -scores varied within the interval from -0.05 to 0.55, so the method validated the accuracy.

According to the obtained results, Ljubo-zeleno mineral fertilizer contains high concentration of calcium, potassium, sodium, as well as elevated concentrations of strontium and barium, which being chemical analogue of calcium, can substitute it in biological systems, causing serious illnesses of animals and human. In Fertika main components are calcium and potassium, although strontium and barium are presented in lower concentrations, than in Ljubo-zeleno mineral fertilizer.

In monopotassium phosphate and ammonium nitrate Fasko mineral fertilizer most of analyzed components (except macrocomponents) are contained in concentrations, lower than the limit of detection of the used method, hence can be recommended to utilization by local population.

Based on data presented in this work obtained by k_0 -INAA and data presented by the producer, we can confirm that content of K in K_2O is in good agreement with stated the producer declaration in Table 1 for Ljubo-zeleno, Fertika and monopotassium phosphate Bujskie udobreniya (see Tables 3, 4 and 6, respectively).

It is necessary to note, that for more precise conclusion, detailed investigations of the bioavailability of minor and trace elements of the investigated fertilizers should be done in future.

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