Verification of chemical composition of phosphorus and complex fertilizers

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Abstract

The purpose of the work is to check the mineral, elemental and radionuclide composition of commercially available complex fertilizers in Ukraine. 14 samples of fertilizers produced in Ukraine, Russian Federation and Belarus were randomly selected: double superphosphate (1 sample), superphosphate (2 samples), phosphorite meal (1 sample), double P–K (3 samples), double P–N (1 sample), double K-N (1 sample) and triple N–P–K-fertilizer (5 samples). The mineral composition of fertilizers was determined by X-ray phase analysis. The common, minor and toxic elements were determined by the method of electron probe microanalysis. Radionuclides ^{226}Ra, ^{232}Th and ^{40}K were found in fertilizers by gamma-spectrometric method.

The studied samples contain minerals corresponding to type of fertilizer. Crystallites of some fertilizer minerals are nanocrystalline. Minor (Mn, Fe, Zn, Sr) and rare-earth (Gd) elements were found. Elements Zn and F belong to the 1^{st} hazard class for soils. The largest amount of minor elements is typical for superphosphate. The registered fluorine concentrations from 34200 to 82500 mg/kg are also quite high in some fertilizer samples. Radionuclides ^{226}Ra, ^{232}Th and ^{40}K were found in fertilizers by gamma-spectrometric method. It is shown that there are direct correlations between C_{ef} and mass fraction of soluble calcium dihydrophosphate between the crystallite size (within the limits of nanocrystallinity) and the fixation of radionuclides by minerals. Fertilizers can be used in agriculture without restrictions, since $C_{ef} \leq 1850$ Bq/kg. The studied fertilizers contain nutrients and the corresponding minerals having a low level of radioactivity. They do not have toxicity and therefore can be used in agriculture for their intended purpose. The results of the work are important from the standpoint of environmental monitoring of industrial products.

Keywords: Phosphorus-containing fertilizers, Chemical composition, Minerals, Heavy metals, Radionuclides.

Introduction

The problem of modern agriculture is the lack of plough lands, impoverishment of soils, the loss of soil fertility and the demand for food products. In this regard, the promising environmentally effective approaches and strict regulatory compliance in the production of fertilizers and the development of new types of fertilizers that will ensure sustainability and productivity of agricultural industry are especially relevant. However, despite the fact that phosphorus-containing fertilizers improve soil fertility and increase crop yield, they have a number of negative factors. This is due to the transition of heavy metals (HM) and radionuclides from raw materials (phosphorus ores) to fertilizers. HMs are determined in phosphorus and multicomponent fertilizers.

The source of Cd, Cr and Zn in phosphorus fertilizers is phosphorite raw material and the source of Ni in multicomponent fertilizers is impurity of ground dolomite[5]. The presence of HM in fertilizers causes damage to the environment, HMs accumulate in the plough layers of the soil, pass along the food chains to the plants and are leached into the ground and surface waters[6,15]. Cd is the most toxic HM; As, Cr, Pb, Hg, Ni and V are also dangerous, they are recorded in plough horizons of the soil[11].

The average content of Cd, Cu, Zn, Cr, Pb, Ni, As and Hg in Chinese phosphorus fertilizers is mg/kg: 0.77, 35.6, 102.7, 24.1, 16.6, 15.4, 19.4 and 0.08[8]. Verification of commercial brands of superphosphate and urea in Nigeria showed the presence of high concentrations of Cd and Zn and the presence of Cu and V impurities in superphosphates and Ni, Pb and Cd in urea[2].

After prolong use of phosphorus fertilizers, the series of decreasing HM concentrations in soils is as follows: Mn > Zn > Pb > Cu > Cd[1]. In many studies, the determined metals are divided into groups: common elements (K, Na, Mg), minor elements (Ni, Zn, Mn, Co) and toxic elements (Pb, Cd, Cr, Cu)[12,14]. In addition to these elements, rare-earth elements: Rh, Pr, Gd, Tb and Tm were found in fertilizers[7].

It was proposed to coordinate national measures and to normalize the maximum concentration of Cd in mineral P-fertilizers in order to reduce the Cd content in soils[11]. However, there is still some confusion regarding the level of such restrictions.

One of the danger factors is the presence of radioactive properties in phosphorus fertilizers. The concentrations of natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K in different chemical fertilizers were analyzed using gamma spectrometry[3]. Authors measured the concentration of major element oxides by X-ray fluorescence analysis.

Table 1
Characteristics of fertilizer samples and results of X-ray diffraction analysis

S.N.	Fertilizer name; manufacturer	Results of X-ray diffraction analysis		
		Phase formula, mineral name	Wt% of the phase	The average crystallite size, nm
1	Double granular superphosphate; PAO Sumykhimprom, Ukraine	$CaSO_4$, Anhydrite	69.3	92
		$Ca(H_2PO_4)_2{\cdot}H_2O$	15.6	42
		$CaSO_4{\cdot}0.6H_2O$, Bassanite	15.2	52
2	Superphosphate; PP Tykva, Rivne, Ukraine	$CaSO_4$, Anhydrite	72.2	81
		$Ca(H_2PO_4)_2{\cdot}H_2O$	21.9	46
		$CaSO_4{\cdot}0.6H_2O$, Bassanite	4.84	85
		γ-$CaSO_4$	1.01	70
3	Ammonized superphosphate; PP OVI, Kremenna, Ukraine	$CaSO_4$, Anhydrite	55.3	99
		$Ca(H_2PO_4)_2{\cdot}H_2O$	23.9	38
		$CaSO_4{\cdot}2H_2O$, Gypsum	13.4	76
		SiO_2, Quartz	7.50	57
4	Agrophoska; ZAO Agrophos, Donetsk region, Ukraine	$Ca_5(PO_4)_3((OH)_{0.4}F_{0.6})$, Hydroxylfluorapatite	54.1	55
		SiO_2, Quartz	35.5	98
		$K(Al_{1.91}Fe_{0.9})AlSi_3O_{10}(OH)_2$, Muscovite	7.5	26
		$Al_2Ca_{0.9}Na_{0.1}Si_2O_8$, Anorthite	2.96	30
5	Phosphorite meal; PP OVI, Kremennaya, Ukraine	$Ca_5(PO_4)_3F$, Fluorapatite	76.8	71
		$CaCO_3$, Calcite	12.9	26
		SiO_2, Quartz	5.53	225
		$Ca_2(HPO_4)(SO_4)(H_2O)_4$	4.8	26
6	Complex triple N–P–K-fertilizer; Dnipro Mineral Fertilizer Plant, Ukraine	$NH_4H_2PO_4$, Biphosammite	67.2	78
		$(NH_4)_2SO_4$, Mascagnite	21.3	59
		$K_2H_2P_2O_7{\cdot}0.5H_2O$	1.9	28
		$K_2Ca(SO_4)_2{\cdot}H_2O$, Syngenite	4.35	53
		$CaAl_2Si_2O_8{\cdot}4H_2O$, Gismondine	1.72	68
		$KAl(HPO_4)_2{\cdot}H_2O$	2.6	77
		$K_3P_3O_9$	0.99	127
7	Complex triple N–P–K-fertilizer; PAO Sumykhimprom, Ukraine	$NH_4H_2PO_4$, Biphosammite	40.6	74
		$(NH_4)_2SO_4$, Mascagnite	24.8	63
		$K_2Ca(SO_4)_2{\cdot}H_2O$, Syngenite	28.2	45
		$Al_2PO_4(OH)_3$, Augelite	3.01	52
		$CaSO_4{\cdot}0.6H_2O$, Bassanite	2.03	57
		$KFe(SO_4)_2$, Yavapaiite	1.38	81
8	Double P–N-fertilizer; OAO Gomel HP, Belarus	$(NH_4)_2SO_4$, Mascagnite (with partial substitution of NH_4^+ with K^+ and SO_4^{2-} with HPO_4^{2-})	100	158
9	Nitroammophoska; PAO Sumykhimprom, Ukraine	$(NH_4)_{0.88}K_{0.12}NO_3$	50.6	41
		KCl, Sylvite	21.0	92
		$NH_4H_2PO_4$, Biphosammite	20.5	75
		α-NH_4Cl, Salammoniac	7.2	69
		$Ca(NH_4)_2(P_4O_{12}){\cdot}2H_2O$	0.67	62
10	Nitroammophoska; PP OVI, Kremennaya, Ukraine	$(NH_4)_{0.88}K_{0.12}NO_3$	55.3	44
		KCl, Sylvite	13.4	92
		$NH_4H_2PO_4$, Biphosammite	22.3	74
		α-NH_4Cl, Salammoniac	8.04	73
		$Ca(NH_4)_2(P_4O_{12}){\cdot}2H_2O$	1.1	65
11	Nitroammophoska; AO Mineral Fertilizers, Rossosh, RF	$(NH_4)_{0.88}K_{0.12}NO_3$	56.9	44
		KCl, Sylvite	12.9	92
		$NH_4H_2PO_4$, Biphosammite	22.4	74

		α-NH_4Cl, Salammoniac	7.77	73
12	Potassium monophosphate; LDM company, Kazan, RF	KH_2PO_4	100	108
13	Potassium monophosphate; OAO Buisk Chemical Plant, Bui, RF	KH_2PO_4	100	138
14	Crystalline; PP OVI, Kremennaya, Ukraine	$Mg(NH_4,K)_2(SO_4)_2{\cdot}6H_2O$	84.9	89
		$(NH_4)_2SO_4$	15.3	76

Table 2
Results of electron probe microanalysis

Element	The elemental composition of the fertilizers samples, wt%				
	1	2	5	6	13
Na	0.57	0.3	0.45	0.43	1.61
Mg	0.97	0.24	0.42	1.1	–
K	0.45	0.49	1.05	0.09	29.64
Mn	–	–	0.38	–	0.12
Fe	1.2	0.093	4.17	0.51	0.06
Zn	–	0.037	–	–	–
Sr	–	0.09	–	–	–
Gd	–	0.06	–	–	–
F	–	4.06	3.42	8.25	–

The X-ray diffraction results confirmed the presence of main constituents fluorapatite $Ca_5(PO_4)_3F$, hydroxylapatite $Ca_5(PO_4)_3(OH)$ and chlorapatite $Ca_5(PO_4)_3Cl$ of phosphate fertilizer samples. Results[4] show remarkable wide variation in the radioactive contents for the different phosphate samples.

The purpose of the work is to check the mineral, elemental and radionuclide composition of commercially available complex fertilizers in Ukraine. The fertilizers produced in Ukraine, the Russian Federation and Belarus were purchased from fertilizer markets. 14 fertilizer samples were randomly selected.

Material and Methods

The mineral composition of fertilizers was determined by X-ray diffraction analysis using a Siemens D500 diffractometer. Powder X-ray diffraction patterns were obtained under the following conditions: CuKa radiation (l = 1.54184 Å), a graphite monochromator on a secondary beam and Bragg–Brentano geometry. The primary phase identification was performed using the PDF-1 card index included in the diffractometer software. The X-ray diffraction patterns of the samples were calculated according to the Rietveld method using the FullProf program[13]. The lattice parameters, profile parameters of reflections, the background line and systematic errors were refined. In order to take into account the instrumental function of the profile and calculate the microstructural characteristics, an X-ray pattern of lanthanum hexaboride was used. The results of X-ray phase analysis are shown in table 1.

The elemental composition of fertilizers (Table 2) is determined by means of the method of electron probe microanalysis by the JSM-6390 LV Scanning electron microscope having the INCA microroentgen analysis system. The depth of analysis is up to 5 microns.

Specific activity concentrations of natural radionuclides (*Ci*) were determined by gamma-spectrometric method using a scintillation gamma-spectrometer SEG-001 (Table 3). Based on the results of the gamma-spectrometric study, the values of the specific effective activities of the fertilizers C_{ef} were calculated as the weighted sum of the specific activities of Ra-226 (C_{Ra}) and Th-232 (C_{Th}) according to the formula[10]:

$$C_{ef} = C_{Ra} + 1.2\, C_{Th}, \text{ Bq/ kg} \quad (1)$$

where 1.2 is respectively weighted coefficient for thorium 232 relative to radium 226.

Results and Discussion

Minerals and nutrients of fertilizers: The mineral composition of the studied fertilizers is presented in table 1. The main phosphorus-containing mineral of double superphosphate (sample no. 1) is water-soluble monocalcium phosphate $Ca(H_2PO_4)_2{\cdot}H_2O$ (GOST 16306-80 "Double superphosphate"). Superphosphate is a direct, one-sided, water-soluble phosphorus fertilizer. The main minerals $Ca(H_2PO_4)_2$ and $CaSO_4$ were found in samples nos. 2 and 3. Agrophoska is a phosphorus-potassium mineral fertilizer, represented by sample no. 4.

Phosphate meal belongs to direct one-sided sparingly soluble fertilizers. Sample no. 5 meets the requirements for phosphorite meal[9], namely: phosphorus may be present in the form of medium phosphate $Ca_3(PO_4)_2$, which is part of fluorapatite $3Ca_3(PO_4)_2{\cdot}7CaF_2$, hydroxylapatite $3Ca_3(PO_4)_2{\cdot}Ca(OH)_2$ or carbonatapatite $3Ca_3(PO_4)_2{\cdot}CaCO_3$.

Table 3
Results of by gamma-spectrometric analysis

S.N.	C_i, Bq/kg			C_{ef}, Bq/kg	$C(Ca(H_2PO_4)_2)$, wt%
	^{40}K	^{226}Ra	^{232}Th		
1	245	270	291	619.2	12.01
2	340	496	231	773.2	16.86
3	–	529	254	833.8	18.4
4	–	16.3	319	399.1	–
5	294	280	187	504.4	–
6	90.7	121	272	447.2	–
7	65	163	311	536.2	–
8	282	476	290	824.0	–
9	3590	44.7	262	359.1	–
10	3430	39.8	287	384.2	–
11	3790	32	256	339.2	–
12	8040	38.2	271	363.4	–
13	7940	16.3	270	340.3	–
14	60	35.3	225	305.3	–

The samples no. 6 and 7 refer to complex triple N–P–K-fertilizers and sample No. 8 is for double N–P-fertilizer. A certain content of P in samples no. 6, 7 is achieved mainly due to the mineral $NH_4H_2PO_4$.

Nitroammophoska (No. 9–11) is a complex triple N–P–K-fertilizer. According to GOST 19691-84 "Nitroammophoska", the total content of N, P, K is 17–18 wt% (grade A) and the upper limits of nutrients are allowed to be exceeded which is noted for N in all three samples. According to the concentration of P and K, a deviation to the lower side is recorded.

Potassium monophosphate (No. 12, 13) is a complex double P–K-fertilizer according to the mineral composition of KH_2PO_4. Crystalline no. 14 is a double N–K-fertilizer. In some fertilizer samples, the average size of minerals crystallites is ≤ 30 nm (Table 1) i.e. the phases can be attributed to nanocrystalline, however, this does not always increase soil productivity.

Primary, secondary and toxic elements: These were determined by the method of electron probe microanalysis in several fertilizer samples (No. 1, 2, 5, 6, 13, sample numbers of table 2 coincide with table 1). Table 2 shows the average results for at least three measurements for each sample. Minor (Mn, Fe, Zn, Sr) and rare-earth (Gd) elements were found. Among the elements found, Zn and F belong to the 1st hazard class for soils. Maximum permissible concentrations for agricultural soils according to GN 2.1.7.2041-06 "Maximum permissible concentrations (MPC) of chemical substances in the soil" are: mg/kg: Zn – 23; F – 10 with a translocation limiting hazard index.

Elements Mn and Sr belong to the 3rd hazard class for soils with a general sanitary hazard index (MPC Mn = 1500 mg/kg). The largest number of minor elements in its composition characterizes superphosphate sample no. 2. A certain danger is caused by concentration of Zn of 0.037 wt% or 370 mg/kg which is more than 3 times higher than the average value for Chinese phosphorus fertilizers[8] in fertilizer samples no. 2, 5 and 6.

Radioactivity of fertilizers: The result of gamma-spectrometric analysis is presented in table 3. The radioactivity of phosphate fertilizers is usually higher than that of nitrogen or potash fertilizers. This is due to a number of factors. From the results obtained, the following can be noted. The effective specific radioactivity C_{ef} increases with an increase of soluble calcium dihydrophosphate mass fraction $C[Ca(H_2PO_4)_2]$ in the series of samples no. 1–3 (Table 3). In samples no. 4 and 5, which contain insoluble hydrofluorapatite and fluorapatite, C_{ef} is underestimated. The higher C_{ef} value for sample no. 5 compared to no. 4 is probably due to the fact that it contains the compound $Ca_2(HPO_4)(SO_4)(H_2O)_4$, the solubility of which is higher than that of medium phosphate.

For calcium phosphate minerals, it is possible to trace a definite relationship between C_{ef} (Table 3) and crystallite size (Table 1). Smaller crystallite size of the $Ca(H_2PO_4)_2 \cdot H_2O$ mineral for samples No. 1–3 within 38–46 nm is compared to the size of $Ca_5(PO_4)_3((OH)_{0.4}F_{0.6})$ crystallites in sample no. 4 (55 nm) and mineral $Ca_5(PO_4)_3F$ in sample no. 5 (71 nm) determines a large area of grain boundaries, which serve as "sources" of vacancies for impurities and determine the high energy of the polycrystal. Thus, the smaller is the crystallite size, the greater is the probability of the fixation of radionuclides as different cations on polycrystals. In terms of $C_{ef} \leq 1850$ Bq/kg,[10] the fertilizers can be used in agriculture without restriction.

Conclusion

Fourteen samples of fertilizers produced in Ukraine, Russian Federation and Belarus were randomly selected and checked for compliance with the mineral composition, the presence of toxic elements and radionuclides. The studied samples contain minerals corresponding to this type of fertilizer. The nanocrystallinity of some fertilizer minerals has been recorded.

The common, minor and toxic elements were determined by the method of electron probe microanalysis. Minor (Mn, Fe, Zn, Sr) and rare-earth (Gd) elements were found. Elements Zn and F belong to the 1^{st} hazard class for soils. The largest number of minor elements in its composition characterizes superphosphate sample. The registered fluorine concentrations from 34200 to 82500 mg/kg are also quite high in some fertilizer samples.

Radionuclides ^{226}Ra, ^{232}Th and ^{40}K were found in fertilizers by gamma-spectrometric method. It is shown that there are direct correlations between C_{ef} and mass fraction of soluble calcium dihydrophosphate between the crystallite size (within the limits of nanocrystallinity) and the fixation of radionuclides by minerals. Fertilizers can be used in agriculture without restrictions, since $C_{ef} \leq 1850$ Bq/kg.

The studied fertilizers contain nutrients and the corresponding minerals, have a low level of radioactivity, do not have toxicity and therefore can be used in agriculture for their intended purpose. The results of the work are important from the standpoint of environmental monitoring of industrial products.

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(Received 26th December 2021, accepted 23rd January 2022)