APPLICATION OF ION CHROMATOGRAPHY AND ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY FOR EXAMINATION OF CHEMICAL COMPOSITION OF MINERAL FERTILIZERS

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Abstract: Product quality tests require accurate and precise analytical techniques. Fertilizers belong to a group of products whose chemical composition is of great importance due to health, environmental and economic reasons. The following paper presents the results of the research into the content of selected substances in several mineral fertilizers manufactured in Poland. Ion chromatography (IC) was employed to determine selected inorganic anions and cations, whereas energy dispersive X-ray fluorescence spectrometry (EDXRF) was used to determine the content of selected elements.

INTRODUCTION

Mineral fertilizers are used on both a large and a small scale (agriculture and horticulture, respectively). Their chemical composition is very important for the quality of grown plants as well as cultivation effectiveness. Selected fertilizer macroelements and microelements serve to improve the growth and quality of cultivated plants, which are to be consumed by people. Because of that, the chemical composition of a fertilizer has a great meaning in terms of health, environmental and economic factors.

When it comes to a number of regulations concerning fertilizers, it is the *Fertilizers and Fertilizing Act* (Ustawa o nawozach i nawożeniu) of 10 July 2007 [3] that is in force in Poland. Article 2 of this Act determines that fertilizers (mineral, natural, organic and organic mineral fertilizers) are products meant for providing plants with nutrients, increasing soil fertility or improving fertility of fish-breeding pools. Fertilizers marked with "EC Fertilizer" are those that meet the requirements defined in Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003) [8]. In accordance with the definition, mineral fertilizers are inorganic fertilizers manufactured in the course of chemical and physical transformations as well as mineral processing. An important feature of mineral fertilizer use is the assimilability of selected constituents, such as soluble substances (e.g. inorganic anions and cations), and selected elements

(such as microelements). Various analytical methods and techniques are deployed in order to examine the content of these substances.

Traditional techniques such as titration as well as colorimetric, gravimetric, turbidimetric and electrochemical methods have been used for many years as means of determining inorganic anions and cations. These methods have both certain advantages and disadvantages. The benefits of the classical "wet" methods encompass their availability and relatively low analysis cost, whereas their limitations include the influence of interferences, low detection and selectivity, being laborious. Moreover, it often occurs that highly toxic chemical reagents are necessary for analyses and, what is more, there is no full automation of determinations.

Chromatographic methods are used more and more often to examine not only liquid samples but also solid ones, such as fertilizers. At the beginning, chromatography did not arouse much interest. Its rapid development occurred years after Mikhail Tsvet's milestone discovery [9]. At present, chromatographic methods are among the most common instrumental methods in analytical chemistry due to the possibility of quick separation and determination of a given substance at the concentration level of $\mu g/dm^3$. Ion chromatography is the dominant instrumental method in terms of determination of organic and inorganic anions and cations [10]. Ion chromatography is a standard determination method of main inorganic ions, such as F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} in drinking water, surface water, groundwater, precipitation and mineral water as well as industrial and municipal wastewater [7]. The range of ion chromatography applications is still extending and includes determination of ions in food samples, clinical trials, pharmaceutical and metallurgical industries or semiconductor production.

The most important advantages of ion chromatography are: the possibility of simultaneous determination of several ions within several minutes' time; the limits of detection and quantification at the level of $\mu g/dm^3$; a small amount of the sample necessary for the analysis; the possibility of using various detectors; the option of simultaneous determination of anions and cations or organic and inorganic ions; the determination of ions of the same element with different oxidation states (speciation analytics) [6]. In addition, it enables receiving complete information about ionic composition of the sample (anions and cations) with the employment of solely one analytical method.

When it comes to the determination of total metal content, spectroscopic methods are the most popular, such as various types of Atomic Absorption Spectrometry (AAS) or Inductively Coupled Plasma (ICP). They are quick, exact and relatively cheap. That is why they are especially popular in terms of liquid sample analyses. If, nevertheless, analysts cannot or do not wish to liquefy a solid sample into a solution, then X-ray fluorescence spectrometry (XRF) is one of the direct methods allowing the determination of elements in a given sample.

XRF technique is widely used in the elemental analysis of biological, environmental, geological and industrial samples. X-ray fluorescence is based on (in accordance with the Moseley's law) the relation between the wavelength (or energy) of X-ray radiation emitted by the examined element and its atomic number Z. In recent years Energy Dispersive X-ray Fluorescence (EDXRF) has become the most important method applied for qualitative and quantitative determination of elements in solid metal and powder samples, pressed samples (pellets), fused beads (alloys, pearls) and suspensions.

The qualitative examination of the content of particular analytes in EDXRF consists in the identification of a band characteristic for a particular element. The EDXRF quanti-

tative analysis is a comparative method and requires preparation of calibration curves and hence using certified reference materials [4].

The main advantages of EDXRF technique involve:
– a very short analysis time,
– the possibility of simultaneous determination of several dozen elements,
– simplicity and low analysis cost in comparison with other techniques,
– the possibility of repeated use of the same sample,
– non-destructive analysis.

The main problems occurring while using EDXRF encompass:
– matrix effects,
– particle size effects,
– reinforcement effects,
– sample heterogeneity,
– difficulties in determination of light elements ($Z < 22$).

Examples of ion chromatography applications for heavy metal determination [1] and various phosphorous forms [5] in fertilizers are described in the literature. However, there are no works on EDXRF application discussing this matter as broadly as the following paper. The aim of this research was to determine the content of selected inorganic anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) with ion chromatography and the content of elements with EDXRF technique in several mineral fertilizers available in Poland.

EXPERIMENTAL PROCEDURE

The Metrohm ion chromatograph was used in the course of examinations. It was equipped with: IC 818 pump; IC 837 eluent degasser; IC 820 separation center; Valco injection valve; Metrodata 2.3 software; IC 838 autosampler; MSM suppressor; IC 819 conductivity detector and IC 844 UV/Vis detector. The other apparatus set consisted of Epsilon 5 EDXRF spectrometer manufactured by PANalytical equipped with a 600 W Gd-anode X-ray tube and 100 kV generator, polarized beam optics, secondary targets and germanium detector.

Reagents
$NaHCO_3$ and Na_2CO_3 with analytical purity produced by Merck were used to prepare eluents. The eluent of a suitable composition and concentration was prepared by weighing suitable $NaHCO_3$ and Na_2CO_3 sample masses. Afterwards, they were dissolved in a 1-liter laboratory flask and finally diluted to obtain the demanded value of specified concentration.

Standard solutions of particular anions (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were prepared with reference materials manufactured by Fluka (Steinheim, Switzerland) at the concentration level of 1000 mg/L ± 2 mg/L. The eluent for the determination of inorganic cations was prepared with ultra-pure Ultranal(R) 65% nitric acid manufactured by POCh (Gliwice, Poland). The eluent of an appropriate composition and concentration was prepared by measuring a suitable volume of HNO_3. Afterwards, it was transferred into a 1-liter laboratory flask and finally diluted to obtain the demanded value of specified concentration.

Standard solutions of inorganic cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were prepared with reference materials manufactured by Fluka at the concentration level of 1000 mg/L ± 2 mg/L. Water used for the eluent preparation came from Millipore deionisator (Millipore, Bedford, MA, USA) and had electrical conductivity < 0.05 µS/cm. Calibration solutions were prepared by means of diluting suitable standard solutions just before their application. All solutions were stored in high-density polyethylene (HDPE) vessels at room temperature. PANalytical synthetic wax (STW wax batch 64) was the only reagent used in the process of element analysis with EDXRF technique. A 10% wax addition to the examined sample contributes to a small amount of contamination that results from the wax composition (Table 1). The apparatus was calibrated on the basis of standard sets provided by PANalytical. These sets have the form of pressed pellets or borax pearls of high purity.

Table 1. Binder composition (synthetic wax – STW wax batch 64)

Element	Unit	Concentration
H	[%]	14.1
C		83.9
O		1.3
Na	[mg/kg]	2844
Al.		7
Si		49
S		3107
Cl		474
Ca		25
Cr		5
Fe		5
Ni		15
Cu		5
Zn		1

Preparation of mineral fertilizer samples for the analysis

Samples of the following mineral fertilizers were analyzed: Enriched Superphosphate, Single Superphosphate 19, Single Superphosphate, Calcium-Magnesium Fertilizer, Enriched Superphosphate, Amofoska Fertilizer, Calcium-Magnesium Sulfate, Florofoska Fertilizer, Azofoska Fertilizer, Polifoska Fertilizer and Saletrzak Fertilizer.

2 kg of sample fertilizers were reduced by quartering to obtain a sample weighing about 50 grams, which is then ground in a vibratory mill to a grain size < 200 µm. To meet the requirements of the ion chromatography analysis, a determined sample mass (approx. 0.1 g) was transferred into a 1 liter volumetric flask and exposed to ultrasounds for 30 minutes in order to enable its complete dissolution. Afterwards, it was filtered through a 0.2 µm nitrocellulose filter and then it underwent chromatographic analysis. In the case of EDXRF technique a sample mass of approx. 9 g was ground in a corundum vibratory laboratory grinder. Then, 7.2 g of this sample was mixed with 0.8 g of the binder and pelleted in a manual hydraulic press under the pressure of approx. 20 tonnes within a 3 minute time. Samples obtained in such a way underwent EDXRF analysis in order to determine the content of selected elements.

Analytical conditions

Determination of inorganic ions in mineral fertilizer samples occurred under the following analytical conditions:

Anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-})

Column	–	Metrohm Metrosep A Supp 3
Eluent	–	1.7 mM Na_2CO_3 + 1.6 mM $NaHCO_3$
Eluent flow rate	–	0.85 ml/min
Injection volume	–	20 µl
Detection	–	suppressed conductivity detection

Cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+})

Column	–	Metrohm Metrosep C3
Eluent	–	5 mM HNO_3
Eluent flow rate	–	1.0 ml/min
Injection volume	–	100 µl
Detection	–	non-suppressed conductivity detection

The conditions of EDXRF spectrometer's work are given in Table 2. EDXRF technique uses four different secondary targets with various excitement parameters. Each anode serves to measure different elements ranging between the first anode, which quantifies the lightest elements (such as Ti, V, Cr, Mn, Fe), and the fourth one, used to determine the heaviest elements (Sr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La).

Table 2. X-ray tube and detector parameter settings and secondary target type for specific excitement conditions

Excitement condition	Elements	kV	mA	Secondary target	Detector settings	Measured line used for measurement	Measurement time (s)
Al_2O_3	Sr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Y, Zr, In, I, Ce, Yb	100	6	Al_2O_3	Standard resolution	Kα	1000
Zr	Ga, Ge, As, Se, Rb, W, Pb, U	100	6	Zr	Standard resolution	Kα Lα- W Lβ- Pb Lα - U	300
Ge	Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn	75	8	Ge	Standard resolution	Kα	300

The peak height in the spectrum corresponds to the content of the element in the analyzed sample to a certain extent. Nevertheless, this correspondence is unequivocal as the sum of a few elements often makes peaks in EDXRF and the computer program automatically does concentration calculation.

Validation of the applied analytical methods

The methodology calibration was conducted in accordance with ISO 8466-1 standard [2]. Seven standard solutions with various concentrations of particular ions were prepared to establish the validation parameters of inorganic ion determination methodology. Each solution underwent chromatographic analysis three times under the above-mentioned separation conditions. The obtained peak areas of particular anions served to calculate standard deviation, variation coefficient, limits of detection and quantification as well as correlation coefficient. Validation parameters were calculated in a similar way for the determined inorganic cations. The results are presented in Table 3.

Table 3. Validation parameters of inorganic ion determination methodology

Parameter	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Concentration range [µg/dm³]	0.2–10	0.1–50	0.1–20	0.15–30	1–75	0.2–20	0.2–20	0.5–30	0.5–20	0.5–50
Standard deviation of concentrations [µg/dm³]	0.029	0.108	0.079	0.059	0.126	0.098	0.059	0.102	0.081	0.115
Variation coefficient [%]	1.47	3.24	2.76	2.52	3.95	2.56	1.94	1.84	2.60	3.12
Limit of detection of concentrations [µg/dm³]	0.058	0.064	0.048	0.049	0.331	0.091	0.027	0.095	0.17	0.211
Limit of quantification of concentrations [µg/dm³]	0.174	0.192	0.144	0.147	0.993	0.273	0.081	0.285	0.51	0.633
Correlation coefficient (r)	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999

Table 4. Inorganic ion recovery

Parameter	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Enriched Superphosphate										
Added amount [mg/kg]	0.50	2.50	1.00	2.50	2.50	1.00	1.00	2.50	1.00	2.50
Determined amount	1.79	2.67	0.97	16.94	27.82	0.95	1.06	2.33	0.96	16.41
Recovery [%]	97.8	94.0	97.0	101.0	99.2	95.0	106.0	93.2	96.0	97.5
Amofoska Fertilizer										
Added amount [mg/kg]	0.50	2.50	1.00	2.50	2.50	1.00	1.00	2.50	1.00	2.50
Determined amount	2.13	13.19	1.28	18.94	47.34	7.47	1.04	14.18	0.93	20.12
Recovery [%]	102.4	97.9	104.9	100.7	98.4	97.2	104	96.9	93.0	98.5

Ion recovery was examined in water extracts of two selected samples of the analyzed fertilizers. It was performed with the reference material prepared by ULTRA SCIENTIFIC Analytical Solutions. The recovery results are given in Table 4.

EDXRF spectrometer calibration was performed with fundamental parameters method. Thirty-five standards of the determined elements in the form of pressed pellets or borax pearls were measured in order to carry it out. As a result, the optical patch sensitivity was established. It was taken into account in the course of mineral fertilizer samples measurements. Recovery was examined with NIST Standard Reference Material (SRM 695 – Trace Elements in Multi-Nutrient Fertilizer). The results are presented in Table 5.

Table 5. Results of NIST 695 standard measurement

Analyte	Number of measurements	Certified element content in the standard	Mean value	Unit	Recovery [%]
Fe	5	3.99	4.02	%	100.7
Mn	5	0.305	0.298	%	97.7
Zn	5	0.325	0.311	%	95.6
As	5	200	206.48	mg/kg	103.2
Cd	5	16.9	15.88	mg/kg	93.9
Cr	5	244	251.15	mg/kg	102.9
Co	5	65.3	69.12	mg/kg	105.8
Cu	5	1225	1241.83	mg/kg	101.3
Hg	5	1.955	2.02	mg/kg	103.3
Mo	5	20	18.9	mg/kg	94.5
Ni	5	135	137.52	mg/kg	101.8
Pb	5	273	280.58	mg/kg	102.7
Ti	5	310	302.36	mg/kg	97.5
V	5	122	119.73	mg/kg	98.1

RESULTS AND DISCUSSION

The results of selected inorganic anion (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and cation analyses (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) are given in Tables 6 and 7.

Examples of anion and cation chromatograms of the Amofoska Fertilizer sample are shown in Figures 1–2. The analysis results of selected elements determined with EDXRF technique are given in Table 8. Examples of spectra (for each anode) obtained for one of the analyzed samples (Enriched Superphosphate) are presented in Figures 3–5.

The limits of detection for the determined ions and elements are presented in Table 9.

The research revealed that the content of fluoride ions ranged between detection limits and 1.58 mg/L. Chloride content was between 0.03 and 10.97 mg/L while nitrate content ranged between detection limits and 1.58 mg/L. The content of phosphates ranged between detection limits and 50.11 mg/L while sulfate content was between 1.34 and 38.18 mg/L. In general, the highest content results of determined inorganic ions were obtained for Amofoska Fertilizer. This fertilizer had also the biggest number of water-soluble inorganic cations. Calcium was the cation found in all the analyzed fertilizers.

Table 6. Results of selected ions determination in mineral fertilizer samples [mg/L]

Sample	Sample mass [mg]	Anions					Cations				
		F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Enriched Superphosphate	115.1	1.33	0.34	<0.048	14.26	24.54	<0.091	<0.027	<0.095	<0.17	14.33
Single Superphosphate 19	105.7	1.68	0.25	<0.048	23.92	37.79	<0.091	<0.027	<0.095	<0.17	20.54
Single Superphosphate	106.0	1.39	0.31	0.07	23.34	38.18	<0.091	<0.027	<0.095	<0.17	22.06
Calcium-Magnesium Fertilizer	100.8	0.67	0.41	0.09	0.22	12.14	<0.091	<0.027	<0.095	2.10	4.36
Enriched Superphosphate	118.0	1.25	0.31	0.07	50.11	11.39	<0.091	<0.027	<0.095	<0.17	11.77
Amofoska Fertilizer	132.6	1.58	10.97	0.22	16.31	45.60	6.68	<0.027	12.12	<0.17	17.92
Calcium-Magnesium Sulfate	97.3	<0.058	0.39	0.05	<0.049	51.60	<0.091	<0.027	<0.095	5.49	13.15
Florofoska Fertilizer	101.0	0.29	1.12	23.13	7.18	27.21	<0.091	10.62	13.08	1.67	0.65
Azofoska Fertilizer	100.5	0.33	1.14	23.15	6.77	27.89	<0.091	10.45	13.44	2.15	<0.221
Polifoska Fertilizer	96.4	0.50	16.19	1.35	18.35	12.08	0.49	5.12	16.64	1.67	1.45
Saletrzak Fertilizer	106.9	<0.058	0.03	69.42	<0.049	1.34	<0.091	20.76	<0.095	1.59	1.74

Table 7. Results of selected ions determination in mineral fertilizer samples [dag/kg]

| Sample	Sample mass [mg]	Anions					Cations				
		F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Enriched Superphosphate	115.1	1.15	0.29	< 0.04	12.39	21.32	< 0.08	< 0.02	< 0.08	< 0.15	12.45
Single Superphosphate 19	105.7	1.59	0.24	< 0.04	22.63	35.75	< 0.09	< 0.03	< 0.09	< 0.16	19.43
Single Superphosphate	106.0	1.31	0.29	0.07	22.02	36.02	< 0.09	< 0.02	< 0.09	< 0.16	20.81
Calcium-Magnesium Fertilizer	100.8	0.66	0.41	0.09	0.22	12.04	< 0.09	< 0,03	< 0.09	2.08	4.32
Enriched Superphosphate	118.0	1.06	0.26	0.06	42.47	9.65	< 0.08	< 0.02	< 0.08	< 0.14	9.97
Amofoska Fertilizer	132.6	1.19	8.27	0.17	12.30	34.39	5.04	< 0.02	9.14	< 0.13	13.51
Calcium-Magnesium Sulfate	97.3	< 0.06	0.40	0.05	< 0.05	53.03	< 0.09	< 0.03	< 0.10	5.64	13.51
Florofoska Fertilizer	101.0	0.29	1.11	22.90	7.11	26.94	< 0.09	10.51	12.95	1.65	0.64
Azofoska Fertilizer	100.5	0.33	1.13	23.03	6.74	27.75	< 0.09	10.40	13.37	2.14	< 0.22
Polifoska Fertilizer	96.4	0.52	16.79	1.40	19.03	12.53	0.51	5.31	17.26	1.73	1.50
Saletrzak Fertilizer	106.9	< 0.05	0.03	64.94	< 0.05	1.25	< 0.08	19.42	< 0.09	1.49	1.63
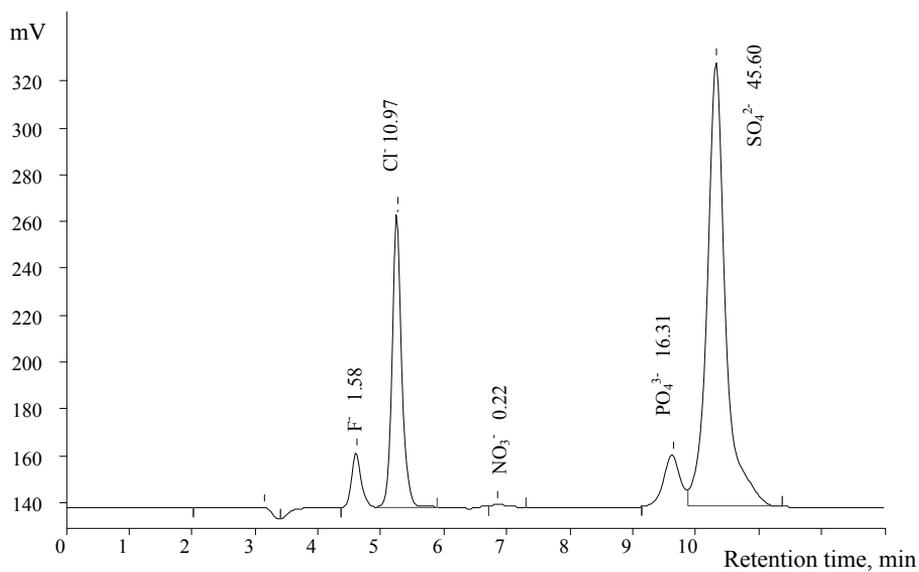
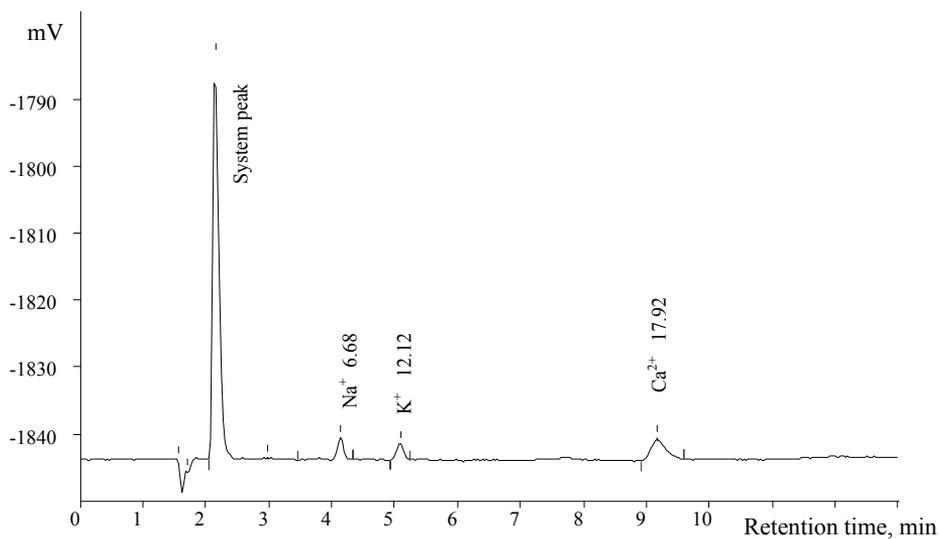Fig. 1. Chromatogram of anions - Amofoska Fertilizer sample

Fig. 2. Chromatogram of cations - Amofoska Fertilizer sample

Table 8. Results of EDXRF determination of selected elements in mineral fertilizer samples [mg/kg]

| Analyte	Enriched Superphosphate (fertilizer)	Single Superphosphate 19	Single Superphosphate (fertilizer)	Calcium-Magnesium Fertilizer	Enriched Superphosphate	Amofoska Fertilizer	Calcium-Magnesium Sulfate	Florofoska Fertilizer	Azofoska Fertilizer	Polifoska Fertilizer	Saletrzak Fertilizer
Ti	< 15.5	< 15.5	52.20	131.97	< 15.5	< 15.5	141.46	89.83	186.71	211.44	71.88
V	246.59	85.21	219.29	< 5.49	278.03	120.00	< 5.49	43.02	57.00	101.56	6.23
Cr	< 8.51	314.29	275.11	96.97	260.90	224.67	< 8.51	78.34	125.98	337.00	17.65
Mn	< 6.1	40.99	68.71	533.41	15.54	118.84	407.47	68.50	6155.00	190.04	924.64
Fe	3300	5000	2200	4100	3100	6200	3500	1800	5700	9100	7900
Ni	98.33	28.45	35.44	< 2.16	68.74	278.08	< 2.16	12.70	5.40	247.08	< 2.16
Cu	9.19	10.77	36.95	9.22	47.60	23.89	< 2.99	37.09	4770.00	18.02	28.55
Zn	421.70	192.35	268.21	99.43	712.96	330.69	55.95	110.20	1352.13	237.57	241.84
As	8.60	3.96	16.73	< 0.91	15.35	7.60	< 0.91	2.82	0.47	5.55	3.07
Br	7.18	5.85	< 0.91	< 0.91	11.04	427.63	< 0.91	29.47	46.19	907.33	< 0.91
Rb	< 0.72	4.11	< 0.72	13.55	< 0.72	6.40	7.10	17.86	23.81	19.77	6.94
Sr	2690.00	2533.00	1019.91	300.82	2446.00	1250.64	115.13	74.77	118.27	263.22	96.81
Y	148.14	184.73	244.48	9.64	81.92	34.05	< 1.17	23.24	19.06	35.40	< 1.17
Zr	< 1.34	< 1.34	< 1.34	15.59	< 1.34	< 1.34	13.25	14.42	12.27	24.01	7.36
Ag	< 0.79	< 0.79	< 0.79	< 0.79	< 0.79	< 0.79	< 0.79	0.87	< 0.79	< 0.79	4.07
Mo	19.00	< 1.04	< 1.04	< 1.04	< 1.04	< 1.04	< 1.04	< 1.04	1101.13	< 1.04	< 1.04
Cd	33.13	20.77	24.79	< 0.83	44.86	19.24	< 0.83	9.54	4.84	8.25	5.13
In	< 0.94	< 0.94	< 0.94	< 0.94	< 0.94	< 0.94	< 0.94	2.17	< 0.94	< 0.94	5.53
Sn	< 0.87	< 0.87	< 0.87	< 0.87	< 0.87	< 0.87	< 0.87	2.50	1.82	1.35	5.41
Sb	< 0.98	< 0.98	< 0.98	< 0.98	4.56	< 0.98	< 0.98	2.60	3.41	2.35	5.48
I	< 1.09	< 1.09	9.31	< 1.09	10.32	< 1.09	< 1.09	6.09	2.67	3.49	33.48
Cs	< 1.16	< 1.16	< 1.16	< 1.16	< 1.16	< 1.16	< 1.16	16.51	< 1.16	9.97	< 1.16
Ba	395.00	70.63	117.16	57.28	606.28	305.26	35.16	26.27	< 1.33	52.14	58.89
La	118.89	166.77	122.17	< 1.17	34.52	24.10	< 1.17	< 1.17	< 1.17	26.15	< 1.17
Ce	136.45	199.25	72.97	< 4.03	< 4.03	< 4.03	< 4.03	< 4.03	< 4.03	36.07	< 4.03
Yb	194.27	< 6.15	< 6.15	< 6.15	204.01	184.21	< 6.15	< 6.15	< 6.15	169.94	246.11
Hg	< 0.92	< 0.92	< 0.92	< 0.92	< 0.92	< 0.92	< 0.92	< 0.92	< 0.92	< 0.92	< 0.92
Pb	11.45	9.05	8.31	17.99	7.61	6.04	15.92	8.98	7.69	9.93	54.89
U	139.42	80.97	180.73	< 2.91	325.36	85.55	< 2.91	58.58	< 2.91	48.43	< 2.91
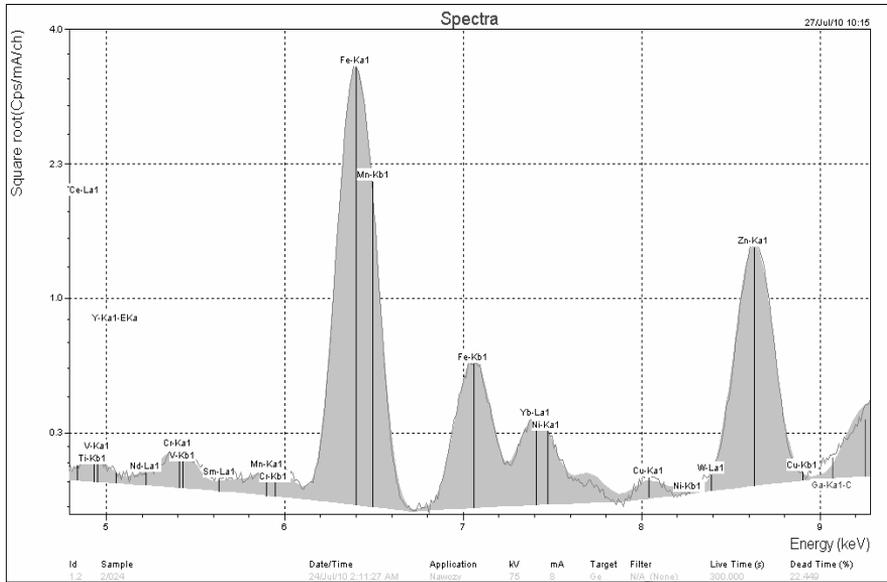
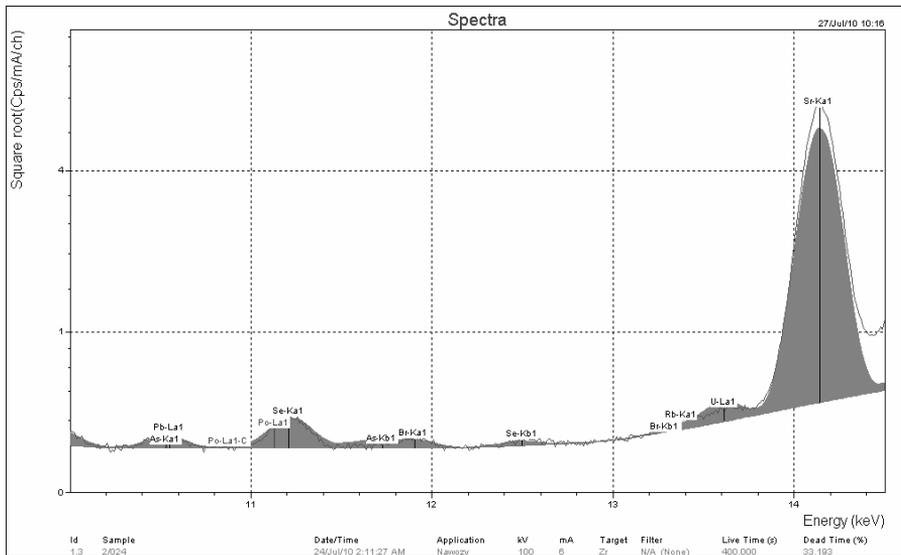Fig. 3. Spectra of Enriched Superphosphate sample obtained for Ge anode

Fig. 4. Spectra of Enriched Superphosphate sample obtained for Zr anode
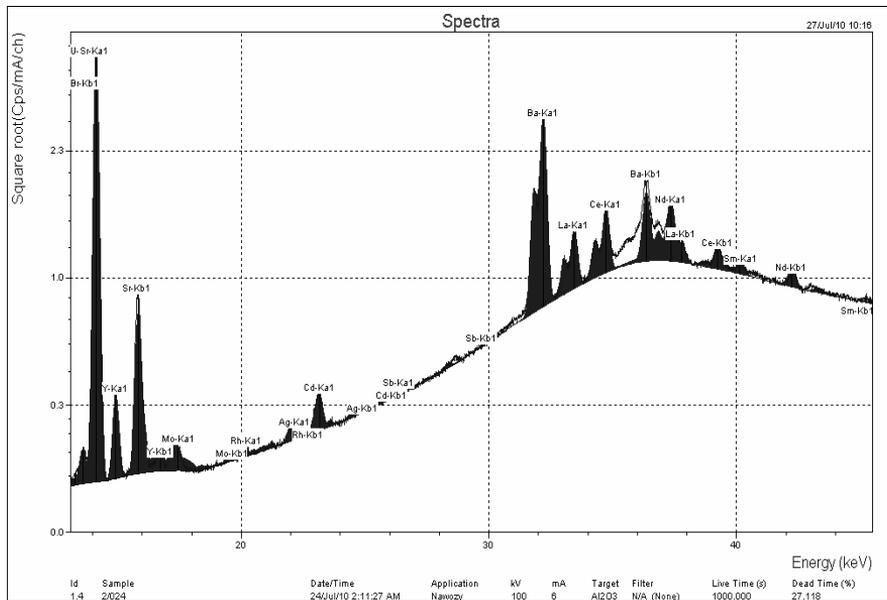
Fig. 5. Spectra of Enriched Superphosphate sample obtained for Al_2O_3 anode

Table 9. Limits of detection of determined analytes

Ion chromatography [mg/L]			
Analyte	Limit of detection	Analyte	Limit of detection
F^-	0.058	Na^+	0.091
Cl^-	0.324	NH_4^+	0.027
NO_3^-	0.078	K^+	0.095
PO_4^{3-}	0.169	Mg^{2+}	0.170
SO_4^{2-}	0.331	Ca^{2+}	0.221
EDXRF [mg/kg]			
Ti	15.5	Mo	1.04
V	5.49	Cd	0.83
Cr	8.51	In	0.94
Mn	6.1	Sn	0.87
Fe	7.76	Sb	0.98
Ni	2.16	I	1.09
Cu	2.99	Cs	1.16
Zn	2.25	Ba	1.33
As	0.91	La	1.17
Br	0.91	Ce	4.03
Rb	0.72	Yb	6.15
Sr	1.34	Hg	0.92
Y	1.17	Pb	1.47
Zr	1.34	U	2.91
Ag	0.79	-	-

Ammonium, potassium, magnesium and sodium ions were found in a few of the analyzed fertilizers.

Several dozen elements were determined in the analyzed fertilizers with EDXRF technique. Many of them play a very important part in the process of soil fertilization and plant cultivation. The Polish law regulates the maximum admissible content of selected elements in mineral fertilizers [3]. Such requirements concern As, Cd, Pb and Hg, whose admissible contents equal to 50 mg/kg, 50 mg/kg, 140 mg/kg and 2 mg/kg respectively. The maximum acceptable concentration of these elements was not exceeded in any of the examined samples. The highest As content was found in Single Superphosphate (16.73 mg/kg). In the case of Cd, the highest concentration was determined in Enriched Superphosphate (44.86 mg/kg), whereas Saletrzak Fertilizer sample revealed the highest Pb concentration (54.89 mg/kg). The Hg concentration was below the limit of detection (< 0.92 mg/kg) in each analyzed sample.

Interesting results were obtained for other elements whose admissible contents are not regulated by the law. Nevertheless, due to their characteristics, these elements are of significant importance for the applied mineral fertilizers.

The highest concentrations of the following elements were found in these fertilizers:
–   Ti – Amofoska Fertilizer (186.71 mg/kg) and Polifoska Fertilizer (211.44 mg/kg),
–   V – Enriched Superphosphate (278.03 mg/kg),
–   Fe – Polifoska Fertilizer (9100 mg/kg),
–   Ni – Amofoska Fertilizer (278.08 mg/kg),
–   Zn –Azofoska Fertilizer (1352.13 mg/kg),
–   Rb –Amofoska Fertilizer (23.81 mg/kg),
–   Sr – Enriched Superphosphate (2690.00 mg/kg),
–   Y – Single Superphosphate (244.48 mg/kg),
–   Zr –Polifoska Fertilizer (24.01 mg/kg),
–   Ag, In, Sn, Sb, I –Saletrzak Fertilizer (4.07, 5.53, 5.41, 5.48 and 33.38 mg/kg respectively),
–   Cs – Florofoska Fertilizer (10.51 mg/kg),
–   Ba – Enriched Superphosphate (606.28 mg/kg),
–   La and Ce – Single Superphosphate 19 (166.77 and 199.25 mg/kg respectively),
–   Yb and U – Enriched Superphosphate (204.01 and 325.36 mg/kg respectively).

The above-mentioned elements were present to a various extent in the majority of analyzed mineral fertilizer samples. Some samples revealed high concentrations of a few characteristic elements, i.e. Mn, Cu and Mo. Their high concentrations were present in Azofoska Fertilizer (6155.00 mg/kg, 4777.00 mg/kg and 1101.13 mg/kg respectively). Another "atypical" example was Br content in Polifoska Fertilizer that amounted to 907.33 mg/kg.

CONCLUSIONS

Chemical composition of fertilizers is a matter of great importance. It does not only influence the plants grown but also cultivation effectiveness and contaminants transferred into the soil. Specific and specialized institutions conduct quality tests of fertilizers in the limited range defined with the corresponding regulations [3].

The results of the research into several fertilizers available in Poland given in this paper embrace a far broader analytical examination range. Isocratic ion chromatography with suppressed conductivity detection was used to determine the content of selected inorganic anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) in mineral fertilizer samples. Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) was employed to determine selected elements (Ti, V, Cr, MN, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr, Ag, Mo, Cd, In, Sn, I, Cs, Ba, La, Ce, Yb, Hg, Pb and U) in these samples.

To sum up, ion chromatography enabled quick and precise determination of soluble mineral elements such as inorganic anions and cations that are important for the plant cultivation. EDXRF technique allowed for quick determination of several dozen elements and did not require expensive and time-consuming sample preparation methods.

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ZADSTOSOWANIE CHROMATOGRAFII JONOWEJ ORAZ
SPEKTROMETRII FLUORESCENCJI RENTGENOWSKIEJ Z DYSPERSJĄ ENERGII DO BADANIA
SKŁADU CHEMICZNEGO NAWOZÓW MINERALNYCH

Badania jakości produktów wymagają stosowania dokładnych i precyzyjnych technik analitycznych. Do produktów, których skład chemiczny ma ogromne znaczenie zarówno ze względów zdrowotnych, ekologicznych, jak i ekonomicznych, należą nawozy mineralne. W pracy przedstawiono wyniki badań zawartości wybranych substancji w kilkunastu nawozach mineralnych produkowanych w Polsce. Do oznaczania wybranych nieorganicznych anionów i kationów wykorzystano technikę chromatografii jonowej (IC), a do badania zawartości wybranych pierwiastków technikę spektrometrii fluorescencji rentgenowskiej z dyspersją energii (EDXRF).