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X-ray fluorescence equipment and method, nutrient content analysis in solid NPK compound fertilizer

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ABSTRACT

The paper presented two X-ray fluorescence analysis methods applicable to element content analysis in mixed fertilizers. The applied addition method determined the content of each ingredient in the fertilizer. The fundamental parameter method was applied for quick analysis, and at the same time, the content of ingredients on the fertilizer production line. X-ray fluorescence analysis methods and equipment have been researched and developed by the Institute of Materials Science - Vietnam Academy of Science and Technology and put into the gold and silver field for more than 30 years. The machines fabricated after 2014 applied TCVN 7055:2014, the 2nd edition "gold and gold alloys – Determination of gold content by X-ray fluorescence method". The national gold standard sample set, managed by the Vietnam Metrology Institute, was used to calibrate the machine, which has standard association with NIST (USA) and Krastsvetmet (Russia). Up to now, there are nearly 100 machines operating in more than twenty provinces and cities across the country, used to check the content of alloying components in gold jewelry processing, production and trading. The aim of new research and development in the field of fertilizers, in the coming time, is to transfer equipment and analysis methods to fertilizer production and trading enterprises.

Introduction

Solid NPK compound fertilizers are most commonly used because they have all the essential nutrients for plants, including: macronutrients (N, P, K), medium nutrients (Mg, Si, S, Ca) and trace elements (B, Mn, Fe, Co, Cu, Zn, Mo) [1]. Determination of the contents of the main macronutrients of N, P, and K in NPK mixed fertilizers is obeyed by TCVN 5815-2018 [2]. The determination of the contents of medium nutrients and micronutrients is also available in other TCVNs. However, these measurements use mainly chemical analysis methods and some physical analytical methods are combined with chemistry such as: atomic absorption, emission spectroscopy, flame photometer, spectrophotometry, etc. These analytical methods require a variety of pure chemicals for sample digestion, sample preparation with long analysis time,

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and analysts must be required to be well-trained and experience to analyze to obtain accurate results. The XRF method does not require pure chemicals, and sample preparation is not too complicated. When determined the elemental contents of a compound fertilizer, this method only needs to select a suitable pure chemical containing the element to be analyzed with a certain amount of cellulose to perform. Rapid analysis method as welll as essential elements and toxic elements for plant needed to be controlled in small amounts such as: As, Cd, Hg, Pb, etc were developed by the X-ray fluorescence spectrometer [3]. Compact, easy-to-use equipment is very suitable for fertilizer production and trading enterprises, the purpose of technological research, decoding technology and manufacturing new mixed fertilizers. The device can check the content of elements for many types of raw materials, the stages of fertilizer production and ensure the quality of fertilizer produced.

Experimental

Xray fluorescent spectrophotometer of VietSpace 5006-2020

Energy-dispersive X-ray fluorescence spectrometer system VietSpace 5006 – 2009 [4], is the product of the project: "Design and fabrication of X-ray fluorescence spectrometer system to analyze material composition applied in mining and mineral processing". Management level was Vietnam Institute of Science and Technology and acceptance result was excellent in December 2009. In order to meet the analysis of elemental contents in mixed fertilizers, the device was upgraded and replaced with the FAST SDD detector in 2020. The energy resolution (FWHM) of FAST SDD detector was better than that of previous SDD detector and collection speed of X-ray receiver of FAST SDD detector was 5 times larger than that of previous SDD. Xray fluorescene spectrophotometer was named VietSpace 5006-2020. Main technical parameters of equipment was shown on figure 1:

- Detector: FAST SDD.
- FWHM ≈ 125 eV at 5.9 keV.
- X ray tube with continuous power 50 W/50 kV max
- Ambient measurement: air of vacuum.
- Identified elements: from Mg to U ($12 \leq Z \leq 92$).
- Lowest detectable concentration: a few tens of parts per million (ppm)
- XRF-FP analysis program for Amptek's PX5 electronic module [5].
- Power consumption: 200 W/220 V (AC).

The program in analyzing the contents of elements in mixed fertilizers was set in the mode: X-ray tube 35 kV, anodic current 200 μA, time of spectrum acquisition 90 seconds.

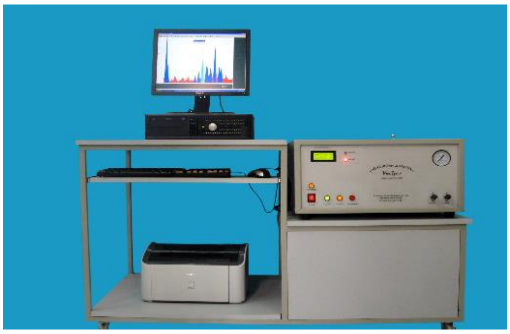

Figure 1: X ray fluorescene spectrophotometer VietSpace 5006-2020

Standard addition method

The standard addition method was applied to the analysis of the contents of each element in the sample by adding a known amount of the analysis element to the sample. Fluorescence intensities I_1 and I_2 before and after added were used to calculate unknown concentrations in the sample either by extrapolation or by calculation. If the result was linear as hypothesized, then the line was the solid line in figure 2 [6].

$$\frac{C_i}{\Delta C_i} = \frac{I_1}{I_2 - I_1} \qquad (1)$$

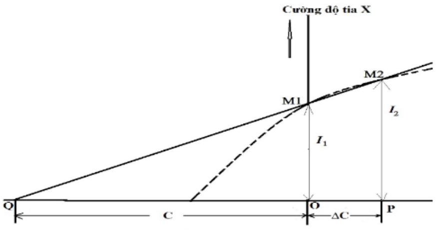

Figure 2: Principle of standard addition method

If the element to be added was not an element, content of the element was calculated by compound.

$$\frac{C_i}{\sigma C_\sigma} = \frac{I_1}{\left(1 + \sigma \frac{\mu_A}{\mu_S}\right) I_2 - I_1} \qquad (2)$$

Form of equation (2) had the same as that of equation (1) when σμA/μS was approached zero. This was

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corresponded that the amount of element was small when element in the analytical object had low content.

To analyze the high content object requires two types of pure chemicals: A_0 which did not contain the element of interest and A which contained the element to be analysed with a defined concentration of C_σ. Both samples were prepared by mixing the same amount of analyte sample S into σ part of A_0 and σ part of A. Since the background compositions were constant, it was assumed that the fluorescence intensity was linear with the added element content. The unknown content was calculated by I_1' and I_2.

$$C_i = \frac{I_1'}{I_2 - I_1'} \sigma C_\sigma \qquad (3)$$

Equation (3) is similar to Equation (1) but it was applicable to analyze elements in fertilizers with high content.

Sample preparation and standard mixture sample

The NPK compound fertilizer was prepared to analyze according to the standard TCVN 10683:2015 [7]. Fertilizer samples and pure chemicals such as: Cellulose $C_6H_{10}O_5$ (XT), $NH_4H_2PO_4$ (MAP), KNO_3, $(NH_4)_2SO_4$ (SA), etc were prepared by drying, grinding to particle size ≤ 75 µm, storing in a plastic bag with a clip and keeping in a desiccator.

A series of stock phosphorus standard mixtures were prepared from $C_6H_{10}O_5$ mixed by compound $NH_4H_2PO_4$. Phosphorus content in the mixture were increased exponentially corresponding to the addition of the $NH_4H_2PO_4$ content in the mixture as shown in table 1.

Table 1: A series of stock phosphorus standard mixtures

Label	SP0	SP1	SP2	SP3	SP4	SP5	SP6
%MAP	0	2	4	6	8	10	12
%XT	100	98	96	94	92	90	88
%P	0.00	0.55	1.10	1.64	2.19	2.74	3.29

Table 2 was a series of standard mixtures of potassium. The potassium compound was used as KNO_3.

Table 2: A series of standard potasium mixtures

Lable	SK0	SK1	SK2	SK3	SK4	SK5	SK6
$\%KNO_3$	0	2	4	6	8	10	12
%XT	100	98	96	94	92	90	88
%K	0.00	0.77	1.55	2.32	3.09	3.87	4.64

Table 3 was a series of standard sulfur mixtures with the sulfur compound used by $(NH_4)_2SO_4$. The original standard mixtures were stored in a plastic bag with a clip and stored in a desiccator.

Table 3: A series of standard sulfur mixtures

Lable	SS0	SS1	SS2	SS3	SS4	SS5	SS6
% SA	0	2	4	6	8	10	12
% XT	100	98	96	94	92	90	88
% S	0.00	0.49	0.97	1.46	1.94	2.43	2.91

When determined the content of any element in the fertilizer (PB), 1g of the fertilizer sample was mixed with 4 g of the original standard mixture containing the analyzed element. Mixture was mixed well, then put it in the mortars of the planetary mill, and dried for 15 minutes in a drying cabinet with a ventilation fan at 55 ^oC. After dried, the mortars must be covered in the drying cabinet, removed and put in a planetary mill, ground at 650 rpm during 30 minutes. After ground, sample was taken and put it into a press. The sample was pressed into a 3 cm diameter tablet with a pressure of 3 tons/cm^2.

The X-ray fluorescence spectra of tablet samples were analyzed by VietSpace 5006-2020. Each sample was measured on both sides and the results were obtained by averaging the two-sided measurement results. The everage results were used to calculate the elemental content in the analyzed compound fertilizer.

Results and discussion

Determination of total phosphorus content

Table 4 was the lable of analytical samples to determine phosphorus content in fertilizers. The mass of the analyzed sample were equal to the total weight of the fertilizer and the mass of the phosphorus standard mixture with the phase ratio of 1/4 between the Xray fluorescent intensity (I c/s) of the spectra peak $P(K_\alpha)$ and their error (σI c/s). Figure 3 was shown that the X-ray spectrum of samples 2PB8XP0, 2PB8XP1, 2PB8XP3 and 2PB8XP5 were compared.

Table 4: Phosphorus determination samples

No.	Lable	0.8 × δP%	I (c/s)	σI (c/s)
1	2PB8XP0	0.00	2372	22
2	2PB8XP1	0.44	3059	24

3	2PB8XP2	0.88	3756	27
4	2PB8XP3	1.32	4376	29
5	2PB8XP4	1.75	5356	32
6	2PB8XP5	2.19	6043	34
7	2PB8XP6	2.63	6700	36
8	δP(PB)	-1.44	0	
9	P(PB)	5.76		
10	P_2O_5(PB)	13.20		

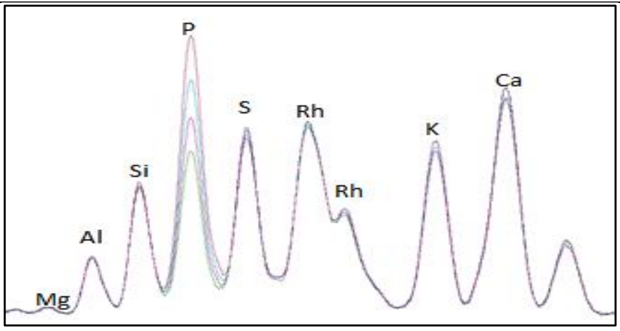

Figure 3: Spectra of phosphorus analysis samples

Based on diagram of the Xray fluorescent intensities (I c/s) of the P(Kα) spectral peak, phosphorus content was depended on 80 % phosphorus content in the original phosphorus standard mixtures. The graph was the equation: y = 1647x + 2372 with the regression coefficient R^2 = 0.9987. Extending the straight line of the graph intersected the horizontal axis at a negative value by solving equation 1647x + 2372 = 0. The value of x was -1.44. Its absolute value was phosphorus content in the fertilizer sample mixed with the standard phosphorus stock mixes, in this case 1.44 %. Phosphorus content was 5.76 % by multiplyling by this value with 4. Converting to phosphorus oxide with a conversion factor of 0.4364 was obtained P_2O_5 = 13.20±0.05 %.

Potasium content determination

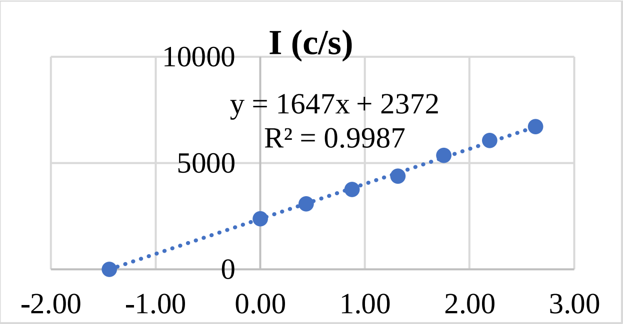

Figure 4: X ray fluorescent intensity depended to phosphorus content

Table 5 was the lables of analytical samples to determine the potassium content in fertilizers. The mass of the analyzed sample were equal to the total weight of the fertilizer and the mass of the phosphorus standard mixture with the phase ratio of 1/4 between the Xray fluorescent intensity (I c/s) of the spectra peak $P(K_\alpha)$ and their error (σI c/s).

Table 5: Potasium determination samples

No.	Lable	0.8×δK%	I (c/s)	σI (c/s)
1	2PB8XK0	0.00	2965	22
2	2PB8XK1	0.62	4561	26
3	2PB8XK2	1.24	6021	30
4	2PB8XK3	1.86	7588	34
5	2PB8XK4	2.48	8904	37
6	2PB8XK5	3.09	10391	39
7	2PB8XK6	3.71	11357	41
8	δK(PB)%	-1.26	0	0
9	K(PB) %	5.03		
10	K_2O(PB)	6.06		

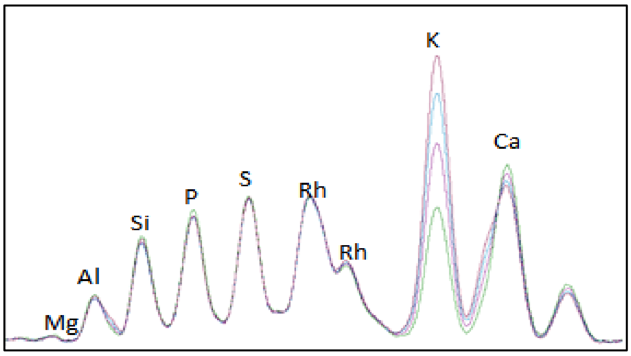

Figure 5: Spectra of potasium analysis samples

Figue 5 compared Xray spetra among 2PB8XK0, 2PB8XK2, 2PB8XK4 and 2PB8XK6 sample. Based on diagram of the Xray fluorescent intensities (I c/s) of the P(Kα) spectral peak, potasium content was depended on 80% potasium content in the original phosphorus standard mixtures. The graph was the equation: y = 2358.6x + 2965 with the regression coefficient R^2 = 0.9975. Extending the straight line of the graph intersected the horizontal axis at a negative value by solving equation 2358.6x + 2965 = 0. The value of x was -1.26. Its absolute value was potasium content in the fertilizer sample mixed with the standard potasium stock mixes, in this case 1.26 %. Phosphorus content was 5.04 % by multiplyling by this value with 4.

Converting to potasium oxide with a conversion factor of 0.8302 was obtained K_2O = 6.07±0.01 %.

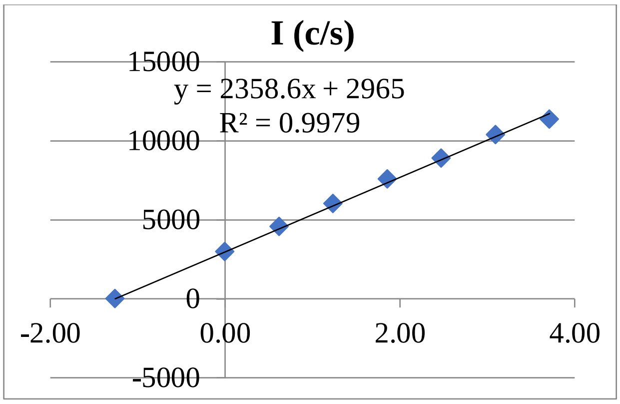

Figure 6: Xray fluorescent intensity depended to potasium content

Analysis of sulfur content

Similar to phosphorus and potassium determination, the sulfur content of the fertilizer added to the standard sulfur mixture was 0.95 %. The sulfur content in the fertilizer was 3.80±0.004 %.

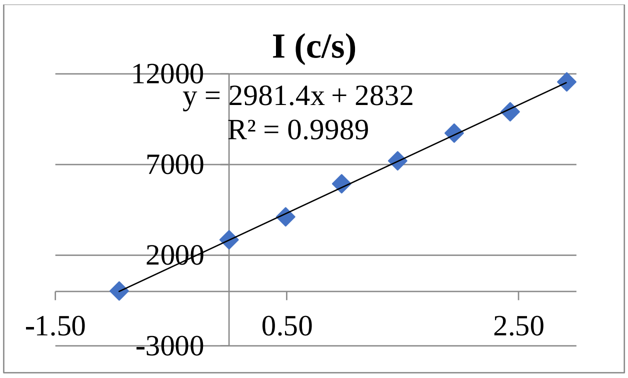

Figure 7: Xray fluorescent intensity depended to sulfur content

Determination of effective phosphorus

The XRF method was built to determine effective phosphorus based on TCVN 11049:2016 [8]. However, crystalline citric acid and concentrated ammonium hydroxide (NH_4OH) solution were needed to make ammonium citrate solution pH 7.

Synthesis principle: dissolve the sample in water to remove phosphorus dissolved in water, filter to take the first residue, continue to dissolve the first residue in ammonium citrate to remove the phosphorus insoluble in the citrate, filter to take the second residue and dry, weigh to determine the weight of the residue. XRF analysis determined the phosphorus content of the second residue. The effective phosphorus content was determined by the total phosphorus content analyzed in section 3.1 that deducted the phosphorus content in the second residue.

30 g of crushed fertilizer were added into 500 mL of water in a 1000 mL beaker, the beaker was placed on a magnetic stirrer and heated to 40 °C, water was added to the 1000 mL mark, the stirrer was turned on and maintained the temperature at 40 °C, baker was removed the stirrer after 60 minutes, solution was filterred by vacuum filter funnel with filter paper, the filter paper and water-insoluble residual were removed from the filter funnel, put it in a 500 mL beaker contained 200 mL of heated ammonium citrate solution pH = 7 at 40 °C, filter was removed when the residue were completely dissolved in the solution, the beaker was placed on the stirrer and added ammonium citrate solution to the 500 mL mark, the solution was stirred and maintained the temperature at 40 °C for 60 minutes, the baker was removed from the stirrer and filterred the solution through a vacuum filter funnel, filter paper containing the residue was removed from the funnel, placed in a clean porcelain dish, the dish was placed in the drying cabinet at 55 °C about 60 minutes until the sample is completely dry, the sample dish was taken out and put in a desiccator to equilibrate the temperature with room temperature and then balanced.

The mass of the citrate-insoluble residue were equal to the mass of the filter paper containing the sample that deducted the mass of the filter paper. The residue was removed from the filter paper, re-ground by mortar and then analyzed to determine phosphorus content followed section 3.1.

(%) HLPKT = (%) HLMC×(KLMC/KLDC)

HLPKT: Insoluble phosphor..rus content.

HLMC: Phosphorus content in residue.

KLMC: Residue weight.

KLDC: Fertilizer weight extracted (30 g).

With the above method, it has been determined that the amount of P_2O_5 insoluble in ammonium citrate was 0.88 %. P_2O_{5hh} content was equal 12.32 % (13.20-0.88).

Control analysis

The XRF method was performed simultaneously with the chemical analysis method of the Department of Inorganic Materials, in accordance with the TCVN. The analytical results of the two methods and some analytical criteria, are compared with the analytical results of the Quality Assurance and Testing Center 1 (Quatest1), table 6.

The XRF method was performed simultaneously with the chemical analysis method of the Department of Inorganic Materials, in accordance with the TCVN. The analytical results of the two methods and some analytical units were compared with those of the Quality Assurance and Testing Center 1 (Quatest1), table 6.

Table 6: Analytical results of laboratories

No.	Units	XRF	Chemical	Quatest1
1	Nts	-	5.53	4.60
2	P_2O_{5TS}	13.20	13.23	13.60
3	P_2O_{5hh}	12.32	12.43	11.80
4	K_2O	6.06	6.21	6.20
5	S	3.80	3.04	-

Basic parametric method

Mixed solid fertilizers, after grinding, had from 12 to 30% that could not go through the seize with hole diameter 150 µm depending on the type of fertilizers. The part that could not be passed through the sieve was called the hard part (H) and the part that was passed through the sieve was called the soft part (S). The H and S ater grinding were sieved with a hole diameter of 75 µm, dried and pelletted. X-ray spectrometry found that Xray fluorescent intensities of the element compositions of the two parts were very different and shown by Figure 8. According to TCVN 10683-2015, two separate analysises must be performed by this fertilizer. The analysis result of the fertilizer was the average of the ratio of the hard part and the soft part.

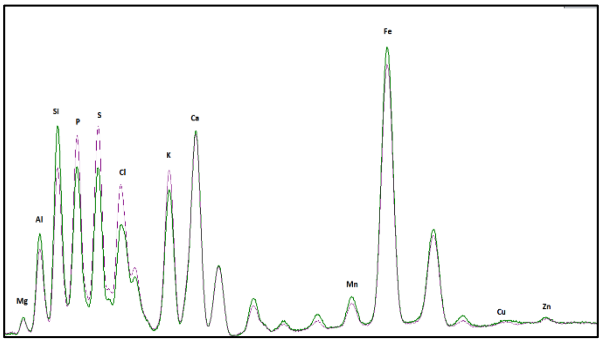

Figure 8: Spectra of hard part and soft part of fertilizer

Mixed fertilizers analyzed by the above standard addition method had hard part 28 % (labeled H100S0) and soft part 72 % (labled H0S100). Inital fertilizer labled H28S72 was determined contents by standard addition method. Components were analyzed by standard addition method for two samples H100S0 and H0S100 and created by 2 more samples with ratio H50S50 and H72S28. Thus, five standard samples with known content of components were used to analyze the component contents on the fertilizer production line by using the basic parametric method [9-11]. Table 7 was a set of 5 standard samples with nutritional element contents.

Table 7: A set of 5 standard samples

Lable	%Mg	%Si	%P	%S	%K	%Ca
H100S0	0.60	9.73	4.94	2.92	4.14	4.24
H0S100	0.65	6.27	6.10	4.27	5.46	4.67
H28S72	0.63	7.25	5.75	3.80	5.03	4.55
H50S50	0.63	8.00	5.52	3.59	4.80	4.46
H72S28	0.61	8.76	5.26	3.30	4.51	4.36

The standard curves of nutrient elements were equations with regression coefficients:

where Mg: $y = 0.0095x - 0.0938,\ R^2 = 0.9425$

Si : $y = 0.0014x - 1.0755,\ R^2 = 0.9993$

P : $y = 0.0005x - 2.3692,\ R^2 = 0.9963$

S : $y = 0.0004x - 0.6264,\ R^2 = 0.9991$

K : $y = 0.0009x - 0.5417,\ R^2 = 0.9986$

When analyzing the content of components according to the basic parametric method, H28S72 was taken as the standard sample and the remaining four samples were used as test samples. The errors in the content of components P, K, S between the calculation and the analysis results of the four test samples were less than ±3 %. This error and the analytical methods were met the requirement of the national technical regulation on root mixed fertilizers: deviation between the registered level of quality criteria (%) = (Value according to test results in units of registration level/registration level) x 100, with a total of three components Nts + P_2O_{5hh} + K_2O_{hh} ≥ 93 %, of which Nts ≥ 90 %; P_2O_{5hh} ≥ 90 % and K_2O_{hh} ≥ 93 %.

Conclusion

The VietSpace 5006-2009 spectrometer system was upgraded and replaced the FAST SDD detector to become the VietSpace 5006 - 2020, which has met the quantitative analysis of elements in solid NPK mixture fertilizers.
The standard addition method quantitatively analyzed the major macronutrients P_2O_5, K_2O, the major medium nutrient elements such as sulfur in fertilizers with error that was accepted by regulatory less than ±5 %. The other ingredients in the fertilizer needed to determine were applied by standard addition method.

VietSpace 5006-2020 X-ray fluorescence spectrometer system with basic parametric method, built a quick and simutaneous analysis process of the content of ingredients in solid NPK mixture fertilizer on the production line and ensured the right quality of fertilizer.

Acknowledgments

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