

ON-LINE ANALYSIS OF PHOSPHORUS IN AGRO-CHEMICAL & MINERAL
PROCESSING PLANTS BY RADIATION TECHNIQUES

By

Ette, A.O., V.I. Umogbai, and D.I.U. Ogo

Faculty of Engineering

University of Agriculture

Markudi, Benue State, Nigeria

ABSTRACT

Phosphorus is economically important for the manufacture of fertilizers, chemicals, animal feed and matches. The conventional method of analysis for phosphorus is the ANSI/ASTM standard test method E278-71. The large amount of time involved in the analysis causes concern for a comparatively accurate analytical method with shorter analytical time. Work has been carried out to establish quantitative detectability of phosphorus in flotation concentrate using Neutron Activation Analysis (NAA). It takes about five minutes to complete a quantitative determination of phosphorus using NAA while the wet chemical methods require many hours. Results from this investigation were discussed and compared with X-ray and standard (wet chemical) methods. Design considerations for an on-line analytical instrument were also discussed.

INTRODUCTION

About two million tons of phosphorus is produced annually of which 70% is used for production of various chemicals and 5% is used in the production of animal feed. The need to accurately determine the concentration of phosphorus in these products for quality assurance and control cannot be overemphasized. Conventional methods of analysis are too slow and incompatible with the requirements for on-line applications. To ensure homogeneity of mix and the attainment of product specification, a technique with short analytical time and independent of sample preparation is required. It is to this problem that our studies have been directed.

X-ray fluorescence analysis has the potential of meeting the analytical speed requirement but suffers from strong dependence on sample type, mineralogy, particle size and sample preparation. The use of neutron activation analysis (NAA) offers both speed and accuracy without the attendant problems associated with X-ray fluorescence and wet chemical analyses. In the use of NAA, recognition is given to possible interference from Silicon and Aluminum. This problem is reduced by appropriate choice of radiation source and application of correction factor (Turner, 1956). It is hoped that the successful determination of phosphorus by this method will be useful in process control in the fertilizer, animal feed, and related phosphorus based manufacturing industries.

REVIEW OF ANALYTICAL METHODS FOR TOTAL PHOSPHORUS IN THE AGRICULTURAL SECTOR

Difficulty in the analysis of phosphorus was blamed for the extreme variability in soil organic phosphorus (Barrow, 1961; Larson, 1967). Methods in common use include ignition, fusion, acid digestion and a combination of these techniques.

IGNITION METHOD: Beckwith and Little in 1963 (Maida, 1973) ignited the soil at 550°C for one hour and then extracted the soil for four hours with dilute hydrochloric acid at 100°C. Saunders and Williams (1955) ignited the soil for one hour at 550°C and extracted the total phosphorus by shaking the ignited soil for 16 hours with 0.2 N H₂SO₄. Given the significant amount of time involved in this technique, fusion has used as an alternative method of analysis.

FUSION METHOD: This method is carried out by melting the soil in Na₂CO₃ and dissolving the melt in water (Pearson et al., 1940; Maida, 1973). H₂SO₄ was used in dissolving the melt (Jackson, 1958). The fusion method depends on the type of soil (Siliceous soils are highly favoured) and also involve significant analytical time.

ACID DIGESTION METHOD: Highly aggressive acids are needed to solubilize the soil sample. Hence, perchloric and hydrofluoric acids are commonly used. The fumes from the digestion process are very dangerous, therefore limiting the use of this method. It should be noted that in spite of the dangers mentioned above, perchloric acid is favoured due to its simplicity and adaptability to most soil samples (Hesse, 1971).

Agbede (1984) has given a summary of the various methods commonly employed in the determination of total phosphorus in soil sample and is displayed in Table 1. These methods have inherent deficiencies due to volatilization

Table 1: Some methods used for extracting soil organic phosphorus, (Agbede, 1984)

Authors	Consecutive Extractant	Performance
Mehta et al. (1954)	1. Hot Conc. HCl, 1 hr 2. 0.5M NaOH, 1 hr 3. Hot 0.5M NaOH, 8 hr	Increased accuracy and recovery over previous extraction methods. No comparison given with ignition methods.
Kaila and Virtanen (1955)	1. 4M H ₂ SO ₄ , 18 hr 2. 0.2M NaOH, 18 hr 3. Hot 0.5M NaOH, 4 hr	97% of "Kjeldahl digested" organic P 93% of "Ignition method" organic P
Saunders and Williams (1955)	1. Hot 0.1M HCl, 16 hr 2. Double extraction with 0.1M NaOH, 16 hr	83% of "Ignition method" organic P
Anderson (1960)	1. 0.3M NaOH overnight subsequently analysed on same day as Mehta et al.	90% recovery of RNA glucose-, inositol- and glycerol- phosphate added to the soil
Dormaar and Webster	1. 1:1 acetone, 4 hr 2. 0.3M NaOH, 4 hrs	86% recovery of RNA, DNA, lecithin, Phytin, glucose-1-phosphate

(Melting point of $P_2O_5 = 572.7^\circ C$); (complete calcination); oxidation and complete mineralization.

INORGANIC PHOSPHORUS ANALYSIS:

Soil Sample:

The sample is consecutively extracted with different extractants, aimed at removing the phosphorus from a specified mineral. This procedure was developed by Chang and Jackson (1957) and was modified by Petersen and Corey (1966). The extraction requires about 21 hours excluding analytical time.

Non-soil Sample:

The standard test method ANSI/ASTM E278-71 (Snell and Leslie; ASTM, 1978) has been widely used for phosphorus analysis. The basic analytical steps include:

1. Dissolution of sample in HCL and HNO_3
2. Addition of perchloric acid
3. Evaporation to hydrate silica
4. Ignition of insoluble residue
5. Addition of ammonium molybdate
6. Dissolution of precipitate in excess NaOH
7. Titration with HNO_3

Depending on the type of sample to be analyzed, the above procedure could take several hours and up to 48 hours.

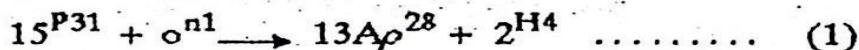
Production of fertilizers, animal feed mixing, and other chemicals containing phosphorus require accurate and fast analysis of the phosphorus in their production plants to ensure good quality control. The existing methods outlined above, are time consuming and therefore can not meet the effective on-line analysis requirements. Instrumental and non-destructive method of analysis would eliminate tedious sample preparation, lengthy extraction procedures and loss/interruption of flow streams due to sampling. The techniques which are capable of meeting these requirements include quantitative X-ray methods and radiation methods.

X-RAY AND RADIATION METHODS FOR PHOSPHORUS ANALYSIS

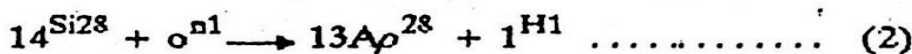
The attractiveness of x-ray and radiation methods of analysis rest in their speed, adaptability to most sample source, absence of elaborate sample preparation, and reliability of results. X-ray methods are seldom used in on-line analysis due to the bulky nature of the generating and analytical equipment.

Radiation, therefore, appears as the most plausible method and will be further explored.

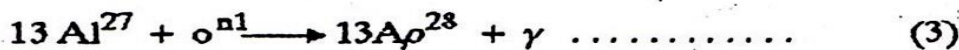
Radiation Techniques: Various techniques of irradiating samples with radio



neucleides (α, β, γ , etc.) to produce radio-active particles are commonly encountered in physics, nuclear engineering and analytical chemistry. The induced activity in the sample is a measure of the concentration of its radioactive



and,



component. More details on this subject can be obtained from common text books on Atomic Physics including Wehr and Richards (1967). For the purpose of this paper, Neutron Activity (NAA) is further reviewed.

Quantitative detectability of Phosphorus by NAA is based on the reaction:

This reaction has a γ -energy of 1.78MeV and a half-life of 2.3 minutes (Turner, 1956; Lenihan et al., 1969; RHH, 1970). The possible interference for this reaction arises from two related reactions:

Reactions represented by equations (1) and (2) occur in a fast-neutron bombardment or when the electrons have 1MeV or more energy. On the contrary, reaction (3) is a slow-neutron reaction and therefore will not occur if fast neutrons are used. This means that interference from silicon, equation (2) will affect phosphorus analysis using fast neutron source. After irradiation of the sample it is analyzed for phosphorus and appropriate correction for silicon interference can be made.

ANALYSIS:

The general decay equation is used for analysis of irradiated samples.

$$I = I_0 e^{-\lambda t} \dots\dots\dots (4)$$

where I = intensity of radio active particles of the element

I_0 = induced intensity at the end of irradiation

$\lambda = 0.693/\tau =$ decay constant

$\tau =$ half-life of radio active particle

t = decay time

The above equation gives activity at specific time (t) after irradiation and can be used to measure the released activity after a given time interval ($t_1 - t_2$).

$$N_r = I_0 (e^{-\lambda t_1} - e^{-\lambda t_2}) \dots\dots\dots (5)$$

$N_r =$ activity released at interval t, to $t_2 =$ Area of photopeak

t_1 = time at start of measurement

t_2 = time at end of measurement (all times measured from end of irradiation)

Since I_0 is a characteristic function of material and instrument parameters (as given below), its accurate determination is crucial to the accuracy of the analysis of the sample.

$$I_0 = \left(\frac{W}{A}\right) N \sigma f \epsilon (1 - e^{-\lambda t}) \dots \dots \dots (6)$$

where W = weight of element in sample

A = atomic weight of element

N = Avogadro's number

σ = effective neutron cross section

f = effective flux

ϵ = counter efficiency

x = isotopic fraction

t = irradiation time

From equation (5) and (6), I_0 can be considered as a constant for a given instrument setting and sample selection. If two values of N_T are measured and their ratio determined, I_0 can be eliminated and the value of λ can be calculated. With known value of λ , the value of I_0 for the element can be calculated. Using known standards and comparing the measured released activity with that of the sample, the concentration of the element in the sample can be determined.

Correction for Si Interference:

Correction for silicon is achieved by dividing the measured weight of the element by the summation of the Relative Specific Activity of the element and potential interference elements.

$$W_T = \frac{W_m}{\frac{\mu(P)}{\mu(P)} + \frac{\mu(Si)}{\mu(P)} + \frac{\mu(Al)}{\mu(P)}} \dots \dots \dots (7)$$

where,

W_T = True weight of element (P) in sample

W_m = measured weight of element in sample

$\mu(P)$ = Specific activity of element (P) = $\frac{1.88 \times 10^{11}}{\tau(\text{Atomic Weight})}$

$\frac{\mu(Si)}{\mu(P)}$ = Relative specific activity of silicon (Si) to phosphorus (P) for τ minutes

From equation (7) $\frac{\mu(Al)}{\mu(P)} = 0$ for fast neutron.

Hence,

$$W_T = \frac{W_m}{\frac{\mu(p)}{\mu(p)} + \frac{\mu(si)}{\mu(p)}} \dots\dots\dots (8)$$

By inserting appropriate values of μ in equation (8) above, the true weight of phosphorus is given by the relationship:

$$W_T = \frac{W_m}{2.1} \dots\dots\dots (9)$$

The above analyses imply that an independent means of determining the presence of the interference elements in the sample must be used. Radioactivity is easy to detect and small amounts can be traced through successive chemical processes.

EXPERIMENTAL

Phosphorus flotation concentrates were obtained from the International Mineral Company, Florida. Known weight of each sample was irradiated for 60 seconds at the nuclear reactor facility of the Michigan Technological University. The sample was then allowed to cool off for 120 seconds. Short lived products would completely within this interval. The sample is counted for 200 seconds. The area under each photopeak was instrumentally measured and the background subtracted. This corrected area (count) gave the value of the consumed activity within the 200 seconds and the integrated areas instrumentally determined.

A second batch of samples were sent to the University of Michigan for analysis at their nuclear reactor facility. Only three samples were successfully analyzed in this facility.

To compare the radiation technique, a set of samples was analyzed using X-ray fluorescence equipment [AXS - Philips, VRG 3100 X-ray generator with Tektronix 4006-1 computer and Diable Printer]. Boric acid was used to dilute the samples and to simulate the presence of water in the process stream.

Finally, a set of samples was analyzed using the standard wet chemical method (E278-71). Standards used in each method of analysis was prepared from Certified Standard Phosphorus Sample, Tennessee Brown 56a Phosphate Rock. Results from each technique are analyzed and compared with one another.

RESULTS AND DISCUSSION

The first batch of samples analyzed by NAA techniques were standard (Reagent grade 56a Phosphate Rock) and two industrial samples designated A1 and A2. The areas of photopeaks measured at 1.778 MeV, 1.273 MeV, and 1.268 MeV for the Standard and A2, A1, and A2 respectively were determined for series of counting intervals. The results appear in Figure 1. From the figure, the values of I_0 for the various samples were graphically determined by extrapolating the plot to one minute on the time axis. Also calculated from the graph were

values of lambda and tau for the three samples. Table 2 displays the results obtained.

Table 2: Characteristic parameters for $P^{31}(n, \alpha)Al^{28}$

Sample	I_0	λ	τ (min)
Standard	2.34×10^5	0.293	2.36
A1	3.30×10^4	0.297	2.33
A2	3.04×10^5	0.294	2.36

It can be seen that the value of λ and τ are basically the same for the three samples and independent of the peak energy value (see Figure 1). This indicates that the parameters λ and τ are material's characteristics and depict a specific mechanism. Also using the instrumental integration of the areas under the photopeaks and equation (5), the value of λ was determined for the standard sample to be 0.298. The value of τ was obtained from continuous approximation analysis. Corresponding value of tau was found to be 2.33 minutes. This confirms the value obtained from graphical solutions. The value of τ for the reaction $P^{31}(n, \alpha)Al^{28}$ is given as 2.31 minutes in the literature. Considering the fact that the samples were not chemically pure, it is evidenced from the above analysis that the prevailing reaction was $P^{31}(n, \alpha)Al^{28}$ as given in equation (1).

The standard sample was irradiated five consecutive times and the value of phosphorus was measured after each irradiation as % P_2O_5 . Values obtained were: 32.63, 33.0, 33.01, 33.01, and 33.06. The mean value of 32.94 and a standard deviation of 0.175 were calculated. The results show good repeatability and the relative accuracy was found to be 99.82% with an Average Precision of 0.309%.

The analysis of 10 samples are displayed in Table 3. These samples cover a wide range of concentrations with some variation in sample size. The equivalent weight of P_2O_5 shown in Table 3 as well as the actual weight were calculated using equations (4) and (9) in the text

Comparison of this result with the other methods of analysis is displayed in Table 4.

It can be seen that the result for each sample was effectively the same from the three techniques. Only A22 showed lower value for wet chemical analysis. It however showed identical values in X-ray and NAA.

It was decided to statistically compare the results from NAA with that of wet chemical methods. The paired difference statistics was used for the analysis. The main difference (\bar{d}) was calculated to be 0.261 with a standard deviation (s) of 1.64. The calculated students' t value was 0.477 for ten samples. The calculated values of t at $\nu = 9$ (degree of freedom) and α (confidence level) = 0.20 and 0.01 were 1.384 and 3.250 respectively. Hence, the Null hypothesis, $H_0: \mu = \mu_0$ (where $\mu =$ population mean and $\mu_0 =$ fixed value usually taken as zero) could be subjected at $\alpha = 0.20$ or $\alpha = 0.010$ since measured t-value was less than $t_{\alpha/2}$ from the tables. This means that there is no difference between NAA and wet

al analysis. Similar results were obtained from comparison of the x-ray

Results of analysis of 10 samples

Wt of (g)	Measured activity (counts /sec)	Equivalent weight of P ₂ O ₅ (g)	Actual weight of P ₂ O ₅ (g)	% P ₂ O ₅
0.7210	3.83×10^5	0.7210	0.7210	100.00
1.250	4.95×10^5	0.9318	0.4236	33.89
1.250	4.97×10^5	0.9356	0.4253	34.02
1.250	4.90×10^5	0.9224	0.4193	33.54
1.250	5.06×10^5	0.9525	0.4330	34.64
1.250	4.83×10^5	0.9092	0.4133	33.06
1.250	9.01×10^5	0.1696	0.0771	6.16
1.250	4.62×10^5	0.0870	0.0395	3.16
1.250	1.64×10^5	0.3087	0.1403	11.22
1.250	3.04×10^5	0.0572	0.0260	2.08
1.100	4.82×10^5	0.9074	0.4124	33.00

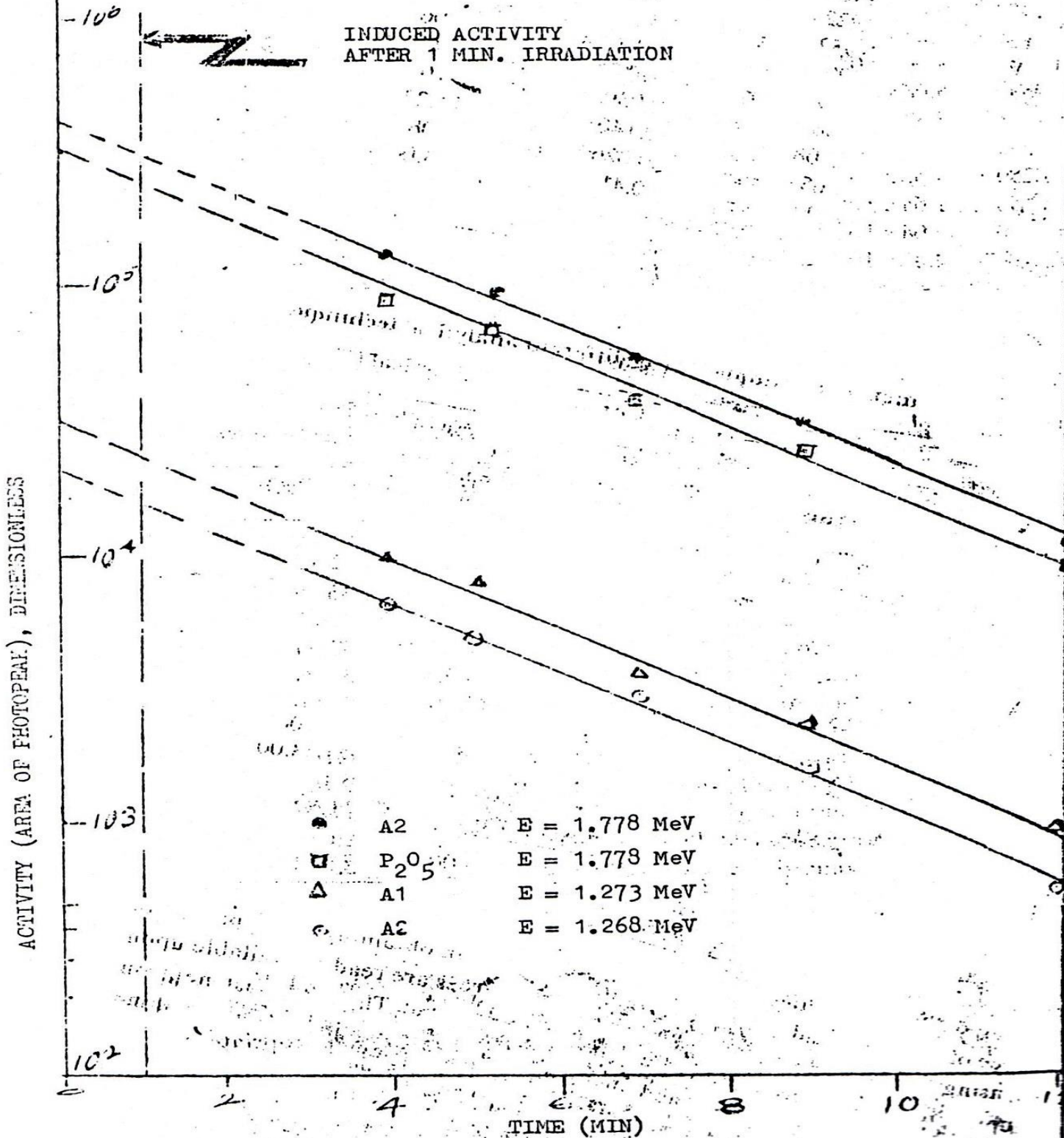
Analysis of P in industrial samples using different analytical techniques

Sample ID	Description	Concentration of P as % P ₂ O ₅		
		X-Ray	Wet chemical	NAA
A1	Plot Conc Bin 9	33.48	34.69	33.89
A2	Plot Conc Bin 8	33.65	34.72	34.02
A3	Plot Conc Bin 7	33.18	34.55	33.54
A4	Plot Conc Bin 11	34.29	34.33	34.64
A13	Standard Tennessee Brown	33.01	33.00	33.06
A18	Noralyn GF-198	6.10	6.40	6.16
A20	Kingsford GG-46	3.13	3.06	3.16
A22	Clear Springs	1.13	6.47	11.22
A23	Kingsford GG-45	2.05	1.94	2.08
A25	Standard + Boric Acid	32.63	33.00	33.00

NOF NAA DEVICE

design of an effective radiation device rest in obtaining the appropriate radiation and a good counter. These sources are readily available upon g and include Co⁶⁰, Am²⁴¹, Sb¹²⁴, Ra²²⁶, and Th²²⁸ for fast neutron ion. Geiger counter is commonly used and sampling could be done

FIGURE 1: ACTIVITY Vs. TIME FOR NAA



intermittently or continuously depending on need. Calibration can be done using known standards or commercially available calibration standards.

CONCLUSIONS

1. The analysis of phosphorus by conventional wet chemical methods is time consuming and cannot be applied for on-line analysis.
2. The use of Neutron Activation (NAA) is much faster than the chemical methods and produce good accuracy and precision.
3. Neutron sources are available and can be acquired through licensing.
4. The speed, adaptability and ease of analysis using NAA make it more appropriate for on-line applications and should be used in fertilizer, and other phosphorus processing plants.

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