

## Technical Note

### RAPID ANALYSIS OF FLORIDA PHOSPHATES BY ENERGY-DISPERSIVE X-RAY FLUORESCENCE

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#### ABSTRACT

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A rapid X-ray fluorescence technique has been developed to determine the BPL ( $\text{Ca}_3(\text{PO}_4)_2$  or Bone Phosphate of Lime) content of various streams in Florida phosphate beneficiation and in supporting laboratory flotation experiments. The method, which requires simple sample preparation, a 100-sec counting, and has an accuracy of better than 2% BPL (0.4% P), employs an  $\text{Fe}^{55}$  radioactive source and a room temperature detector to analyze for calcium. The BPL values, which can not be obtained readily and directly because of the weak fluorescence of phosphorus, are instead derived from a close correlation found to exist between the phosphorus and calcium concentrations.

#### INTRODUCTION

In phosphate mining and beneficiation, the phosphorus content, expressed usually in terms of the BPL values, is analyzed in one of two ways. The first involves the isolation of phosphorus as ammonium phosphomolybdate from nitric acid solutions, followed by dissolution of the molybdate precipitate in an excess of NaOH which is then determined by back titration with standard acids (Rieman and Beukenkamp, 1961); a related photometric method based on the reaction with molybdovanadate reagents is also widely used. The second measures the emitted energy of electronic transition or X-ray fluorescence of phosphorus atoms when they are subjected to incident electromagnetic radiation. Both techniques, although quite accurate, are tedious and time-consuming.

Due to its weak fluorescence, the *direct* determination of phosphorus by the latter method of X-ray spectroscopy is presently difficult, requiring a strong photon source obtainable only by tube excitation, elaborate sample preparation (pulverizing, pelletizing, etc.), detection of emissions under cryogenic conditions, and computer signal enhancement. However, the need for these added efforts to achieve improved precision would be sharply

reduced in analyses of elements having atomic numbers much greater than that of phosphorus. Thus, if one finds in a sample a relation between the concentrations of phosphorus and of an element with sufficiently large atomic number, he can test for the latter with comparatively simple spectrometers and indirectly deduce the value of the former. This note describes a rapid method of BPL assay based on this approach.

## EXPERIMENTAL METHOD

Energy-dispersive and wavelength dispersive spectrometers are both suitable for phosphorus analysis. The first accounts for the X-ray fluorescence by measuring the number of radioactive counts at the characteristic energy of the element; the second, which is slower but has better resolution, does a similar counting by rotating a diffracting crystal and scanning the specimen over the associated wavelength region (Henrich, 1976). In these experiments where speed and sensitivity were stressed, an energy-dispersive unit, specifically, the Princeton Gamma Tech Model 100 Analyzer with an  $\text{Fe}^{55}$  source and a room temperature detector was found to be satisfactory. Due to the softness of the X-rays, some sample preparation was necessary. Air and water significantly attenuated the fluorescence signals and these effects were removed by purging the test window area with helium and by heating the specimens in a fast drying oven. Sample homogeneity, which also influenced test precision, was achieved by a 20-sec grinding in a CRC Micro-Mill. Calcium analysis in the spectrometer, like that of any high atomic number element, was standard and so will not be described here (Henrich, 1976; Barbi, 1978).

Phosphate samples, representing plant streams and mixtures thereof, were obtained from Mobil Chemical Company's facilities at Nichols and Fort Meade, Florida. The analyses for calcium and phosphorus were performed by atomic absorption and the molybdate procedure, respectively.

## RESULTS AND DISCUSSIONS

*Calcium/phosphorus correlation.* Based on prior spectroscopic studies of Florida minerals, we sought a correlation between calcium and phosphorus contents such that calcium fluorescence may be used as an indirect means to determine BPL values. The premise was that the predominant phosphate-containing mineral in the Bone Valley District of Central Florida is apatite ( $\text{CaF}_2 \cdot 3\text{Ca}_3\text{P}_2\text{O}_8$ ) which, on the average, should have a nearly constant ratio of these two elements. This relation should be even more evident for the deslimed plant streams where interfering substances like clay and calcite have already been eliminated.

Figure 1 summarizes the results on a set of 27 samples employed to develop the calcium/phosphorus correlation. Triplet measurements were made for nine specimens to show their typical precision. As indicated, the

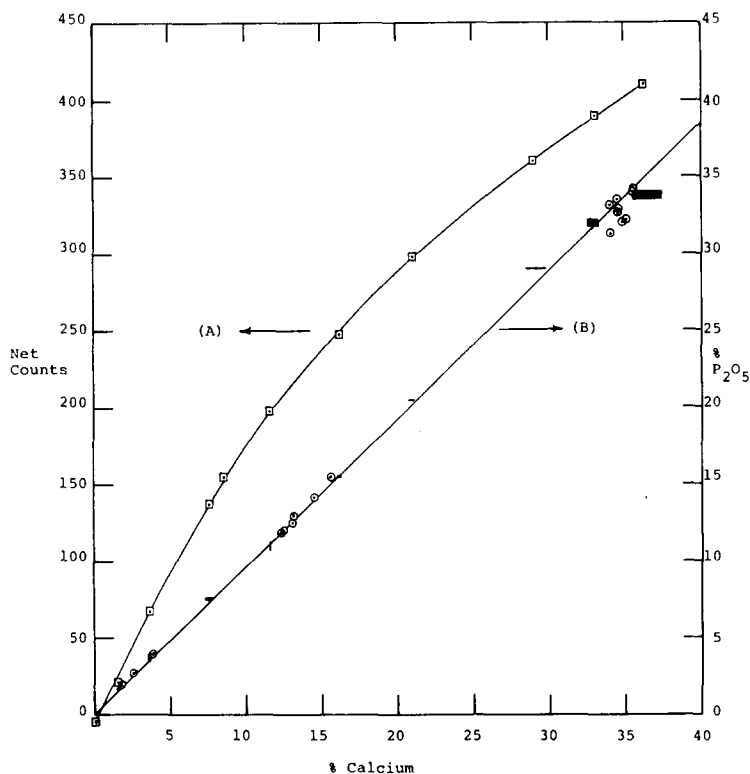


Fig. 1. A: calcium counts in 100-sec vs. calcium concentration in test samples. B: calcium/phosphorus correlation ( $\circ$  represents single analyses in one laboratory;  $\blacksquare$  denotes triplicate measurements in another laboratory; the size of the data points illustrates the range of uncertainties).

variations are small but become somewhat larger at the highest  $P_2O_5$  concentrations. In this region, the data scatter appears to have originated from the fact that these few samples, primarily pebbles and similar products from the Nichols mine, had not undergone the customary desliming in beneficiation; because of the inclusion of calcium-containing minerals in the pebbles, the ratio of calcium to phosphorus tends to vary more than those of normal plant streams. The least square fit of the data provides the following relation:  $\% \text{ Ca} = (1.044) (\% P_2O_5)$ .

**Calcium fluorescence.** The dependence of the number of radioactive counts during a 100-sec interval upon calcium concentration is also given in Fig. 1. The  $Fe^{55}$  source has a half-life of 2.94 years so the equation governing its decay is  $N/N_0 = \exp(-0.2357 t)$  where  $t$  is the time in years,  $N$  and  $N_0$  the respective number of disintegrating atoms at times  $t$  and 0. From this, one finds approximately a 1% decline in the counts every two weeks which must be compensated by the use of the above expression or by prolonging the counting period accordingly. Preferably, a new plot will be generated monthly to insure proper calibration — a task not at all onerous in view of the rapidity of these measurements.

## CONCLUSIONS

The curves in Fig. 1 together provide an indirect means of phosphorus determination. Its central features are easy sample preparation, the strong X-ray fluorescence of elemental calcium, and the calcium/phosphorus correlation observed in the streams of beneficiation plants. This technique, which requires only a 100-sec counting as contrasted to hours for other analyses for phosphates and which can be further "fine-tuned" to a particular ore body through a more specific — and thus even more precise — correlation, has been extensively tested. The results of multiple assays show an accuracy of better than 2% BPL (0.4% P) which is sufficient for most applications associated with phosphate recovery and processing in Florida.

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