any effect on the sign of rotation of the enantiomers, the same conclusion is applicable to debromoleptophos oxon. Therefore, the enantiomer of debromoleptophos oxon with greater anticholinesterase activity and acute toxicity is $(R)_p$ while the enantiomer with greater antineurotoxic esterase activity and delayed neuropathy is $(S)_p$.

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Analysis of Phosphate Ores and Related Raw Materials by X-ray Spectrometry

Wendell D. Wilhide* and Doris H. Ash

Both pressed-powder and fusion sample preparation methods have been compared in the application of an automated X-ray spectrometer to a broad range of phosphate ore types and their products of beneficiation treatments. Emphasis has been on minimum dilution techniques. The methods developed show good precision for six of the more important constituents followed in process control and experimental studies. The X-ray fluorescence (XRF) method is in general agreement with routine chemical methods, although no attempt was made to establish ultimate accuracy. Sample preparation methods are evaluated for the various types of materials studied.

INTRODUCTION

World production of phosphate rock products increased by nearly two-thirds during the past decade to the current production rate of about 150 million metric tons of concentrate product. Domestic U.S. production accounts for about one-third of this total production, mainly from major sedimentary deposits in Florida, North Carolina, and the western U.S. phosphate district (Idaho, Utah, Wyoming) (IFA, ISMA, 1983).

The principal use of phosphate rock products is as raw material for the manufacture of chemical fertilizers and wet-process phosphoric acid (WPA) intermediates. Worldwide market requirements for fertilizers, however, have accelerated rapidly to meet agricultural production needs of food and fiber. This is resulting in increased dependence on lower quality phosphate rock resources as

high-grade reserves are being depleted. As a consequence, the progressive slippage in chemical quality of phosphate concentrate grades is adversely affecting the chemical fertilizer processes and product compositions (Lehr, 1984).

Compositional variations among phosphate rock products may result from a combination of factors. Phosphate rocks occur in a broad range of geological settings ranging from igneous intrusives and metamorphic carbonatites to sedimentary deposits of widely differing geochemical origin. These individual deposits differ in the compositional form of the apatitic phosphate minerals, as well as in the variety of accessory mineral impurities (McClellan and Gremillion, 1980). Furthermore, physical metallurgy treatments to upgrade the phosphate values in raw ores to commercial concentrate grade lead to more or less random rejection of accessory mineral impurities. Consequently, phosphate rock products meeting specific P_2O_5 grade specifications may differ markedly in their chemical compositions, especially for key impurities such as Na, K, Mg, Al, Fe, and Si, that are mainly derived from the accessory mineral matter retained in rock products (Lehr,

Division of Chemical Development, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama 35660.

1984). This results in a serious quality control problem to the phosphate industry.

These widely differing compositional characteristics of commercial phosphate rocks create the need for rapid analysis methods applicable to all stages of rock production from exploration and mining to physical metallurgical beneficiation treatments and quality control of rock reagent feeds for chemical acidulation processes.

Each of these production stages generates a high volume of samples for multicomponent analysis of P_2O_5 and key impurities where a rapid analysis capability is highly desirable to ensure quality control over the production step. To meet these analytical requirements of the phosphate chemical processing industry, it is highly desirable to have an automated analytical instrumental method capable of rapid, routine, multicomponent analysis.

This report describes the Tennesse Valley Authority's (TVA) development of two sample preparation methods that are generally applicable for automated X-ray spectroscopic analysis (X-ray fluorescence, XRF) of phosphatic ores and related beneficiation products. The sample base used in this evaluation included representative ore types and beneficated products from the major U.S. deposit sources.

Several investigators have applied X-ray spectrometric methods to the analysis of natural phosphate ores and beneficiation products. McKinney and Rosenberg (1970) analyzed six elements (P, Si, Ca, Fe, Al, and Mg) in production samples (27.4–33.6% P_2O_5), as well as exploration samples separated into several fractions by physical tests such as screening and flotation (2.4–36.8% P_2O_5). Intensities were collected on pressed-powder specimens by using a vacuum X-ray quantometer interfaced to a small computer to perform calculations. A calibration algorithm was developed based on sample absorption characteristics of chemically analyzed standards prepared from phosphate rock and Ottawa sand. A standard deviation of calibration was given as well as a standard deviation from chemical results for several new samples not used in the calibrations.

Issahary and Pelly (1982) more recently applied a simultaneous wavelength-dispersive X-ray spectrometer to an eight-element analysis of Israeli high-grade phosphate ores and calcination products (33–34% P_2O_5). The elements analyzed were Mg, Na, Al, Si, P, S, Cl, and Ca. Pressed-powder sample intensities were fed to a small interfaced computer and concentrations calculated from a linear algorithm. Short-term sensitivity changes were corrected by use of a stable monitor or "correlation" specimen. Precision was shown for several splits of a calcination product. The general method was stated to be sufficiently accurate for the needs of the phosphate industry, although presumably calibration standards closely matching unknowns in composition would be desirable.

Wankova et al. (1982) developed a method using X-ray spectrometry for determining P and Ca in high grade natural or "raw" phosphates (27.8–38.8% P_2O_5) from deposits around the world. Intensities were collected for seven elements (P, Ca, S, Si, Fe, Al, and K) in order to apply a mathematical interelement correction based on the Lucas-Tooth and Pyne algorithm. Again, a pressed-powder sample preparation was used to analyze ores and calcination products in the range 27.8–38.8% P_2O_5. Compared to chemical analysis, results for both standard deviation and coefficient of variation were slightly better for raw phosphates than for calcined products because of matrix effects. It also was concluded that samples from different deposits probably should be fused to minimize matrix effects.

Finally, in the recent application by Ex et al. (1983), an automated spectrometer was used for an eight-element analysis (P, Ca, Si, Fe, Al, S, Mg, and K) of high grade phosphate ores. A pressed-powder method was used for the minor elements and a fused disk internal standard method was used for Ca and P. As compared to the chemical results using available standards, accuracy of the X-ray method was found to be excellent.

The objective of the present work was to apply an automated X-ray spectrometric analysis to a broader range of ores and beneficiation products than previous investigators had done and to compare precision for a six-element analytical program using both fused disks and pressed-powder pellets. Pressed-powder techniques described in most early studies did not use wet grinding, controlled pressing conditions, or binding additives. It is felt that a combination of these techniques contribute significantly to the present general application. The fusion method was chosen for simplicity, low dilution factor, and general applicability. High dilution, internal standard methods undoubtedly would present an attractive alternative in some cases in which only CaO and P_2O_5 are to be determined. Also, pregrinding of sample and flux are felt to be especially helpful in the present application to high silica ores and beneficiation products.

INSTRUMENTATION AND EXPERIMENTAL SECTION

Apparatus. A Philips automated PW1410 spectrometer (AXS) was used with a chromium target tube. Special equipment to prepare XRF sample specimens included a Claisse automatic fluxer, Angstrom TE-150 swingmill grinder with tungsten-carbide vessels, and Angstrom 4451A press with programmed loading accessory.

Sample and Standard Preparation. The XRF analytical sample was prepared by conventional methods so that a small sample (50 g or less), oven dried at 105 °C for 2 h and reduced to at least –200 mesh, was further treated as outlined below.

Pressed-Powder Method. The sample was mixed with exactly one-ninth its weight of spectroscopic grade boric acid and loaded in a tungsten–carbide grinding vessel, along with enough Freon 113 (trichlorotrifluoroethane) to give a wet grinding mixture of about 1 mL of Freon/g of sample mixture for weights up to 10 g. When sufficient sample was available, 50 g of sample and 20 mL of Freon were used. The small samples were ground 5 min in a 10-mL vessel and the large samples were ground 7 min in a 100-mL vessel. The Freon was evaporated off, and the dry powder packed in a 40-mm aluminum cup half-filled with crystalline boric acid as a backing cushion. The sample pellet was prepared with the programmed loading accessory set for 10-s rise time, 30 000 lbs total pressure, 10-s dwell time, and 10-s release time.

Fused Glass Disks. About 5 g of the dry, powdered analytical sample was placed in a platinum ignition dish and heated for 1 h at 1000 °C in a muffle furnace. The sample was cooled in a desiccator, the weight loss recorded, and about a 1.5-g sample weighted out into an aluminum weighing cup fitted with a lid. Exactly four times the sample weight of spectroscopic grade anhydrous lithium tetraborate was added, along with about 20 mg of potassium iodide wetting agent. The closed cup and contents were shaken vigorously by hand to mix the sample and flux as well as possible. Alternatively, for sand tailings only, the sample and flux mixture were ground together for 2 min in the swingmill grinder, omitting the Freon. This minimizes cracking of high silica materials reported by Houseknecht (1982, 1983). The mixture was transferred to a 25-mL Claisse-form nonwetting platinum–gold alloy

Table I. Ore and Beneficiation Product Standards

	sample description	chemical analysis, wt %					
		MgO	Fe$_2$O$_3$	CaO	SiO$_2$	P$_2$O$_5$	Al$_2$O$_3$
	Group 1						
concentrate grades							
1	central Florida commercial concentrate	0.37	1.3	48.7	4.0	32.9	1.4
2	North Carolina double float concentrate	0.54	0.71	48.5	3.2	30.3	0.47
3	south Florida concentrate	0.43	1.6	48.0	3.9	32.1	1.3
	Group 2						
raw ores							
4	Idaho calciner feed	0.82	0.61	41.8	12.9	27.9	1.8
5	central Florida pebble reject, 12.5% CO$_2$	4.6	0.93	40.1	11.9	22.0	1.2
6	Idaho foot wall shale, 10.3% CO$_2$	4.1	0.98	32.8	21.7	18.1	2.9
7	Tennessee brown high clay	0.51	5.2	25.0	25.8	19.9	10.2
8	central Florida raw matrix	0.88	1.5	29.6	38.5	20.1	2.4
9	central Florida raw matrix, 17.6% CO$_2$	7.4	0.83	21.1	40.0	6.3	2.0
10	south Florida raw matrix, 12.6% CO$_2$	5.3	0.64	18.6	50.2	6.6	2.0
11	central Florida high silica raw matrix	0.57	1.7	19.3	56.4	12.5	3.0
	Group 3						
sand tailings							
12	North Carolina sand tailings	0.15	0.28	8.7	81.5	4.6	0.39
13	central Florida sand tailings	0.05	0.15	4.5	90.0	3.0	0.47

Table II. Comparison of Analytical Results from Pressed-Powder and Fused Glass Disk Specimens, wt %[a]

	MgO		Fe$_2$O$_3$		CaO		SiO$_2$		P$_2$O$_5$		Al$_2$O$_3$	
	pellet	disk	pellet	disk	pellet	disk	pellet	disk	pellet	disk	pellet	disk
					Group 1							
1	0.35	0.37	1.2	1.2	49.2	48.9	4.2	3.4	33.3	33.8	1.3	1.4
2	0.51	0.62	0.67	0.68	49.3	49.0	3.5	2.8	31.1	30.8	0.44	0.45
3	0.40	0.41	1.5	1.5	48.6	48.5	3.9	3.1	32.5	33.4	1.2	1.4
					Group 2							
4	0.88	0.83	0.63	0.62	42.9	41.6	13.3	12.5	29.0	28.2	1.8	1.7
5	4.9	4.5	1.0	0.90	41.3	40.3	11.9	12.8	22.4	21.9	1.1	1.3
6	3.8	4.2	1.0	0.95	34.0	33.5	21.4	21.1	17.6	18.3	2.9	2.8
7	0.49	0.47	5.5	5.3	25.8	25.6	25.4	26.7	20.0	19.4	9.2	9.3
8	1.0	0.84	1.6	1.4	30.2	29.1	39.0	38.4	19.6	20.4	2.4	2.5
9	7.2	7.1	0.81	0.82	22.8	21.4	39.5	39.4	6.3	6.6	1.9	2.0
10	4.9	5.2	0.61	0.62	20.4	18.7	50.6	49.3	6.3	6.8	1.8	1.9
11	0.59	0.54	1.8	1.7	18.7	19.0	56.1	54.1	11.8	12.8	3.0	3.0
					Group 3							
12	0.16	0.15	0.29	0.28	9.1	8.5	78.1	82.3	4.6	4.5	0.37	0.35
13	0.06	0.04	0.14	0.16	4.4	4.4	89.5	91.7	2.7	2.9	0.48	0.43

[a] Values are means of five replicate determinations.

crucible and one to six samples fluxed automatically, finally casting a 40-mm clear glass disk for direct use. The fluxer was operated at medium heat for 5 min and at full heat for 6 min longer, both with moderate agitation. Normally, the individual mold holder assemblies are carefully adjusted beforehand to ensure a level position and evenly filled molds when the molten material is cast. However, we have found that it is easier to make use of the "wait" control–agitation sequence between casting and melt thickening to produce evenly filled molds, even if they are not completely level. The associated timing circuit board was modified for this purpose. The optimum delay varied from 6 to 12 s, depending on melt viscosity, which in turn depends on silica content.

Calibration Curves. Three types of ores and beneficiation products were used to establish calibration programs for both sample preparation methods. Group 1 contained concentrates with less than 20% silica. Group 2 contained raw or natural phosphate ores in the range 20–85% SiO$_2$ content. Group 3 contained the high silica sand tailings. Calibration fits for each group were made during the "run fit" testing of accumulated intensities, as described by Schreiner and Jenkins (1979). Usually a simple straight-line regression fit was adequate; when adsorption or enhancement effects were indicated, the Lachance Traill or Rasberry Heinrich models were chosen.

XRF Measurement Conditions. All X-ray intensities were collected on first-order Kα analyte lines except for calcium, which required attentuation by using the second-order line. Phosphorus was measured with a Ge crystal to eliminate second-order calcium interference; iron was measured with an LiF(200) crystal; magnesium was measured with a TLAP crystal; calcium, silica, and aluminum were measured with a PET crystal. Tube anode voltage was held at 60 kV, and the current varied from 10 to 50 mA to control counting rates. The flow detector used P-10 argon–methane gas, and all measurements were made by the ratio method. The spectrometer was operated in the vacuum mode.

RESULTS AND DISCUSSION

Table I lists the source and types of ores and beneficiation products analyzed (Fe, Al, Si, and Mg were determined by argon plasma spectrographic methods; CaO was determined by oxalate-permanganate titration; P$_2$O$_5$ was determined by colorimetric vanado-molybdate methods). The CO$_2$ content also is given when it is high enough to represent a significant addition to the matrix. All the materials listed were analyzed five times to provide an estimate of precision since the primary objective was to evaluate the precision of the two described sample preparation methods over a range of materials. Table II com-

Table III. Comparison of Precision for Pressed-Powder and Fused Glass Disk Specimens Analyzed by XRF (Coefficient of Variation, $\sigma/x \times 100$)[a]

	MgO		Fe_2O_3		CaO		SiO_2		P_2O_5		Al_2O_3	
	P	F	P	F	P	F	P	F	P	F	P	F
Group 1												
1	5.7	3.3	0.0	3.8	0.26	0.6	3.2	1.6	0.6	0.6	0.0	0
2	1.4	3.8	0.8	2.4	0.31	1.2	3.3	2.9	0.3	1.2	4.0	1.2
3	3.3	4.9	0.0	3.8	0.40	0.51	2.3	1.8	0.4	0.6	0.0	0
Group 2												
4	1.0	2.1	0.8	2.6	0.54	0.47	0.82	0.91	0.7	0.2	0.8	1.1
5	1.4	0.9	0.0	1.0	0.32	0.60	0.46	2.2	0.3	0.9	0.0	1.6
6	1.3	2.0	0.0	0.9	0.44	0.34	0.62	0.58	0.5	1.5	2.1	2.0
7	3.1	2.3	0	0	0.44	0.27	1.0	0.4	0.9	0.8	1.0	1.0
8	0	2.3	1.0	1.0	0	0.4	0.3	0.6	0.3	0.4	1.6	1.0
9	4.5	0.8	1.5	1.0	2.0	0.2	3.3	1.0	1.8	0.9	2.4	1.2
10	3.1	1.4	0.8	4.9	1.3	0.5	0.7	0.3	2.6	0	2.5	1.3
11	1.5	3.9	3.2	0	1.0	0.8	1.0	0.8	1.2	1.6	3.8	1.8
Group 3												
12	5.5	6.0	3.6	5.4	0.5	1.3	1.3	1.4	2.4	1.6	5.3	5.1
13	0	0.3	6.7	4.5	1.3	2.1	0.6	1.1	2.0	0.1	2.0	2.7

[a] P = pressed-powder pellet; F = fused glass disk.

pares the analytical results obtained with the two sample preparation methods and Table III presents the methods' precision.

Slightly better overall precision resulted for the Group 1 concentrate grades by using the pressed-powder method. The bulk matrix does not change very much for this group, and the main difference probably is the degree of dilution involved in the two sample preparation techniques. It also should be pointed out that some silica may be volatilized as SiF_4 (Bertin, 1975) by the fusion process. This particular result thus would be compared to a routine chemical acid-insoluble determination, which often is reported for process control and engineering samples. Standard deviations are somewhat lower for the Group 1 concentrates with the pressed-powder method.

The Group 2 raw ores represent the most extreme matrix variations. Results of the precision tests show a slight advantage for the fused disks, especially for high silica and high CO_2 materials. Also, as Ex et al. (1983) pointed out, best precision is obtained for CaO and P_2O_5 generally by fusion, while the less sensitive determinations of MgO, Al_2O_3, and Fe_2O_3 give better precision for pressed-powder specimens. The one exception is the high dolomitic raw ore; in this case, better precision for MgO is obtained by fusion.

The Group 3 sand tailings also represent a narrow range of matrix variations; precision again is slightly better for the pressed-powder method.

The methods described have been used routinely for ore characterizations, small-scale beneficiation studies, and process control of pilot plant flotation studies. About 25 samples can be analyzed easily during an 8-h shift by either sample preparation technique. The automatic fusion method (in which six samples are fused at one time) can be carried out in about half the time required to grind and press powdered samples individually. For other minor and trace components, the pressed-powder method with minimum dilution is necessary, as pointed out by Ex et al.

(1983). Additional work is being performed in this laboratory to extend such analyses to several other elements of interest in experimental studies. Also, it should be emphasized that in this study no attempt was made to establish the ultimate accuracy of the general XRF methods for all the materials analyzed. This is an ongoing process and is being continually updated to meet the needs of the particular application.

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