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Note

Simultaneous determination of fluoride, phosphate and sulfate in wet-process phosphoric acid by ion chromatography

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In the production of phosphoric acid, frequent, rapid and accurate determinations of sulfate and phosphate are needed to monitor the concentration of product acid, prepare recycle acid of the proper concentration, and maintain the desired amount of free sulfuric acid in the slurry. The density method for phosphate and the barium sulfate-centrifuge method for sulfate, along with various other methods, have been widely used. However, they are not as accurate and reliable as desired because they are affected by changes in the amounts of impurities in the acid. The reactor slurry also contains significant amounts of fluoride, which may affect both the composition and crystalline habit of the by-product calcium sulfate. Thus, a routine, yet accurate, method is needed for the simultaneous determination of anions in wet-process phosphoric acid.

The use of ion chromatography (IC) has grown rapidly in recent years, and a few applications to fertilizer materials have been reported. Phosphate rock^{1–3}, urea^{4–6}, and granular fertilizers⁷ were successfully analyzed, but no reports have appeared on the analysis of wet-process phosphoric acid by IC.

This note describes a simple, rapid, and reliable ion chromatographic method for the simultaneous determination of fluoride (F^-), phosphate (HPO_4^{2-}), and sulfate (SO_4^{2-}) in wet-process phosphoric acid.

EXPERIMENTAL

Materials

The test samples were produced by acidulation of a central Florida phosphate rock with sulfuric acid. The samples included both product acid and the first washing of the filter cake. They contained 0.35–1.16% F, 35.5–68.3% H_3PO_4 , and 0.44–6.82% H_2SO_4 , along with significant amounts of metallic impurities and organic material derived from the humic acid in the rock and the sulfonated tall oil added during the acidulation to control foaming. The composition of a typical acid sample produced by the hemihydrate method is given in Table I.

The acid samples were prepared for analysis by weighing 1-ml portions into 500-ml volumetric flasks. Any precipitates (usually calcium sulfate) in the acid samples were suspended before sampling and then dissolved by treatment with warm, dilute hydrochloric acid in the 500-ml flasks before diluting to volume with water.

TABLE I
TYPICAL COMPOSITION OF PHOSPHORIC ACID MADE BY HEMIHYDRATE METHOD

<i>Component</i>	<i>Concentration (%)</i>	<i>Component</i>	<i>Concentration (%)</i>
H ₃ PO ₄	62.14	CaO	0.10
H ₂ SO ₄	1.84	K ₂ O	0.03
F	1.00	Na ₂ O	0.08
Cl	0.01	SiO ₂	0.40
Fe ₂ O ₃	1.80	U	0.01
Al ₂ O ₃	0.80	C (from defoamer and humic acid)	0.20
MgO	0.50		

Aliquots of 10 ml were then diluted to 250 ml with water and 5 ml of a concentrated eluent solution (0.196 *M* NaHCO₃–0.154 *M* Na₂CO₃) before injection. The eluent was added to eliminate the “water dip” which would otherwise interfere with the fluoride determination.

Reagent-grade NaF, KH₂PO₄ and (NH₄)₂SO₄ were used to prepare aqueous stock solutions containing 1000 ppm F⁻, 1352 ppm HPO₄²⁻, and 1200 ppm SO₄²⁻, respectively. The stock solutions were diluted and mixed to give calibrating solutions which contained 0.5–3 ppm F⁻, 13.5–81 ppm HPO₄²⁻, and 1.2–7.2 ppm SO₄²⁻. Concentrated eluent also was added to the standards to prevent the “water dip”. All solutions were prepared with filtered (0.2 μm) deionized water having a specific resistance of 10 MΩ-cm or higher.

Apparatus and conditions

The determinations were made on an ion chromatograph equipped with a standard anion guard, separator, suppressor and conductimetric detection system. Two precolumns were used to prevent contamination of the separator column with organic material and transition metals. The eluent was a 0.0028 *M* NaHCO₃–0.0022 *M* Na₂CO₃ solution, and the flow-rate was 2.0 ml/min. The volume of the injection loop was 100 μl, and the sensitivity of the conductivity cell was set at 30 μS. The electrical output was fed to a computing integrator. Additional details on the equipment and instrumental conditions are given in Table II. The test solutions were filtered through 0.2-μm syringe filters as they were injected into the sample loop.

RESULTS AND DISCUSSION

In initial operation of the chromatograph, excellent results for fluoride, phosphate and sulfate were obtained on reagent samples. The fluoride analysis accounted for all of the fluoride, even when it was present as aluminum fluoride or hexafluoro-silicate. However, several problems due to the presence of transition metals and organic material (mainly defoamer) were encountered in the analysis of impure wet-process phosphoric acid. These impurities were absorbed on the columns and affected the retention times and the recovery of phosphate. This may explain in part why IC has not been more widely adopted in the fertilizer industry.

TABLE II
EQUIPMENT AND INSTRUMENTAL CONDITIONS

Reference to specific equipment or manufacturers is made for identification purposes only and does not imply endorsement by the Tennessee Valley Authority.

Instrument	Dionex Model 2120 ion chromatograph
Eluent	0.0028 M $NaHCO_3$ -0.0022 M Na_2CO_3
Flow-rate	2.0 ml/min
Precolumns	Dionex MPIC-NG1 (to remove organics), MFC-1 (to remove transition metals) and HPIC-AG4 (standard)
Separator column	Dionex HPIC-AS4
Suppressor	Dionex AFS-1
Suppressant	0.0125 M H_2SO_4
Injection volume	100 μ l
Detector	Conductivity
Integrator	Spectra-Physics Model 4270
Attenuation (AT)	1024 mV (full scale)
Peak width (PW)	18 s
Peak threshold (PT)	10 000 mV/s
Recorder speed	0.5 cm/min

Two new guards, or precolumns, were then installed in front of the regular columns to remove transition metals and organic material. Also, the peak detector setting on the integrator was optimized to improve the precision of replicate analyses. Very good results then were obtained on the wet-process samples. Twenty-three acid samples were analyzed in duplicate or triplicate, and the IC results were in very good agreement with the values determined by standard methods. The IC results for fluoride corresponded to 72–117% of the analytical laboratory values, with a mean of 99.0%. The absolute difference in the two sets of data did not exceed 0.10 and the precision, or coefficient of variation, of replication was 5.20%.

The phosphate results were within 98.9–100.2% of the analytical laboratory values, with a mean of 99.7%. The precision for phosphate was 0.47%.

The sulfate results ranged from 96–119% of the analytical laboratory values. The mean was 102.4% and the absolute difference did not exceed 0.20. The precision was 2.36%.

Because a single sample is used in the simultaneous determination of the three ions, typical chromatograms contain a large peak for phosphate and two much smaller peaks for fluoride and sulfate. Although the small size of these peaks limits the accuracy and precision of the fluoride and sulfate results to something less than that obtainable with a larger sample or smaller dilution, the limitation is necessary to avoid overloading the column with phosphate. Nevertheless, the results compare well with those obtained by standard methods and are entirely adequate for process control.

The ion chromatograph has been used for control purposes in several continuous acid production tests. Slurry samples were centrifuged or filtered to remove the solids. After weighing and diluting a sample, only about 8 min were required for

an analysis. The accuracy was checked periodically with known samples and new calibrations made as needed.

IC has great potential as a tool for the analysis of phosphoric acid and related fertilizer compounds. It is reliable and rapid; it requires little, if any, sample treatment other than dilution; several ions can be determined at the same time; there is little or no interference from other ions; small samples are used (1 ml of strong acid); and it is a cost-effective technique.

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