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Determination of Total Phosphorus Using Two-Dimensional Ion Chromatography

INTRODUCTION

The determination of phosphorus is prescribed by the U.S. EPA (methods 365.1–365.5). These colorimetric methods use an autoanalyzer or spectrophotometer.

Total phosphorus determination is described as a subset of these methods and includes oxidative decomposition of organic phosphates in the sample by heating with persulfate (methods 365.1–365.3, 365.5) or acidic mercuric sulfate (method 365.4) to transform all the phosphates to orthophosphate. The method depends on a color reaction between orthophosphate, ammonium molybdate, and antimony potassium tartrate to form an antimony-phosphomolybdate complex. This complex is subsequently reduced by ascorbic acid to form a blue-colored complex, whose concentration is determined by visible absorption spectroscopy.

Ion chromatography (IC) with suppressed conductivity detection can be used to determine phosphate in the presence of other ions. IC offers a valuable secondary analysis method for total phosphate and serves as a confirmatory technique. IC is preferable to colorimetry due to the elimination of a very toxic reagent, antimony potassium tartrate. However, the presence of a large amount of sulfate from the persulfate digestion and

the inherent complexity of some samples (for example, soil and wastewater) makes IC difficult to perform at the required detection limit of 10 µg/L with a direct injection of the sample and single-dimensional analysis.

A simple, two-dimensional analytical technique is presented for the analysis of total phosphorus. A sample is injected onto an IonPac® AS11-HC column. The phosphate-containing fraction of the separated sample is then directed to an anion concentrator column where the phosphate and other anions in that fraction are trapped. The majority of the sample goes directly to waste while the phosphate and a smaller amount of interfering anions are collected on the concentrator column. The concentrator column is then placed back in line with the original separator column and the trapped anions it contains are re-separated on the column. This process removes the majority of the matrix ions. The sensitivity and accuracy of the analysis is improved since the phosphate analyte now forms a sharper peak with better signal-to-noise ratio and better separation from matrix interferences.

EXPERIMENTAL

Instrumentation

Dionex ICS-3000 Reagent-Free™ Ion Chromatography system with Eluent Generation (RFIC-EG™ system) consisting of:

- SP Single pump (P/N 079819)
- EG Eluent generator module (P/N 079827)
- DC Detector compartment module with conductivity detector (P/N 063772 and P/N 079829)
- Automation Manager with 10-port valve (P/N 079833 and P/N 061962)
- TAC-ULP1 (5 × 23 mm) concentrator column (P/N 061400)

Conditions

Columns: IonPac AG11-HC, 4 mm (P/N 052962) and IonPac AS11-HC, 4 mm (P/N 052960)

Eluent: Electrolytically generated KOH gradient; EGC (P/N 058900), 1 mL/min; 20 mM (0 to 15 min), 40 mM (20 min), 20 mM (20.1 min)

Inj. Volume: 250 μ L

Temperature: 30 °C (column compartment)
30 °C (detector compartment)
35 °C (conductivity detector)

Detection: Suppressed conductivity, ASRS® 300 suppressor (4 mm) (P/N 064554), 100 mA

This application can also be conveniently performed on an ICS-2100 system (P/N 069576) equipped with an auxiliary 10-port valve (P/N 069473).

RESULTS AND DISCUSSION

Water samples were prepared by heating in a laboratory microwave oven with persulfate. Samples were injected onto an IonPac AS11-HC column, which was selected because it exhibits the high capacity needed for this highly concentrated sample. The initial separation is carried out isocratically with 20 mM potassium hydroxide to retain the phosphate on the column and elute most of the matrix ions away from the phosphate. A full-scale chromatogram (Figure 1) shows that the phosphate peak,

approximately 25 nS tall, is not observable on this scale. The amount of phosphate in the sample is approximately 1 part per million of the total anion content, with the vast majority of the remainder being sulfate. Figure 2 shows the expanded scale chromatogram, where the phosphate peak is now observable and elutes at about 13.4 min on the tail of the huge sulfate peak. The phosphate peak is also broad, with a peak width at half height of 0.4 min. If the analysis were carried out using only this separation, quantitative analysis of the phosphate

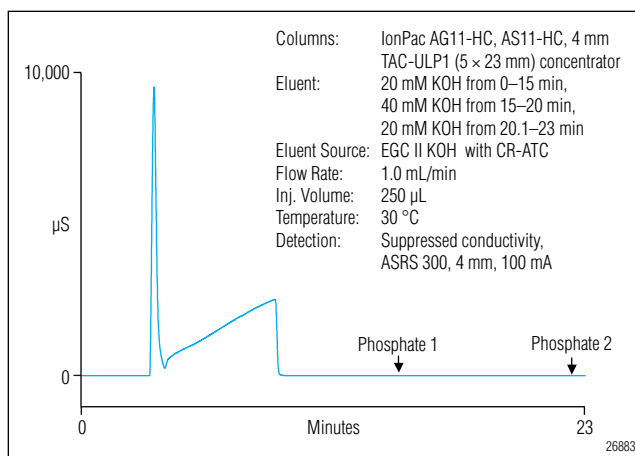


Figure 1. Full-scale chromatogram of digested wastewater showing approximate retention times of the two phosphate peaks.

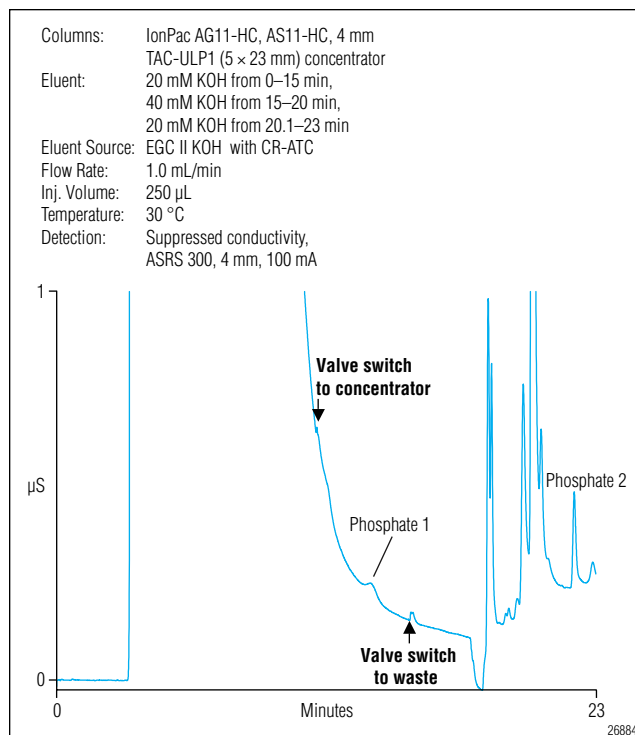


Figure 2. Expanded-scale chromatogram of wastewater digest.

peak on the tail of the sulfate peak would result in lower analytical sensitivity due to the problems of detecting and integrating a small peak on the tail of a very large peak.

The auxiliary valve was switched to collect column effluent onto the concentrator column during the retention time period of 11 to 15 min, as noted in Figures 2 and 3. This traps the phosphate peak and a relatively small amount of other anions, and directs them back to the concentrator column. It is important to note that the sample has passed through the suppressor before being collected on the concentrator. The suppressor converts the hydroxide eluent to water, thus enabling the concentrator

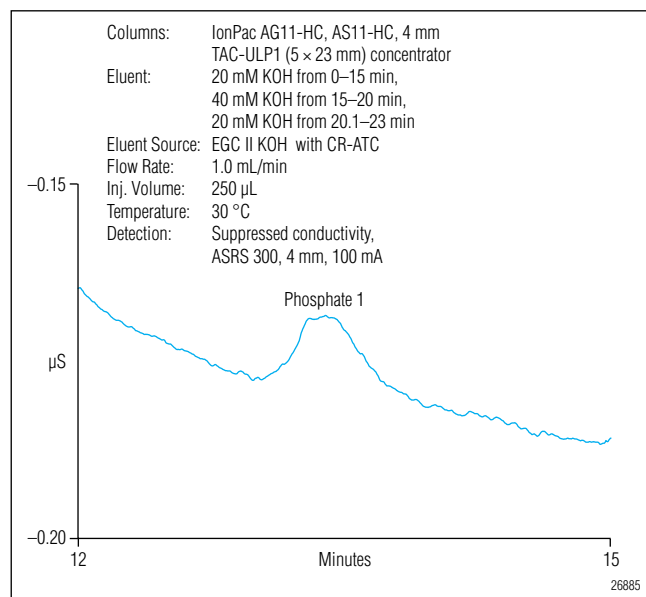


Figure 3. First phosphate peak, 10 µg/L standard.

column to capture the anions in the sample in a narrow band, as there is no eluent to disperse them off the concentrator column.

At 15 min retention time, the auxiliary valve was switched back to its original configuration, which now positions the concentrator column before the analytical column (Figure 4.) At this point, an elution gradient is also started. Gradient elution has the effect of eluting the trapped anions from the concentrator column in a narrow band. The increasing ionic strength also reduces the elution time of the phosphate during this second pass to half of what it was on the first pass through the column.

These effects together produce a second phosphate peak, which is now isolated from contaminants and is

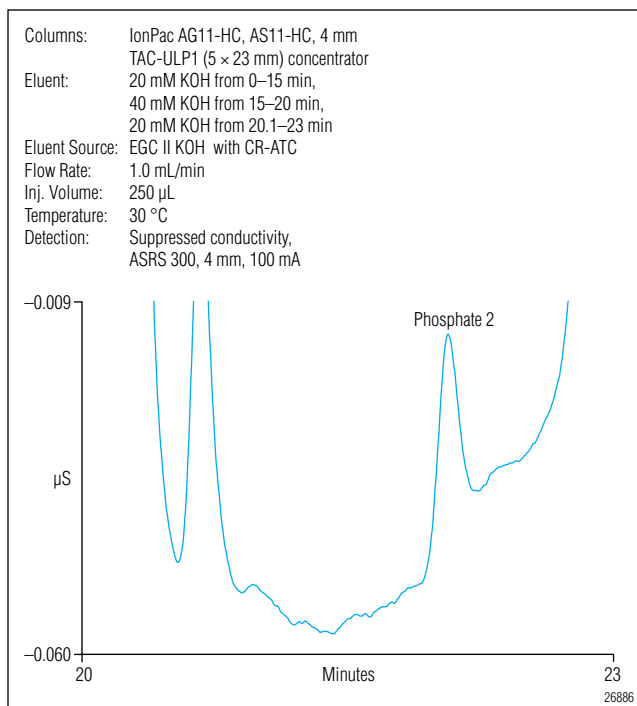


Figure 4. Second phosphate peak, 10 µg/L, same chromatographic run as Figure 3. Note improved peak height and peak shape and resulting improvement in signal-to-noise ratio.

about one-third narrower than the original peak. This sharper peak results in an improvement of signal-to-noise by about three-fold.

A calibration curve from 10 to 30 µg/L is seen in Figure 5. Plumbing diagrams showing the various valve positions and flows at different stages in the analysis are seen in Figures 6–9.

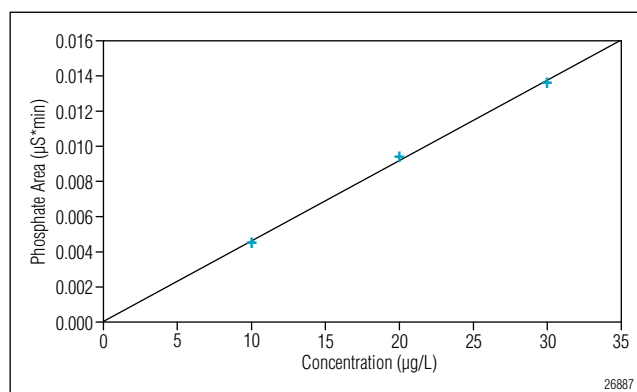


Figure 5. Calibration curve (10 µg/L to 30 µg/L) using second phosphate peak.

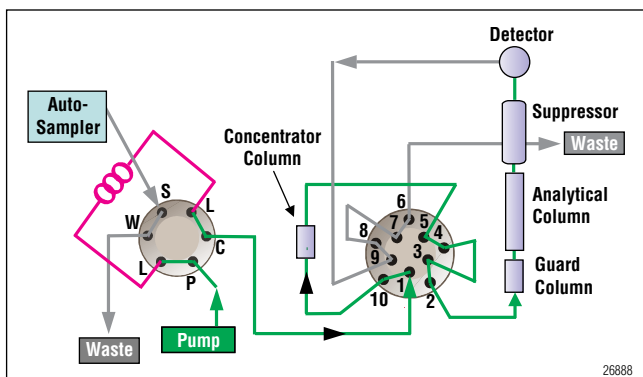


Figure 6. Inject sample.

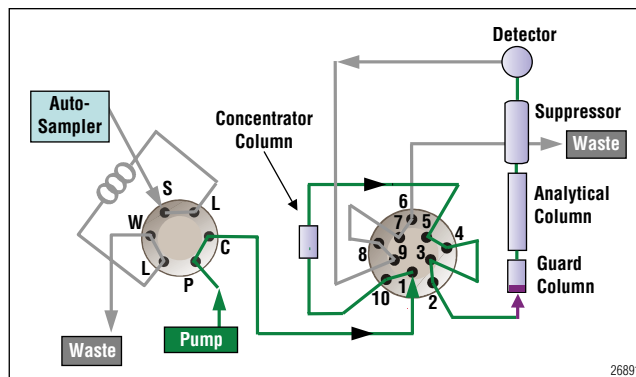


Figure 9. Reanalyze phosphate heart-cut with gradient elution.

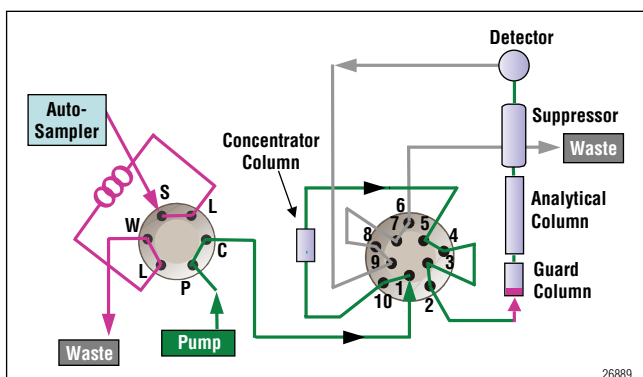


Figure 7. Analyze sample.

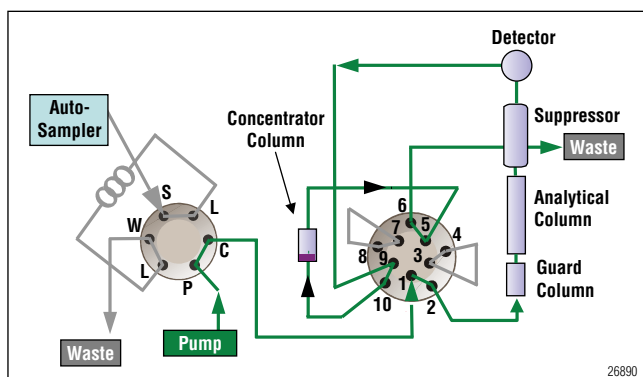


Figure 8. Collect phosphate-containing band on concentrator column.

CONCLUSION

In this application note, a two-dimensional separation technique to isolate phosphate from a huge excess of sulfate is demonstrated. Compared to the first phosphate peak, the second peak is approximately three times taller than the peak resulting from the first pass through the column, thus improving signal-to-noise ratio and detectability by a factor of three (Figures 3 and 4). The technique depends on the flexibility of the application of an auxiliary high-pressure switching valve, along with a concentrator column, to recycle trapped analyte for a second separation run on the analytical column.

This approach provides improved quantitation of the phosphate using only one column. The use of a single column eliminates the need for a second analytical pump and thus, reduces instrument complexity and cost. Integration of the auxiliary sample preparation valve in the ion chromatograph also helps reduce the complexity of software control and hardware management.

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