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Note

Determination of inorganic phosphates in detergents by high-performance liquid chromatography on PRP-1 with phosphorus-selective detection

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The determination of phosphate species is important in the detergent industry, especially because legislation in many areas of the world limits the use of phosphates in detergents. Tripolyphosphate is the desired phosphate because of its superior performance in sequestering water hardness ions. The distribution of ortho-, pyro- and tripolyphosphate must be accurately known, and the undesirable reversion of tripolyphosphate to the smaller forms closely monitored in the raw materials, intermediates, and finished product. This is necessary to maximize product performance while limiting total phosphorus.

Ion-exchange methods are widely used for phosphate species determinations[1,2]. There are two principal problems associated with this approach. First, analyses usually take about 45 min[3]. This limits the total sample throughput of the laboratory (even when automated equipment and overnight runs are used) and is undesirable in a method used for process control. The second problem is detection. It is common to hydrolyze the eluting phosphates to orthophosphate, then determine them photometrically as the molybdenum blue complex. Autoanalyzer technology is well suited for this task[2,3], but adds time and complexity to the otherwise simple separation. Flow-injection analysis has also been used for detection[4]. With it the total analysis time is reduced to less than 15 min from injection using similar ion-exchange conditions. Additional improvements might also be possible, but the ultimate speed of analysis will be limited by the relatively slow kinetics of ion-exchange.

Recently, detergent phosphates have been analyzed in about 12 min by ion-chromatography using post-column reaction with ferric nitrate and UV detection[5]. Unfortunately, orthophosphate cannot be determined with confidence in this time frame since it is not resolved from the void volume peak. Weakening the mobile phase greatly improves the orthophosphate determination but does not allow the elution of tripolyphosphate in a reasonable analysis time. Thus, two analyses may be required for each sample.

Ion-exclusion chromatography has been used successfully for determining condensed phosphates[6]. Unfortunately, it has the same detector problems as the methods already mentioned, and is also inherently slow.

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We have used a faster high-performance liquid chromatographic (HPLC) approach where a hydrophobic counterion is added to a mostly aqueous mobile phase used with a hydrophobic stationary phase. Iskandarani and Pietrzyk[7] showed that the retention of inorganic anions on PRP-1 (a rigid, polystyrene–divinylbenzene packing of 10-μm spheres) with a quaternary ammonium-modified mobile phase follows a dynamic ion exchange process which they called "ion-interaction chromatography".

We have combined this separation approach with an instantaneous detection process, flame-photometry, to produce baseline-resolved peaks for ortho-, pyro-, and tripolyphosphate in about 7 min. In addition, the high selectivity of the detection process allows a very fast sample preparation and reduces the requirements of the separation. Results can be available within 10 min of receiving the sample.

EXPERIMENTAL

Equipment and conditions

A single HPLC pump (M-6000A, Waters Assoc., Marlboro, MA, U.S.A.) and injector (Rheodyne 7125 or Waters WISP) were used. The column was a 150 mm × 4.1 mm I.D. PRP-1 (Hamilton Company, Reno, NV, U.S.A.). The detector was a dual-flame photometric, phosphorus-selective HPLC detector[8]. It uses two flames in series. The first, in an inverted or hydrogen atmosphere configuration, is used to burn and eliminate the organic materials in the solvent, while the second is used for the formation and photometric detection of phosphorus oxyhydride (HPO). Peak areas were measured using one of several electronic integrators (for example, Model 3390A, Hewlett-Packard, Avondale, PA, U.S.A.). The mobile phase was deionized water containing 0.01 *M* tetraethylammonium hydroxide (TEAH, 5.88 g of 25% solution in methanol added per liter) and 0.02 *M* formic acid. The methanol, usually provided by the TEAH solution, strongly affects retention and must be present in the mobile phase. If TEAH was supplied in water, methanol was added to make its content in the mobile phase *ca.* 0.56% by volume (or 0.44% by mass). A flow-rate of 2 ml/min and injection volume of 10 μl were used.

Sample preparation

For detergents, approximately 1 g of base powder or 2 g of finished product (accurately weighed) were dissolved in deionized water to make 100 ml of solution. Then 7 ml of this was injected through a Sep-Pak C_{18} cartridge (Waters Assoc.). A 5-ml aliquot of filtrate was transferred to a 10-ml volumetric flask. A 1-ml volume of buffer (1 *M* TEAH and 2 *M* formic acid, together in deionized water) was added, and the resulting solution diluted, with mixing, to volume.

Sodium tripolyphosphate (STP) raw material was prepared by dissolving 0.4 g of STP in deionized water to make 100 ml of solution. A 1-ml aliquot of TEAH–formic acid buffer was then diluted to 10 ml with the STP solution.

Standards were prepared from reagent grade sodium phosphates by dissolving 0.1 g Na_3PO_4, 0.5 g $Na_4P_2O_7 \cdot 10H_2O$ and 2.0 g $Na_5P_3O_{10} \cdot 6H_2O$ (each weighed to ± 0.005 g) in deionized water to make 1000 l of stock standard. Working standards were prepared for injection by combining one volume of TEAH–formic acid buffer with nine volumes of stock standard. Working standards were made fresh daily. Stock standards were stable for over two weeks.

RESULTS

Typical chromatograms of ortho-, pyro- and tripolyphosphate standard and of STP raw material are shown in Fig. 1. Detergent chromatograms are similar to those of the standard. The peak in the void volume is always present due to (unretained) cations in the sample. (The detector has a slight response to these ions.)

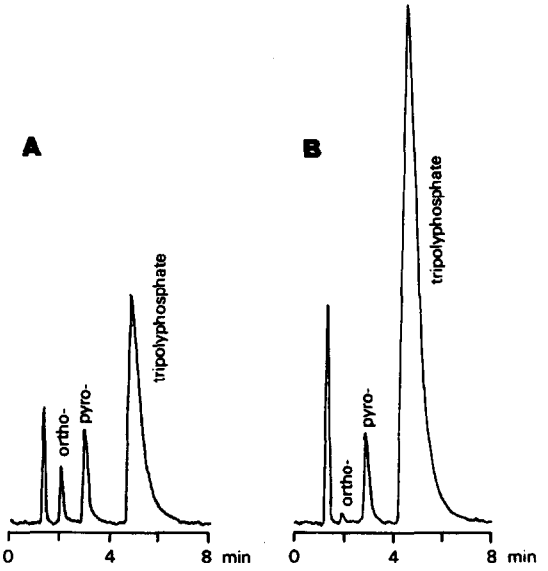

Fig. 1. Chromatograms for phosphate standard (A) and STP raw material (B).

Of the three phosphate species, orthophosphate was found at the lowest concentration in all samples tested. Fortunately, it has the narrowest peak and lowest detection limit: about 0.1 μg injected (as sodium salt). The detection limit for pyro- and tripolyphosphate is slightly higher because of their larger peak widths, but was never a problem because of their higher concentrations in the samples. Peak areas are directly proportional to phosphorus content. No deviation from linearity was observed with STP injections up to 40 μg.

Validation of our HPLC method was done by comparison with an ion-exchange-auto analyzer (IE–AA) method (similar to ref. 3). A cooperative study among eleven laboratories performing the IE–AA method was done on standards, STP raw materials and a detergent base powder. Results are reported as percent of the total phosphorus in each form, and are compared to the values obtained by the present HPLC method in Table I. Results are also shown for a finished product analysis by the HPLC method to illustrate the precision for these samples.

DISCUSSION

Slight, matrix-dependent changes in peak shape made peak height measurements less reliable than peak area. Area measurements were used exclusively in this work.

TABLE I

PERCENT OF TOTAL PHOSPHORUS FOUND IN EACH PHOSPHATE FORM

Sample		*HPLC results (% ± S.D.)*	*Number of determinations*	*IE–AA values (%)*
Standards	Ortho	4.63 ± 0.29	8	4.74
	Pyro	14.49 ± 0.22		14.42
	STP	80.87 ± 0.40		80.83
STP raw material	Ortho	0.46 ± 0.21	9	0.48
	Pyro	5.70 ± 0.26		6.52
	STP	93.73 ± 0.52		92.97
Base powder	Ortho	3.72 ± 0.32	8	3.70
	Pyro	18.13 ± 0.52		18.39
	STP	78.13 ± 0.54		77.81
Finished product	Ortho	2.45 ± 0.11	16	
	Pyro	8.69 ± 0.17		
	STP	88.84 ± 0.20		

It is possible to use conventional, silica-based octadecylsilane columns for this method, but peak shapes are worsened. Presumably, this is because of silanophilic interaction with the phosphates. Even highly deactivated columns of longer length and smaller particle size, such as the Whatman PXS-125 ODS or the Altex Ultrasphere IP, gave poorer resolution than the polymer-based PRP-1 column.

The pH and type of counterion additive strongly influence the separation process. At pH 3.7 each phosphate exists predominantly in one ionic form, but each with a different charge: $H_2PO_4^-$, $H_2P_2O_7^{2-}$ and $H_2P_3O_{10}^{3-}$.

Retention is easily adjusted by changing the methanol concentration. In general, phosphates are not soluble in alcohols. But, with the counterion present, the usual reversed-phase behavior of retention *vs.* methanol content is observed, at least for low methanol concentrations.

Tetraethylammonium was chosen as counterion because it allows minimization of the methanol content in the mobile phase, but still provides control of retention by methanol concentration adjustment. Larger quaternary ammonium ions, such as tetrabutylammonium, work well for ortho- and pyrophosphate, but require as much as 50% methanol in the mobile phase. Tripolyphosphate exhibits concentration-dependent peak distortion under these conditions. Conversely, tetramethylammonium ion does not provide enough retention, even when the methanol is absent.

Our HPLC results agree closely with the ion-exchange referee values for all determinations except pyrophosphate in STP raw material. The reason for this difference is unclear, but is probably due to slight STP hydrolysis somewhere in the IE–AA method. Naturally, this would affect the STP raw material sample most, resulting in an apparent loss of STP and increase in ortho- and pyrophosphate.

In the IE–AA method, the ion-exchange column is regenerated between samples with 1.0 *M* hydrochloric acid. One possible cause of STP hydrolysis could be the systematic, incomplete removal of hydrochloric acid before sample injection. Since the present HPLC method is both isocratic (at pH 3.7) and does not require

column regeneration, there is no opportunity for this kind of systematic error to occur.

In practice, a single column was used continuously over a three-month period to analyze more than 500 samples with no noticeable degradation in performance. With extended use, column backpressure increases somewhat, but can be reduced with an occasional backflush.

In a limited number of cases, when the sample matrix is relatively simple and the phosphate concentrations are high, it might be possible to use a refractive index or conductivity detector. However, the high selectivity provided by the flame photometric detector minimizes sample preparation and separation requirements. With suitable modification of the sample preparation, this method could easily be used in numerous other applications.

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