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# Determination of total phosphorus in soaps/detergents by ion chromatography<sup>☆</sup>

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## ABSTRACT

The quantitative determination of phosphorus in soaps and detergents is a classical analytical problem owing to the complexity of the matrix containing a variety of chemical species (*i.e.*, surfactants, complexones and/or zeolites, optical whiteners, perfumes, etc.). A new method has been developed for the analysis of total phosphorus in soaps and detergents which employs UV photolysis of the analyte. It has the advantages that it is a simple procedure and has very low blank values because of the small amount of reagent required for the sample pretreatment. Different types of soaps and detergents were subjected to oxidative UV photolysis. It was found that the organic matrix was degraded in about 60 min, thereby permitting the quantitative analysis of various inorganic species, especially the phosphate ion. Soaps and detergents of different “types and brands” were found to contain phosphate from a few mg/l or mg/kg to the 1% level. The results were compared with those obtained by conventional alkaline fusion followed by reduction to molybdenum blue, and were found to be in good agreement.

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## INTRODUCTION

The determination of total phosphorus in soaps, detergents and other cleaning agents has gained much importance because of legislation in many parts of the world that limits their use as they are one of the causes of eutrophication. This, in turn, has resulted in demand for sensitive and rapid instrumental analytical techniques for a precise control of the phosphorus content,

not only in the inorganic form, but also present as combined organic derivatives in various forms.

Different techniques are routinely used for the determination of phosphate in detergents. These include gravimetry [1], spectrophotometry [2,3], voltammetry [4] and flow injection analysis [5], but these methods suffer from various drawbacks, such as cumbersome sample preparation and long analysis time.

The remarkable developments in high-efficiency liquid chromatography, in particular ion chromatography, have provided the opportunity to explore a new approach to analyse the total phosphorus content in detergent products. High-performance liquid chromatography with flame photometric detection has been used [6] for the determination of inorganic phosphate in de-

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tergents, but the method is not recommended for the determination of the phosphorus present as organic derivatives.

The present work deals with the development of a new sample treatment method for the analysis of total phosphorus in soaps and detergents which employs oxidative UV photolysis of the analyte to destroy organic matter prior to the ion chromatographic analysis. It has the advantages that it is a simple procedure and has very low blank values because of the small amount of reagent required for sample pretreatment.

When the proposed method was compared with the conventional alkaline fusion method followed by spectrophotometric molybdenum blue detection the results were found to be in good agreement.

#### PRELIMINARY STUDIES

Investigations were performed on a large number of commercially available soaps, detergents and cleaning agents and revealed that the composition of these products varies not only in terms of the total phosphorus content, but also in terms of total chlorine, nitrogen and sulphur content. After UV photolysis, some of the products show a very large peak for chloride, nitrite, nitrate and/or sulphate ions. In some cases the partially photolysed samples were also found to contain one or more carboxylate ions as photolysis products. Some of these ions have retention times very close to that of orthophosphate, and can be confused with the presence of phosphate, even if it is not present in the product. It therefore becomes necessary to study the effect of various ions on the retention behaviour and quantitation of phosphate. Chloride, nitrite, nitrate, sulphate and a number of carboxylate ions were chosen to study the interferences because one or more of these ions are formed after UV photolysis of the commercially available products. Borate and silicate were also included in the list of possible interferents in the determination of phosphate as these are, or might be, present as one of the constituents of soaps and detergents. For this study, a series of solutions containing 1 mg/l phosphate and vary-

ing amounts of possible interferents were prepared. The pH of all the solutions was adjusted to 7.5 by adding dilute ammonia solution and the solutions were then analysed by ion chromatography following the procedure described in the Experimental section. In most cases, a sufficiently high concentration of the added anion did not interfere with the quantitation of phosphate. These findings are summarized in Table I.

#### Effect of pH

The retention time and the peak area of phosphate are very much influenced by the change in pH of the eluent as well as the analyte. This is largely because phosphate undergoes protonation/deprotonation and is present in different forms. The free orthophosphate form is predominant in alkaline conditions, while at acidic pH the protonated form dominates. The carbonate–hydrogencarbonate eluent used for the present chromatographic analysis has a pH of 9.7, at which the divalent form ( $\text{HPO}_4^{2-}$ ) predominates. However, if the sample is too acidic to be neutralized by the eluent, the initial retention of the analyte is disturbed, probably because its valence is continuously changing as the buffer takes effect, and thus its retention time as well as the peak area changes. Experiments revealed that for a sample injection volume of 25  $\mu\text{l}$  the area of the phosphate peak is not affected if the pH of the analyte is in the range 4.5–10.

TABLE I

TOLERANCE LIMITS FOR VARIOUS ANIONS FOR THE DETERMINATION OF 1 mg/l PHOSPHATE (AT pH 7.5)

Ion	Tolerance limit (mg/l)	Ion	Tolerance limit (mg/l)
Oxalate	1000	Palmitate	500
Formate	1000	Oleate	500
Acetate	1000	Laurate	1000
Benzoate	1000	Chloride	1000
Succinate	1000	Nitrite	1000
Salicylate	400	Nitrate	100
Phthalate	250	Sulphate	1000
Malonate	200	Silicate	5000
Stearate	500	Borate	5000

## EXPERIMENTAL

### Reagents and standards

Sodium carbonate and sodium hydrogencarbonate were chromatographic grade (Novachimica, Milan, Italy), hydrogen peroxide (30% m/m, without stabilizer), hydrochloric acid (37%), ammonia solution (30%) and sodium hydroxide were Erbatron electronic grade (Carlo Erba, Milan, Italy), sulphuric acid, ammonium molybdate, sodium nitrate, sodium sulphite and *N-p*-methylaminophenol sulphate were analytical grade (Carlo Erba), and sodium hydrogensulphite was analytical grade (Janssen Pharmaceutica, Geel, Belgium). Ultrapure water with conductivity  $<0.1 \mu\text{S}$  (DI water) was obtained from a Milli-Q (Millipore, Bedford, MA, USA) four-bowl deionization system.

Working standards were prepared daily by dissolving pH standard-grade potassium dihydrogenphosphate and reagent-grade potassium pyrophosphate (Carlo Erba).

Quartz test tubes and all glassware were cleaned in concentrated nitric acid and carefully washed with DI water. Normal precautions for trace analysis were observed throughout.

### Eluent and regenerant solutions

A solution of 2.0 mM sodium carbonate and 0.90 mM sodium hydrogencarbonate (pH 9.7) was prepared by dissolving the requisite amounts in DI water and used as chromatographic eluent at a flow-rate of 1.5 ml/min. The regenerant solution for the anion micromembrane suppressor was 125 mM sulphuric acid at a flow-rate of 8 ml/min.

### Spectrophotometric solutions

**Reducing solution.** A 250-g amount of *N-p*-methylaminophenol sulphate, 1.25 g of sodium sulphite and 37.5 sodium hydrogen sulphite were dissolved in DI water and make up to 500 ml. Since this solution deteriorates in contact with air, it was prepared freshly when needed.

**Ammonium molybdate solution.** A 12.5-g amount of ammonium molybdate was dissolved in 125 ml of 10 M sulphuric acid and diluted to 500 ml.

### Instrumentation

Samples were subjected to UV photolysis in a Metrohm (Herisau, Switzerland) 705 UV digester equipped with a 500-W high-pressure mercury lamp. The temperature of the sample was maintained at  $85 \pm 5^\circ\text{C}$  with the aid of a combined air–water cooling system.

Chromatographic analyses were performed on a Dionex (Sunnyvale, CA, USA) 2000i ion chromatograph equipped with an EDM eluent degassing module, a GPM gradient pump, a 25- $\mu\text{l}$  injection loop, an IonPac AG9 guard column and an IonPac AS9 separator column, an AMMS anion micro-membrane suppressor and a CDM conductivity detector.

All measurements were made at  $25 \pm 1^\circ\text{C}$  and, in all cases, injection of the sample was done at least in triplicate.

Precautions were taken to ensure that the analyte did not remain either on the column or on the injection loop overnight. The injection loop was washed with DI water prior to every analysis.

Peak areas were obtained using AI-450 Dionex software and background correction was applied wherever necessary.

Spectrophotometric analyses were performed on a Baush & Lomb (Rochester, NY, USA) Spectronic 21 UV-D spectrophotometer.

### Sampling

An appropriate sampling procedure is essential to ensure that the sample taken represents all the characteristics/properties of the bulk material, because only a small amount is required for the analysis.

The sampling of commercially available soaps, detergents and cleaning agents was done on the basis of their physical form. Transparent liquid detergents free from deposit and suspensions were used directly without any sampling treatment. But the liquid products containing insoluble deposit or suspended matter were heated to  $40^\circ\text{C}$  with constant stirring to homogenize all the components present in the product. Powdered products were sampled using a conical divider such as the Pascall Rotary Cascade Sample Divider. Products in the form of cakes were homogenized by warming with water at  $40^\circ\text{C}$ .

### *Ion chromatographic procedure*

A 0.05-g amount of sample was mixed with 0.5 ml of hydrogen peroxide in a quartz tube, which was closed with conical PTFE stoppers that tapered to a point. The stoppers acted as cooling fingers, and thus prevented solution losses and also protected the sample from contamination. The sample was subjected to UV photolysis at  $85 \pm 5^\circ\text{C}$  for 60 min, then it was diluted to 25 ml (100 ml in case of samples containing a relatively large amount of phosphate) and analysed by ion chromatography. Under the present chromatographic conditions, the retention time for phosphate was found to be 7.7 min.

### *Spectrophotometric procedure*

For comparison purposes, the spectrophotometric method for the determination of phosphate, as proposed by Longman [7], was used: 0.5 g of the detergent/soap sample were

mixed with an equal amount of sodium nitrate, and heated gently in a platinum cap to oxidize the organic matter. When cold, the fuse was treated with 10 ml of hydrochloric acid (25%) and evaporated to dryness. The addition of hydrochloric acid was repeated and the mixture again evaporated to dryness. The residue was dissolved in 5 ml of hydrochloric acid (25%) and filtered into a 500-ml flask. The cap and filter were washed with hydrochloric acid, and the washings were added to the flask. The solution was neutralized with 10% sodium hydroxide solution (using phenolphthalein as indicator) and diluted to 500 ml. A 45-ml aliquot of this solution was transferred to a 100-ml flask and mixed with 10 ml of ammonium molybdate solution and 20 ml of the reducing solution. This mixture was diluted to 100 ml with DI water and its optical density was measured at 720 nm, employing DI water as the blank.

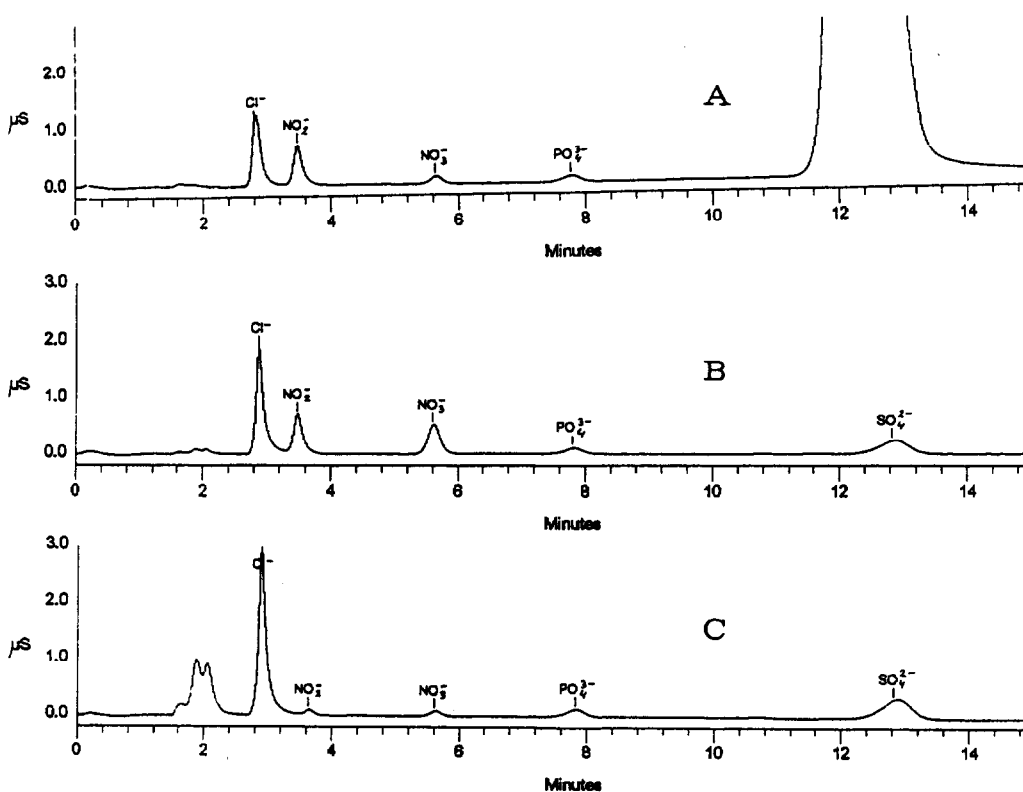


Fig. 1. Determination of phosphorus (as  $\text{PO}_4^{3-}$ ) in detergent (A), soap (B) and shampoo (C). Eluent: 2.0 mM  $\text{Na}_2\text{CO}_3$  + 0.9 mM  $\text{NaHCO}_3$ .

## RESULTS AND DISCUSSION

Fig. 1 shows typical chromatograms obtained for three different detergent samples, which had been subjected to UV photolysis prior to chromatographic analysis.

The commercially available soaps, detergents and other cleaning agents contain phosphorus in a variety of chemical forms, including simple phosphates, pyro- and polyphosphates, alkyl or phenyl phosphates and their derivatives, imidophosphates, alkylphosphonates, etc. These chemicals are hydrolysed during the course of UV photolysis in the presence of hydrogen

peroxide. Experiments were performed by analysing a mixture of potassium dihydrogenphosphate and potassium pyrophosphate, after it had been subjected to UV photolysis. The chromatogram of this solution gave only one peak at 7.7 min and the peak area was in agreement with the area that would be obtained with the equivalent amount of orthophosphate. Similar studies could not be made on organic derivatives of phosphorus, since the compounds were not available in pure form.

At the same time, it is interesting to note that for different soaps, detergents and cleaning agents analysed after 1 h of UV photolysis, at pH

TABLE II

THE PHOSPHORUS CONTENT OF VARIOUS COMMERCIALY AVAILABLE SOAPS, DETERGENTS AND CLEANING AGENTS

Category	Determined by	
	Ion chromatography (ppm) <sup>a</sup>	Spectrophotometry (ppm) <sup>a</sup>
Toilet		
(A) Cake	260	257
(B) Liquid emulsion	275	277
Shampoo		
(A) Liquid clear	174	180
(B) Liquid emulsion	202	207
Laundry soap		
(A) Cake, white	0	0
(B) Cake, yellow	9	9
(C) Flakes	44	45
Detergent		
(A1) Liquid, wool	0	0
(A2) Liquid, wool	0	0
(B1) Liquid, hand washing	72	71
(B2) Liquid, hand washing	259	257
(B3) Liquid, hand washing	631	628
(C1) Powder, machine washing	181	175
(C2) Powder, machine washing	197	191
(C3) Powder, machine washing	919	920
Fabric softener		
(A) Liquid emulsion	0	0
Fabric whitener		
(A) Powder	7495	7500
Dishwasher detergent		
(A) Liquid, hand washing	74	70
(B) Powder, machine washing	2813	2850

<sup>a</sup> Liquid detergents, ppm = mg/l; solid detergents, ppm = mg/kg.

greater than 7, the retention time for phosphate changed by only 5%, thus suggesting that phosphorus present in different forms (inorganic as well as organic) is converted to orthophosphate after UV photolysis.

Apart from the determination of phosphate, the present method can be successfully used to determine the total chlorine and sulphur content of detergents in the form of chloride and sulphate ions, as good separation of their peaks is achieved. The method is not recommended for the determination of the nitrogen content of soaps and detergents, as nitrogen is oxidized to nitrite and nitrate, which are broken down during UV photolysis.

The reproducibility, working range and sensitivity of the present method were evaluated by spiking one phosphate-free detergent sample with different amounts of standard phosphate and pyrophosphate solutions, and subjecting it to UV photolysis prior to analysis. The reproducibility of the successive injections of the same sample solution was better than 2% R.S.D. In the concentration range 0.2–100 mg/l phosphate. Peak area was found to be linearly related to phosphate concentration for the spiked solutions covering the entire working range of 0.2–100 mg/l.

The total phosphorus content as determined for different "types and brands" of soaps and detergents varies from product to product. Most of the toilet soaps and a few shampoos were

found to contain phosphate in low amounts (<1000 mg/l or mg/kg). Interestingly, dishwasher detergents were found to contain very large amounts of phosphate compared with other types of detergents, while the detergents for cleaning woollen clothes were free from phosphate. The comparison of the proposed ion chromatographic method with the conventional spectrophotometric procedure has shown good results. These results are reported in Table II.

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