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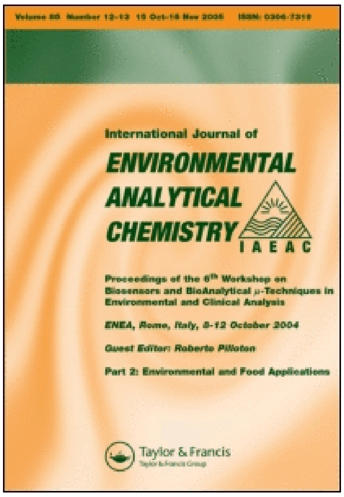

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The Determination of Phosphates using Ion Chromatography: An Evaluation of Influential Factors

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The factors that influence ion chromatographic measurements of phosphates have been evaluated using a system equipped with anion suppressor. If an equilibrium condition prevails in the suppressor column, only one form of phosphate will be detected regardless of the eluent pH. The solution pH controls the interactions of phosphates with other chemical species, such as cations, that might be present. These interactions render the phosphates undetectable. Under optimum conditions with a 50-μL sample loop, a detection limit of 0.02 μg/mL phosphorus can be achieved.

Upon comparing ion chromatography (IC) with direct current plasma spectrometry (DCP), IC can only provide information on ionic phosphates while DCP can allow the determination of all forms of phosphorus. However, a combination of the two techniques can provide a powerful tool for separating, identifying, and measuring all forms of phosphorus.

KEY WORDS: Ion chromatography, phosphate determination, DC plasma, speciation, analysis of natural waters.

INTRODUCTION

The development of ion chromatography (IC) has proved to be an important addition to the techniques available for measuring ions in

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solution. In many cases, this approach appears to be superior to conventional wet chemical methods especially with respect to measurement sensitivity, speed, sample requirements, and the inherent capability for speciation measurements.

Several articles have appeared in the literature describing the hardware and the principles of operation of IC[1–9]; some of the areas in which the technique has been applied[10–20]; and its potential for speciation measurements.[20] In general, however, ion chromatography is, in many respects, a very new technique and thus its capabilities are yet to be exploited fully.

One area in which IC has received a very wide application is the determination of the five common anions, namely Cl^-, F^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}. In general, the analytical measurement of these and other ions determinable by IC must be evaluated on the basis of four distinct processes that occur inside and outside the chromatographic column. The first of these processes is the dissociation and the lability of the analyte in the sample. If the species of interest is labile, it will equilibrate with the eluent rapidly upon injection. Thus, the magnitude of the analytical signal obtained will not depend upon whether or not the sample is injected directly or after equilibration with the eluent.

The second process to be considered is the ion exchange process occurring in the separator column. For those procedures utilizing bicarbonate/carbonate eluent, the exchange process is influenced by the HCO_3^-/CO_3^{2-} ratio, among other things. This ratio not only controls the eluent pH but also influences the competition between the analyte and the eluent anions for the exchange sites on the resin. The retention time as well as measurement sensitivity, if peak heights are measured, are affected the most by changes in the HCO_3^-/CO_3^{2-} ratio.

The third process involves the exchange occurring in the suppressor column, if anion suppression is employed. Here, the analyte anions are converted into their acid forms and the eluent anions are converted into nonconducting species as shown in Table I. For weak acid anions, such as PO_4^{3-}, the suppressor action may result in the formation of several species, e.g., HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4 depending on the concentration of the suppressor and whether or not an equilibrium is reached in the suppression system. If an equilibrium exists, then only one species will be formed and detected regardless of the suppressor concentration.

TABLE I

Processes occurring in ion chromatographic suppressor column[a]

A. Eluent anion suppression	
$R\text{-}H + NaOH \rightarrow R\text{-}Na + H_2O$	(1)
$R\text{-}H + NaHCO_3 \rightarrow R\text{-}Na + H_2CO_3$	(2)
$2(R\text{-}H) + Na_2CO_3 \rightarrow 2(R\text{-}Na) + H_2CO_3$	(3)
B. Analyte anion conversion	
$R\text{-}H + NaX \rightarrow R\text{-}Na + HX$	

[a] Processes applying to anion separation IC employing $NaHCO_3/Na_2CO_3$ mixture as eluent. HX can be a weak acid or a strong acid.
R = Exchange resin.

The fourth process that may influence ion chromatographic measurements of anions is the interaction of the analyte with other chemical species such as cations. Such interactions can occur in the sample solution, the separator column, and also in the suppressor column rendering the analyte undetectable by conducivity measurement. The solution pH will determine the type of material formed during these interactions.

Even though the chemical literature shows some reported articles on the ion chromatography of phosphates,[9,10] none of these articles has evaluated the extent to which the weak acid/base characteristics of phosphates influence the ion chromatographic measurements of these species. Further, no data have appeared in the literature showing the influence of other chemical species, especially metal ions, on ion chromatographic measurements. Therefore, the purpose of this work was twofold: (1) to investigate the factors that influence the IC determination of phosphates; and (2) to compare IC with direct current plasma spectrometry (DCP) relative to their application in the determination of phosphates in solution.

EXPERIMENTAL SECTION

Instrumentation

All measurements were done with a Dionex Model 2010i Ion

Chromatograph, Dionex Corporation, Sunnyvale, California. In all cases, chromatograms were recorded on a stripchart recorder, Linear Instruments Corporation, Model 215. The analytical signal measured was obtained with a conductivity detector, Model CDM-1, Dionex Corporation.

The chromatography module of the system consisted of a guard column (3 × 50 mm), Model HPIC-AG4; a separator column (3 × 150 mm), Model HPIC-AS4; and a suppressor column, Anion Fiber Suppressor, all supplied by Dionex Corporation. The eluent used consisted of mixtures of varying concentrations of $NaHCO_3$, and Na_2CO_3. The fiber suppressor column, which provided a continuous suppressor regeneration, was used with varying concentrations of dilute H_2SO_4 as the regenerant. A $50\,\mu L$ sample loop was used throughout this study.

The operational features of the direct current plasma used in this work have been described elsewhere.[21]

Reagents and chemicals

Hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid and sodium phosphate tribasic (all Baker analyzed) were obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Sodium bicarbonate, sodium carbonate, potassium chloride, boric acid, aluminum nitrate, ferric nitrate, calcium nitrate, and magnesium nitrate (all analytical Reagents) were obtained from Mallinckrodt, Inc., Paris, Kentucky. Deionized water was obtained by passing distilled water through a series of ion exchange cartridges obtained from Barnstead Company, Boston, Massachusetts.

Procedure

This study employed phosphate solutions of known concentrations as well as natural water and wastewater samples obtained from various sources. Solutions of known concentration were prepared by using both distilled-deionized water, and the HCO_3^-/CO_3^{2-} eluent as solvents. In each case, dilutions were made from 1,000 ppm P stock solutions. Two sources of phosphate were used, H_3PO_4 providing solutions with pH around 2.6 and Na_3PO_4 which provided solutions of pH around 9.3.

The effects of sample pH were evaluated by preparing two sets of analytical curves; one using the H_3PO_4 solution and the other using the Na_3PO_4 solution. The influence of eluent pH was investigated by monitoring the signal of 10 ppm P at varying ratios of $NaHCO_3/Na_2CO_3$.

In order to evaluate the influence of the suppressor on the analytical signal obtained, the concentration of the reagenerant was varied, providing 1,000-fold concentration differential, while monitoring the peak heights obtained with 10 ppm P samples.

The effects of cations such as Al, Ca, Fe, and Mg, which are common in natural waters, were studied by spiking a constant concentration of phosphorus (10 ppm) with incremental amounts of each of these cations. In each case, the phosphate peak height was measured. Spikes were made in low pH samples, using H_3PO_4 as the sample, and in high pH samples using Na_3PO_4 as the sample.

The data obtained with IC were compared to those obtained with DCP for orthophosphate and total phosphorus measurement in water samples.

RESULTS AND DISCUSSION

Sample pH effects

The effects of sample pH were investigated by preparing two analytical curves, one with sample solution maintained at pH 2–4 using H_3PO_4 as the sample; and the other with samples maintained at pH 8–9.5 using Na_3PO_4 as the sample. In each case, two modes of sample preparation were used. In the first mode, the sample solution was made with distilled-deionized water as the solvent and in the second mode the eluent was used as the solvent. In all cases, peak heights and retention times were measured. As shown in Table II, the analytical curves and the retention time measured at the two pH regions were practically identical. Thus, it appears that relative to sample pH, it is inconsequential whether the sample is injected directly or after mixing with the eluent. Normally, direct sample injections should be preferred as this minimizes the probability of sample loss and contamination.

TABLE II

Analytical curve data for phosphate solution at pH range 2.0–4.0 and pH range 8.0–9.5.[a]

	Peak height (μS-Cm)	
Phosphorus concentration (ppm)	pH range 2.0–4.0 (analyte = H_3PO_4)	pH range 8.0–9.5 (analyte = Na_3PO_4)
(a) Analyte solution injected directly using distilled-deionized water as solvent.		
0.10	0.25 ± 0	0.28 ± 0.1
1.00	2.10 ± 0	1.90 ± 0.1
10.00	22.40 ± 0.4	21.40 ± 0.1
50.00	137.00 ± 0.2	138.60 ± 0.5
100.00	261.50 ± 0.1	267.30 ± 0.4
(b) Analyte dissolved in eluent before injection.		
0.1	1.0 ± 0.1	0.53 ± 0.1
1.0	2.4 ± 0.0	2.57 ± 0.1
10.0	24.2 ± 0.6	23.5 ± 0.0
50.0	132.9 ± 0.4	134.5 ± 0.2
100.0	278.9 ± 0.2	256.6 ± 0.1

[a] Eluent composition: 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3; eluent pH = 8.9.

Measured retention time at solution pH range 2.0–4.0 = retention time at solution pH range 8.0–9.5 = 3.4 min.

± values are standard deviations of the mean.

Measured detection limits (based on twice the standard deviation of the background signal) = 0.02 μg/mL P.

Eluent pH effects

Eluent pH was varied by changing the molar ratios of $NaHCO_3$ and Na_2CO_3 providing a working pH range from about 8.3–9.3. With each eluent composition, an analytical curve similar to the ones discussed above was prepared. The data obtained for pH 8.3 and 9.3, indicating the peak heights measured, are shown in Table III; and Table IV shows the corresponding retention times. Two things are evident from these data: (1) as the eluent becomes more basic due to an increase in CO_3^{2-} concentration, the analyte retention time decreases; and (2) a corresponding increase in the analytical signal (peak height) measured occurs. The increase in pH as CO_3^{2-} concentration increases should favor an increase in the concentration of the divalent HPO_4^{2-} species. This should be retained longer than the monovalent $H_2PO_4^-$. The observed decrease in retention as

TABLE III

Effect of eluent pH on phosphate peak height[a]

Phosphorus concentration (ppm)	Peak height at eluent pH[b]	
	8.3	9.3
0.1	0.2 ± 0.0	0.5 ± 0.06
1.0	1.1 ± 0.0	2.3 ± 0.06
10.0	11.4 ± 0.4	26.2 ± 0.06
50.0	54.0 ± 0.4	114.0 ± 0.03
100.0	87.5 ± 0.1	194.7 ± 0.00

[a] In each case, the eluent was used as the solvent.

[b] ± values are standard deviations of the mean.

shown in Table IV suggests therefore, that the CO_3^{2-} is significantly more effective as a competitor for the exchange sites than both HCO_3^- and HPO_4^{2-} even when the concentrations of the latter two species are more than ten times as high.

Effects of suppressor concentration

The use of a suppressor column is a common practice in ion chromatography even though some articles have appeared in the literature reporting on the feasibility of nonsuppressed ion chromatography.[2,3,6,7,12] For suppressed IC, two processes occur in the suppressor column: (1) the conversion of the highly conductive eluent anions (HCO_3^-, CO_3^{2-}, and OH^-); and (2) the conversion of the sample anion to its corresponding acid. For anions of weak acids, the species formed are likely to be less conductive as they will possess more of a molecular character than their corresponding anion. In the case of orthophosphate, if we assume that the species eluting from the separator column is predominantly in the HPO_4^{2-} form, then the interaction of this species with the suppressor solution would result in the formation of $H_2PO_4^-$ which would be less conductive than HPO_4^{-2}. Clearly then, the process of using a suppressor column is, at least in theory, unfavorable in the ion chromatographic separation of anions of weak acids.

TABLE IV

Effect of eluent composition on pH and retention time

$NaHCO_3$ concentration (added) M	Na_2CO_3[a] concentration (added) M	Measured[b] pH	Retention time (min.)	$HPO_4^{2-}/H_2PO_4^-$[c] (calculated)
3.0×10^{-3}	0.0	8.3	8.6	13:1
3.0×10^{-3}	2.4×10^{-3}	8.9	3.4	50:1
0.0	2.4×10^{-3}	9.3	4.2	125:1

[a] Solution may contain HCO_3^- from the hydrolysis of CO_3^{2-}.

[b] The measured pH values are lower than would be expected from calculations due to high acidity of the water used.

[c] Ratio calculated on the basis of the measured solution pH.

A recent innovation that appears to circumvent this drawback is the development and employment of anion fiber suppressor.[22] This type of suppressor is not only continuously regenerated but also its configuration avoids direct contact between the regenerant and the eluent. This, apparently, should minimize the protonation of the anions of weak acids therein. In the present study, a fiber suppressor column was used. The concentration of the regenerant (dilute H_2SO_4), was varied over three orders of magnitude while monitoring its effect on the peak height of a 10 ppm orthophosphate solution. As shown in Table V, the peak heights measured did not vary significantly over the wide regenerant concentration range used. This suggests the existence of an equilibrium in the suppression system.

TABLE V
Peak heights of 10 ppm P at different regenerant concentrations

Regenerant concentration ($M\ H_2SO_4$)	Average peak height: (μS-Cm)
2.5×10^{-4}	—
2.5×10^{-3}	11.0 ± 0.1
2.5×10^{-2}	21.5 ± 0.2
5.0×10^{-2}	16.3 ± 0.1
2.5×10^{-1}	—

Eluent: 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$.

The effects of cations in solution

The underlying factor to analytical measurements in conventional IC is the conductivity of the ionic species in solution. Therefore, any substance or process that acts to deplete the population of the conducting species in the sample solution, the analytical column, or the suppressor column will ultimately give rise to poor analytical data. As was discussed above, pH changes can bring about a reduced population of the conducting species by hindering the dissociation process. Another factor that can deplete the population of these species is the formation of insoluble material between the analyte anions and other chemical substances in solution, such as cations. Shown in Table VI is a listing of the various phosphorus compounds that can be formed with Al, Ca, Fe, and Mg, and their solubility characteristics. It is apparent from this table that for elements such as Ca and Mg, the solubility of the phosphate formed depends on the type of compound which, in turn, depends on the phosphate species present. Thus for example, in the presence of HPO_4^{-2}, Ca will form an insoluble $CaHPO_4$ compound. On the other hand, moderately soluble species will be formed in the presence of $H_2PO_4^-$, while PO_4^{-3} will form an insoluble substance with Ca. Since solution pH influences the formation and persistence of these phosphate species, it will influence the type of compound formed with Ca as well.

The degree to which the solution pH and cation concentration interact to influence the concentration of phosphate species was investigated for each of the four cations by spiking constant concentrations of PO_4^{-3} (from H_3PO_4 and Na_3PO_4) with incremental

TABLE VI

Phosphorus compounds and hydroxides of Al, Ca, Fe, and Mg (Ref. 23, 24)

Cation	Phosphorus compound	Properties	Hydroxides
Al	$AlPO_4$	Insoluble in water ($K_{sp} = 10^{-18.2}$ var.)	$Al(OH)_3$; $K_{sp} = 10^{-31.2}$
Ca	$CaHPO_4$	Insoluble in water ($K_{sp} = 10^{-6.6}$)	
	$Ca(H_2PO_4)_2$	Moderately soluble in water.	
	$Ca_3(PO_4)_2$	Insolute in water ($K_{sp} = 10^{-26}$)	
Fe	$FePO_4$	Insoluble in water ($K_{sp} = 10^{-21.9}$ var.)	$Fe(OH)_3$; $K_{sp} = 10^{-38.7}$
	$Fe_4O_{21}P_6$	Insoluble in water ($K_{sp} = 10^{-22.6}$)	
Mg	$MgHPO_4$	Slightly soluble in water	$Mg(OH)_2$; $K_{sp} = 10^{-9.2}$
	$Mg_3(PO_4)_2$	Insoluble in water ($K_{sp} = 10^{-27.2}$)	

amounts of Al, Ca, Fe, and Mg. Spikes were made at pH 2.6 (pH of H_3PO_4 solution); pH 9.3 (pH of Na_3PO_4 solution); and at pH 12 which was done by preparing Na_3PO_4 solution in pH 12 buffer. Shown in Figure 1 are the data obtained showing the effects of Ca spikes on the measured peak height. At pH 2.6, the predominant phosphate species is $H_2PO_4^-$. Table VI shows that $Ca(H_2PO_4)_2$ is moderately soluble in water and therefore no significant depletion of the conducting species ($H_2PO_4^-$) should occur as Ca spikes are made. Thus, the peak heights measured should remain unchanged as depicted in Figure 1. At higher solution pH, however, pH 9.3 and pH 12, the predominant species are HPO_4^{-2} and PO_4^{-3} both of which form insoluble compounds with Ca. Thus, as Ca spikes are increased, the species HOP_4^{-2} and PO_4^{-3} are depleted, and the peak heights diminish as shown.

The data obtained for Mg are shown in Figure 2. Since the predominant phosphate species at pH 2.6, i.e., $H_2PO_4^-$, forms a

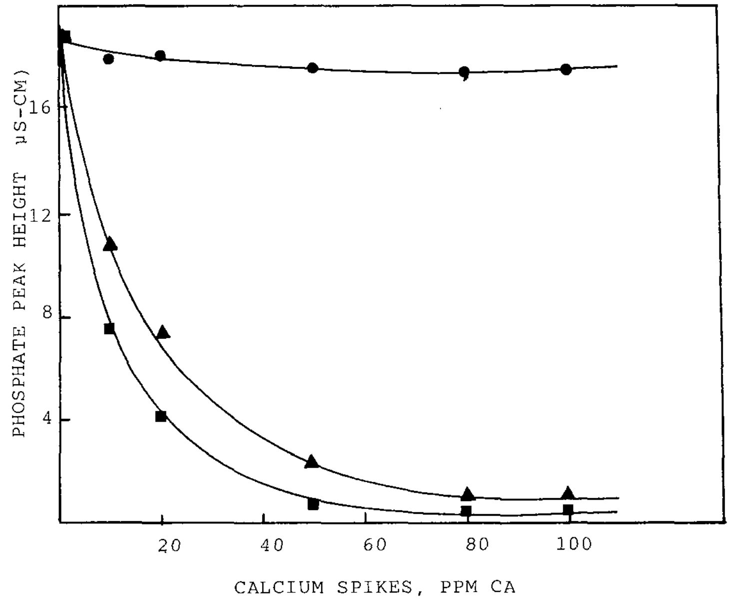

FIGURE 1 Effects of calcium on phosphate peak height. Solution pH = 2.6 (●); solution pH = 9.3 (▲); solution pH = 12.0 (■).

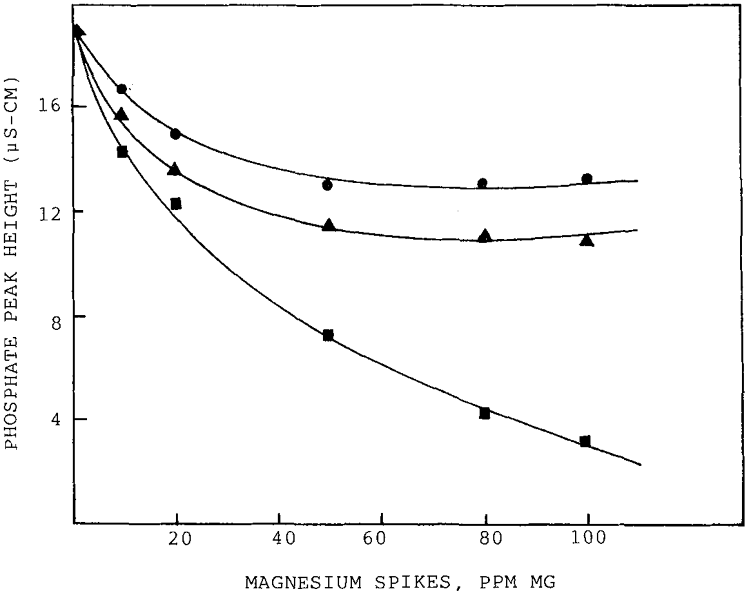

FIGURE 2 Effects of magnesium on phosphate peak height. Solution pH = 2.6 (●); solution pH = 9.3 (▲); solution pH = 12.0 (■).

soluble compound with Mg, no decrease in peak heights should be expected. The slight decrease observed can be attributed to the presence of HPO_4^{-2} which forms a slightly soluble compound with Mg, i.e., $MgHPO_4$. Steeper decrease in peak height occurred at pH 9.3 and 12 where the concentration of PO_4^{3-} was higher, hence favoring the formation of $Mg_3(PO_4)_2$ which is insoluble. On comparing the data shown previously for Ca and the data shown in Figure 2 for Mg, it is apparent that the suppressive effects observed in the presence of Ca are more pronounced than those observed for Mg. This is probably due to the fact that two out of three ionic phosphates form insoluble species with Ca whereas only one forms insoluble species with Mg. Thus, the probability of formation of insoluble species is greater in the presence of calcium. It should be added that even though Mg has a tendency to form insoluble hydroxides, the K_{sp} of $Mg(OH)_2$ is much larger than that of $Mg_3(PO_4)_2$ (see Table VI). If this were not the case, the formation of hydroxide could be used as a means of sequestering the PO_4^{-3}.

Shown in Figure 3 are the data obtained when phosphate solution was spiked with incremental amounts of Fe. According to the data in Table VI, $Fe(OH)_3$ is many times more insoluble than $FePO_4$. Thus, at high pH, the formation of $Fe(OH)_3$ should be favored over the formation of $FePO_4$. Therefore, no Fe suppressive effects should be expected at pH 12. This indeed was found to be the case, for as shown in the figure, the measured peak heights remained practically unchanged even in the presence of up to 100 ppm Fe. At pH 2.6 and 9.3, a sharp decrease was observed due to a decrease in OH^- concentration, allowing the formation of $FePO_4$.

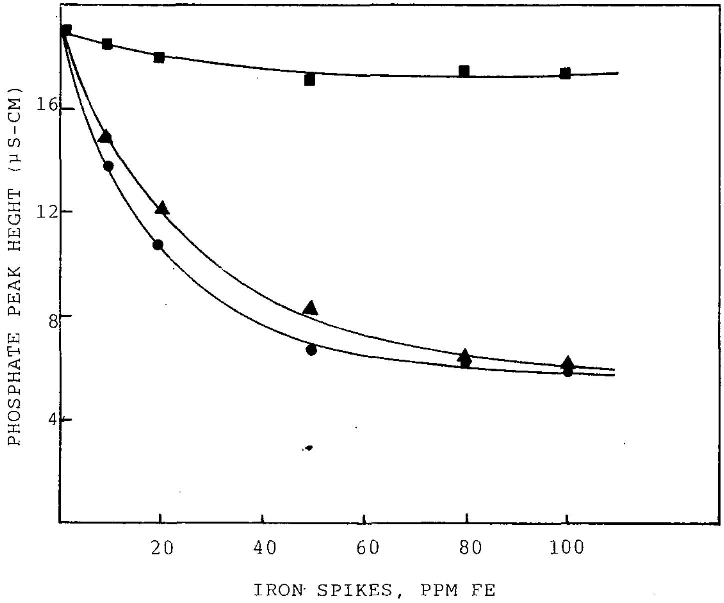

FIGURE 3 Effects of iron on phosphate peak height. Solution pH = 2.6 (●); solution pH = 9.3 (▲); solution pH = 12.0 (■).

Aluminium forms an insoluble $Al(OH)_3$ which is many times more insoluble than $AlPO_4$. Thus, as with Fe, at high pH no Al suppressive effects should be expected; and this was found to be the case experimentally. However, as solution pH decreased the OH^-

concentration diminished and the probability of formation of $AlPO_4$ increased. This led to a decrease in peak height as shown in Figure 4. No decrease was observed at pH 2.6 since at this pH the concentration of PO_4^{-3} is negligible.

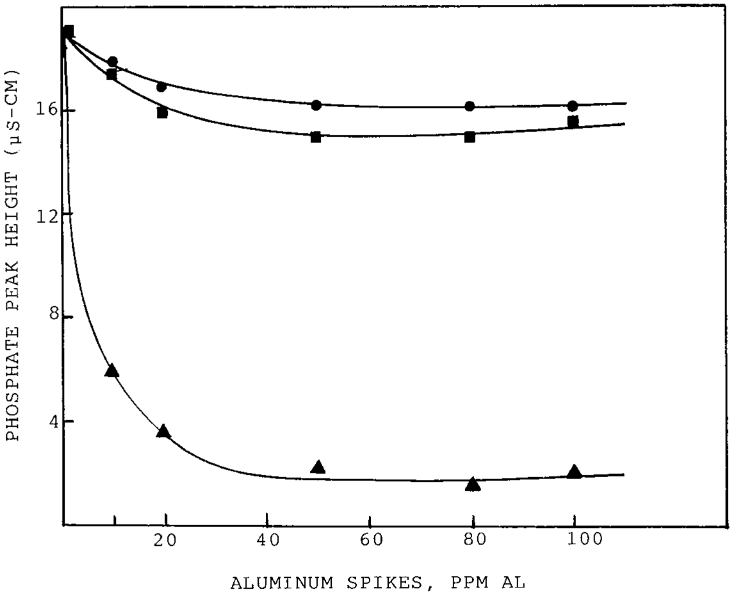

FIGURE 4 Effects of aluminium on phosphate peak height. Solution pH = 2.6 (●); solution pH = 9.3 (▲); solution pH = 12.0 (■).

It is evident from Figures 1–4 that the presence of cations in the sample solution can influence measurement of total phosphate in solution. The extent to which this occurs depends on the cation involved and the phosphate species in solution, which in turn depends on the solution pH as discussed earlier.

The data presented above point to the influence of solution pH on ion chromatographic measurements of phosphates. The solution pH controls not only the dissociation of the orthophosphates but also the reaction of orthophosphates with cations in solution to form insoluble material which ultimately influence the analytical signal measured. This pH influence, however, is more significant as a control of the reaction of phosphates with metallic species than as a control of phosphate dissociation because the latter process is mainly controlled by the eluent in the analytical column.

Comparison of IC with direct current plasma spectrometry

Ion chromatographic data can provide information on phosphates in the ionized form only. For total phosphorus determination including other forms such as meta, pyro, and organic phosphorus and insoluble species such as $AlPO_4$, $FePO_4$, $Ca_3(PO_4)_2$, and $Mg_3(PO_4)_2$, other analytical techniques must be utilized. Direct current plasma emission spectrometry (DCP) has been found to be particularly suitable for this.[21] In the present study, however, comparative data for IC and DCP were obtained using orthophosphates only. Shown in Table VII are the recovery factor data for 10 ppm P (Na_3PO_4) solution after spiking with incremental amounts of Al, Ca, Fe, and Mg. For each cation, spikes were made at a solution pH 9.3 which reflected a decrease in phosphate peak heights with increase in the amount of cation added. It is evident that with DCP, no significant change occurs in the presence of up to 100 ppm of these cations even though in some cases the IC measurement signal was reduced to almost the background level.

TABLE VII

Recovery of 10 ppm P in the presence of incremental amounts of Al^{+3}, Ca^{+2}, Fe^{+3}, and Mg^{+2} at pH 9.3

Cation concentration (ppm)	DCP: % recovery of P in the presence of:				IC: % recovery of P in the presence of:			
	Al^{+3}	Ca^{+2}	Fe^{+3}	Mg^{+2}	Al^{+3}	$Ca^{+3}2$	Fe^{+3}	Mg^{+2}
0	100	100	100	100	100	100	100	100
10	101	92	99	95	15	63	53	93
20	97	90	98	90	18	37	30	89
50	91	94	100	100	31	13	0.1	68
100	92	85	97	95	—	0.1	0.2	60

Analysis of water samples

Water samples were obtained from various sources including wastewater and natural surface waters. For each sample, the phosphorus concentration was determined with IC and DCP. Also, pH and cation (Al, Ca, Fe, Mg) determinations were made to serve as an indication of what phosphate compounds might be in the samples.

The data obtained are shown in Table VIII. Only calcium was found to be present at a concentration that might effect the ion chromatographic signal measured. The rest of the cations (Al, Fe and Mg) were all below 1 ppm. It is apparent that the phosphorus concentrations obtained with IC and DCP differ by less than 20%. This is despite the fact that Ca was at a concentration level sufficient to cause a significant decrease in the IC peaks (Figure 1). This apparent discrepancy can be explained on the basis of the solution pH. For most of the samples the solution pH was below 5. As was shown in Figure 1, the suppressive effects observed with calcium are minimal at acidic pH since Ca forms a moderately soluble compound, ($Ca(H_2PO_4)_2$, with the predominant phosphate species at such conditions.

Summarizing, this research was aimed at evaluating the ion chromatographic properties of phosphate in solution. The study included an evaluation of the processes that may occur in the sample

TABLE VIII

Concentration of phosphorus in water samples: Comparison between IC and DCP data

Sample I.D.	pH	Phosphorus concentration (ppm) IC	Phosphorus concentration (ppm) DCP	Calcium concentration (ppm)
WWSI	4.5	2.47±0.01	2.90±0.1	27.3±0.1
WWSII	4.3	2.78±0.01	2.93±0.1	27.3±0.1
WWS III	4.4	2.62±0.01	2.89±0.05	27.0±0.5
WWS IV	4.5	2.75±0.02	2.90±0.06	27.7±0.3
TW I	5.5	0.25±0.03	0.42±0.01	27.8±0.2
NW I	6.2	0.96±0.02	1.44±0.06	25.2±0.1

solution before injection, the separator column; and the suppressor column. On the basis of the data obtained, the following conclusions can be made: first, considering the analytical signal measured, it does not matter whether the sample is injected directly or after equilibrating it with the eluent. However, in those cases where sample is limited, direct injection is preferred to avoid dilution. Second, the eluent pH has the most influential effect on phosphate determination with respect to its retention in the seperator column and the peak heights measured. The HCO_3^-—CO_3^{2-} equilibrium controls the prevailing pH in the column. Third, for those systems equipped with suppressor columns, and more specifically, hollow fiber suppressor columns, an equilibrium is maintained over a wide range of regenerant concentration. This equilibrium condition determines the type of phosphate species that is ultimately detected. Fourth, the presence of certain cations in solution can form insoluble material with phosphate that render the phosphate species undetectable. The formation of these insoluble substances is dependent upon the pH of the solution and the eluent used. Fifth, since cations such as Ca can form insoluble material at the operational pH, it is imperative that in order to avoid the formation of these materials which can permanently damage the analytical column, chemicals of high purity must be used. Sixth, a combination of the capabilities of IC for ionic phosphate and those of DCP for total phosphorus can provide a powerful approach for distinguishing between and measuring orthophosphate and other forms of phosphorus.

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