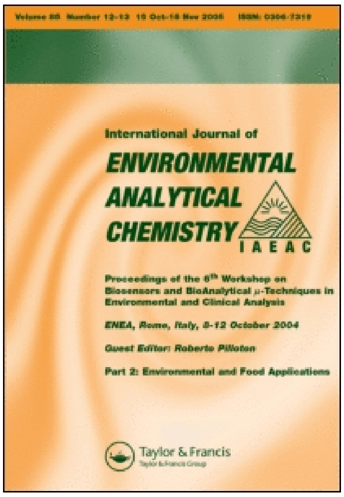

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POTENTIAL CONTAMINATION FROM GLASSWARE IN THE DETERMINATION OF PHOSPHORUS IN NATURAL WATERS

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Phosphorus was determined in samples of glass from laboratory glassware, using a hydrofluoric digestion followed by colorimetry. Glass from such sources is shown to contain up to 0.002% of phosphorus. Experiments on storage of samples in glass bottles show that glassware may contribute significant phosphorus contamination to natural water samples, particularly seawater, as a result of partial dissolution of glass into the sample during storage. The release of phosphate from glassware into the sample is greater than the concentration expected from the P/Si ratio in glass and the silicate dissolution in the sample. This is attributed to the formation of a leached layer at the surface of the glass in contact with the water. Under the alkaline digestion conditions applied in this work for the total phosphorus determination, the dissolution of glass does not appear to be a source of measurable phosphate contamination. Nevertheless each analyst must satisfy himself that no phosphate contamination occurs under his particular working conditions with his own glassware.

KEY WORDS : Phosphorus, contamination, glass, sea water.

INTRODUCTION

Glass bottles are frequently recommended in preference to plastic for storing water samples, particularly seawater, for the determination of different forms of phosphorus[1,2], since several authors have made reference to the possible adsorption of phosphate to plastic surfaces[3-6]. However Koroleff[7] has expressed similar reservations for glass. Despite these, marine samples preserved with mercury in polypropylene containers[8] or autoclaved in glass bottles[9], have shown good stability for phosphate concentrations over several months. However, this apparent inertness of the container material towards phosphate under sterile conditions does not preclude container-sample interaction and bias resulting from leaching of the container material into the sample. Glass is attacked by natural waters, especially seawater, as already demonstrated[10] in connection with the determination of silicate, therefore traces of phosphorus in the composition of the glass of the container may contribute to its concentration in the contained sample. Although it is undesirable to store seawater samples for the determination of phosphate for a long period, extended storage is unavoidable for reference material, especially in intercomparison exercises[11], or in preservation studies. In neither case must the container material bias the results. In addition to storage, oxidative procedures used to determine total phosphorus may release some phosphate from the container walls into the sample.

This work sets out to assess the contamination risk posed by using glass vials when phosphorus is to be determined in samples. Using bottles of various origins, types of glass, shape and volume, experiments were performed on the dissolution of glass vial walls by seawater and total phosphorus digestion reagents in order to evaluate the potential contamination of samples by phosphate leached from glass. In order to relate this leachage to the composition of glass, selected bottles were analysed for their major constituents and for their phosphorus content.

EXPERIMENTAL SECTION

Glass digestion

The phosphorus content of various glasses was determined colorimetrically after digestion. So that the phosphomolybdate colorimetric procedure for phosphate could be applied without the risk of interference from silicate, a heated hydrofluoric/perchloric acid digestion procedure was applied to the ground glass samples, resulting in the total volatilisation of silica[12]. The residue was dissolved in hydrochloric acid 1 mol l^{-1} (hereinafter referred to as 'final solution').

Merck concentrated acids were used: hydrofluoric acid (334), perchloric acid (519) and hydrochloric acid (317). The phosphate content of these acids was found to be respectively 3.3 µmol l^{-1}, < 0.5 µmol l^{-1} and < 1 µmol l^{-1}, within manufacturer's specifications.

Bearing in mind the low concentrations under examination in this work, all possible precautions were taken to ensure sample integrity and to avoid contamination due to handling[13]. The bottles to be analysed were machine cleaned, including washing with phosphate-free detergent, then acid (0.02 mol l^{-1} H_2SO_4) and rinsing with distilled water. Before crushing and grinding, bottles were once more rinsed inside and out with Milli-Q deionised water. Gloves were worn for all these manipulations. In addition, any contamination by phosphate on the surface of the glass powders was checked by stirring the powders in demineralised and seawater. The concentrations measured after half an hour (and verified after 6 hours) correspond to less than 0.17 µmol l^{-1} PO_4 in the final solution: this was considered negligible in comparison with the concentrations of phosphate in blanks and digested samples (2-20 µmol l^{-1}). Residual silicate remained at very low and non-interfering concentrations (<1.3 µmol l^{-1}).

The above procedure was applied to three of the seven types of glass bottle used in this work, bottles A, B and E in Table 1. Two samples of each glass and two blanks were treated.

Table 1 Characteristics of glass bottles tested in the present work. Types of glass: SL = soda-lime, BS = borosilicate.

Bottle reference	*Type of glass*	*Capacity (ml)*	*Remarks*
A	SL	200	Rectangular, screw cap. Full of seawater for months, then washed and stored dry for months. Certain bottles (A') kept full of seawater up to 2 years prior to the experiment.
B	SL	200	Cylindrical screw cap. Full of seawater for months, then washed and stored dry for months.
C	SL	100	Cylindrical, screw cap. Unused previously.
D	SL	20	Serum bottles, aluminium seal with silicone/teflon liner.
E	BS (Pyrex)	100	Cylindrical, screw cap, manufactured by SOVIREL. Various laboratory uses before experiment.
F	BS (Duran)	100	Cylindrical, screw cap, manufactured by SCHOTT. Unused previously.
G	BS	20	Cylindrical, screw cap, SUPELCO vials. Unused previously.

Glass dissolution during seawater storage or digestion

Experiments were undertaken to evaluate the dissolution of silicate and phosphate from the walls of glass vials during seawater storage and during the digestion of samples for total phosphorus determination.

In the examination of the dissolution by seawater, bottles were filled with filtered coastal water (salinity close to 34 PSS) depleted in phosphate and silicate and poisoned with 20 mg l^{-1} of mercury. All bottles, except bottles D (Table 1), were used, but a wider set of conditions was applied to bottles A, B and E, those previously analysed for phosphate. In order to enhance the dissolution of glass, thus expecting measurable phosphate leaching in a reasonable time scale, the main test was performed at 50 °C using three bottles of each kind, all of them pre-treated with 1 mol l^{-1} HCl overnight. To compare with normal storage conditions, an additional series of HCl pre-treated bottles A, B and E was tested as follows: two bottles of each kind at 5 °C (fridge) and three bottles B at 20 °C. Finally, three of each kind (A, B and E) were pre-treated with sulfochromic acid overnight (instead of HCl) and tested at 50 °C. Silicate and phosphate concentrations were determined at various intervals up to eight weeks. Normally, total phosphorus, rather than phosphate, should be determined in order to demonstrate the leachage of phosphorus from glass since phosphate could be generated internally in the sample by the transformation of organic or polymerised forms. However, this determination would have consumed too much water from each sample, consequently total phosphorus was measured only at the end of the experiment in typical samples covering various experimental conditions.

The experiment on dissolution of glass during the digestion for total phosphorus was performed using the procedures described by Koroleff[7].

Analytical methods

Analysis of major elements in glass was performed by X-ray dispersive fluorescence (XRDF) using a fully automated Siemens SRS 303 sequential spectrometer. A glass-disc is prepared by fusing 1.5 g of finely ground glass with 8.0 g of Flux 120 A (a mixture of 90% LiB_4O_7 and 10% LiF) in a platinum crucible. Standardisation employs international geochemical reference standards and synthetic pure-oxides. Inter-element effects are mathematically corrected.

In water samples, phosphate and silicate were determined by Technicon AAII equipment using methods described by Tréguer and Le Corre[14]. The only modification (to the phosphate method) consisted of a reduction of the reagent pumping rate from 0.8 to 0.42 ml min^{-1} in order to comply more closely with the conditions originally stated by Murphy and Riley[15]. The computerisation of the output signal of the colorimeter allows a repeatability of ± 0.002 μmol l^{-1} PO_4 in the lower range.

During the experiment on dissolution of glass by seawater, phosphate and silicate were determined by pumping the water directly from the bottles by manually introducing the sampling probe into the necks of the vials. Great care was taken to prevent contamination from skin contact[13]. When a dilution was required for silicate, the aliquot was taken using an automatic pipette.

Potential silicate interference in the determination of phosphate was checked by spiking phosphate standards with hexafluorosilicate up to 2 000 μmol l^{-1} Si, with due attention to reaction pH conditions. No interference was detected (detection limit: 0.005 μmol l^{-1})in this range. Acidic digestion solutions were diluted in such a way that correct reaction conditions prevailed. Additionally, each determination was internally standardised by spiking.

RESULTS

Glass composition

The composition of the three selected glasses is summarised in Table 2.

Silica accounts for about 70% of the composition of ordinary soda-lime glasses (A and B) and 80% for the borosilicate glass (E) which is in agreement with approximate data given by manufacturers. Very few differences are noted on major elements between both ordinary glasses.

The phosphorus concentration, determined after the digestion of glasses, exhibits a precision of 15-30%. Despite this uncertainty inherent in the method, the results can be considered adequate for the aim of the project. The results show that phosphorus may reach 0.002% in glass (*i.e.* close to 0.7 μmol P per gram of glass), which corresponds to a P/Si ratio (by atom) of 56.10^{-6}.

Table 2 Composition of commercial bottle glasses. Bottle types refer to Table 1. Major oxides are determined by XRDF; results are in percent and B_2O_3 is obtained by difference. Phosphorus is determined after a digestion procedure; results are in percent × 10^4. The P/Si ratio is expressed by atom.

Constituent	*Bottle Type* *A* *(ordinary)*	*B* *(ordinary)*	*E* *(Pyrex)*
SiO_2	70.0	71.5	79.7
Na_2O	13.1	13.1	3.1
K_2O	0.7	0.3	1.1
CaO	9.0	9.7	0.0
MgO	2.6	2.0	0.0
Al_2O_3	2.2	1.6	2.0
B_2O_3	-	-	13
P(× 10^4)	20	9.3	< 3
P × 10^6/Si	56	25	< 7

Glass dissolution in seawater samples

The dissolution of glass in seawater samples, illustrated by the increase of dissolved silicate (figure 1), must not be considered a negligible process since concentrations of around 1 000 µmol l^{-1} are reached in 5 weeks at 50 °C. At laboratory or fridge temperature, the dissolution is of course considerably slower and the silicate concentration does not exceed a few tens of micromoles per litre over that period.

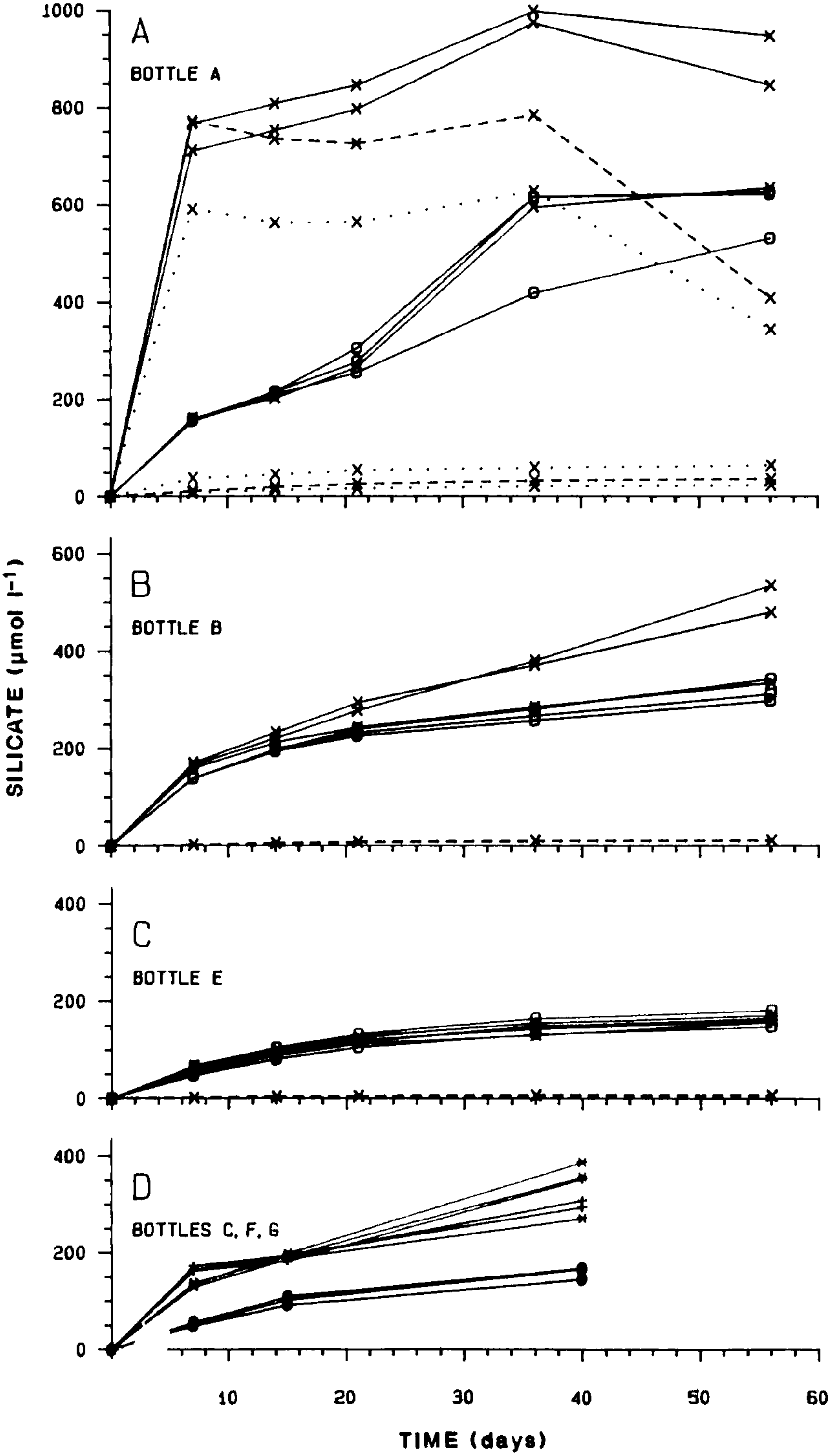
Various dissolution rates were observed depending on the bottle type. The borosilicate glasses used dissolve more slowly in seawater than ordinary soda-lime glasses. This is particularly noticeable with Pyrex and Duran glasses. Compared with the later glasses, Supelco (G) and other soda-lime glasses (except bottle A) dissolve twice as rapidly. The glass of bottle A dissolves four times faster than Pyrex (E) and Duran (F). In each series of bottles the dissolution kinetics appear very similar.

The pre-treatment of the bottles before the experiment (hydrochloric or sulfochromic acid) does not seem to affect the dissolution process while certain conditions of use and storage have a noticeable effect. This is illustrated by the behaviour of certain bottles A (see Figure 1A), identified as A'. These bottles had already been full of seawater for some time (up to 2 years) prior to the experiment. In these bottles, the dissolution of silicate was not temperature-dependent and was particularly fast during the first few days, reaching 600-800 µmol l^{-1} Si in one week. Their subsequent behaviour exhibited irregular variations, sometimes with decreases in concentration.

Phosphate leachage from glass into seawater

The concentration of phosphate in the seawater contained in glass bottles is summarised in Figure 2.

The general feature is an increase of phosphate in the samples, the magnitude of which depends on the bottle type.


A
BOTTLE A
B
BOTTLE B
C
BOTTLE E
D
BOTTLES C, F, G
SILICATE (µmol l⁻¹)
TIME (days)
0
200
400
600
800
1000
10
20
30
40
50
60

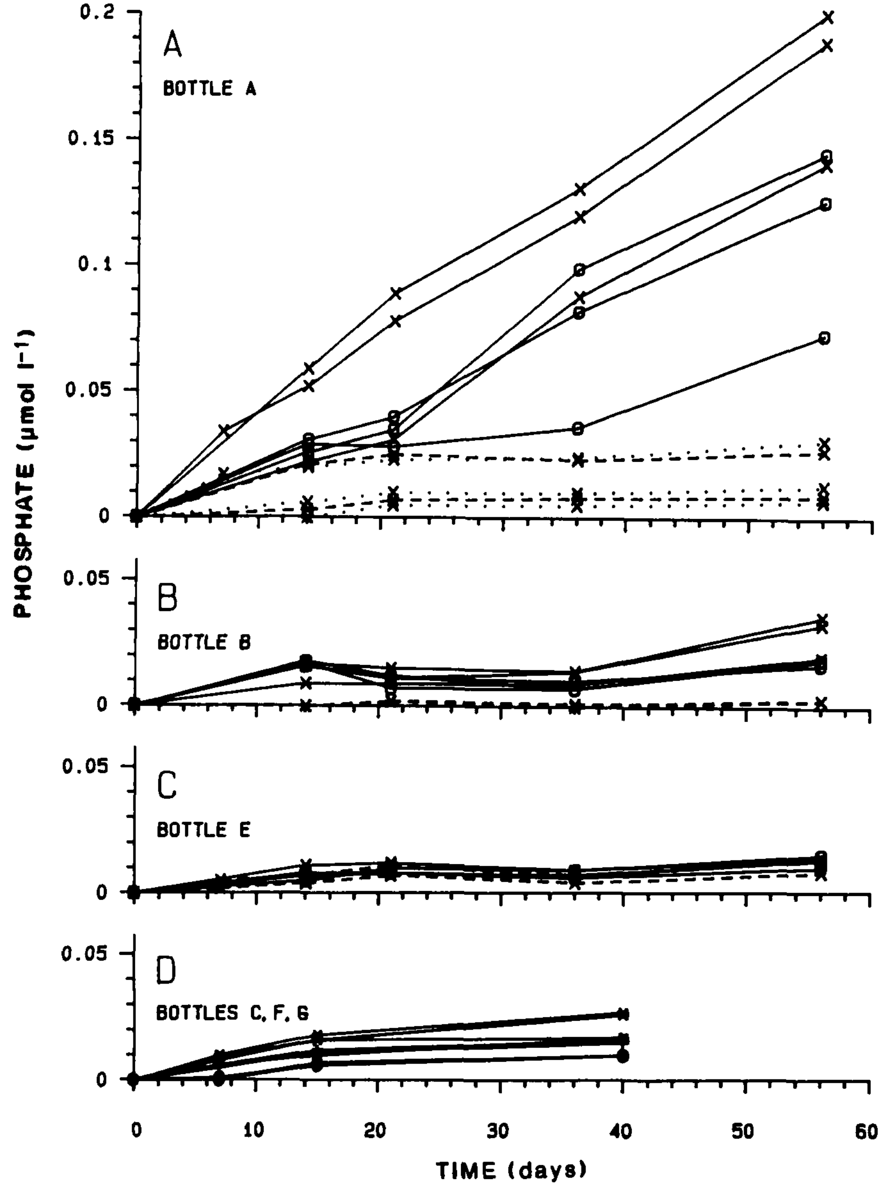


Figure 2 Leachage of phosphate from glass in seawater stored in bottles of various types (see Table 1) as a function of time. Line and point symbols as in Figure 1.

Figure 1 Dissolution of silicate in seawater stored in glass bottles of various types (see Table 1) as a function of time.

Line symbols: full line = storage at 50 °C; dotted line = storage at 20 °C; dashed line = storage at 5 °C.

Point symbols in A, B and C: X = pre-treated with hydrochloric acid; O = pre-treated with sulfochromic acid.

Point symbols in D:* = bottle type C; • = bottle type F; + = bottle type G.

Note the four above curves in fig. A which correspond to the bottles A' kept full of seawater for 2 years.

Table 3 Total phosphorus (TP) and dissolved organic plus polymerised phosphorus (DOP + DPP) in seawater samples at the end of the experiment (8 weeks) about glass dissolution in seawater (all samples preserved with mercury).

Bottle type	*Temperature °C*	*TP µmol l⁻¹*	*DOP + DPP µmol l⁻¹*
Polypropylène	20	0.11	0.09
Ordinary glass (A)	5	0.09	0.07
	5	0.08	0.07
Pyrex (E)	50	0.26	0.07
	50	0.21	0.07
	50	0.27	0.06

However, in order to confirm the phosphate leachage from glass, it is necessary to demonstrate the stability of organic plus polymerized forms of dissolved phosphorus (DOP + DPP) in the samples. The determination of these forms, by subtracting phosphate from total phosphorus, was performed at the end of the experiment in the following selected set of samples: the original seawater stored in polypropylene at 20 °C, two samples stored in Pyrex bottles (E) at 5 °C and three samples stored in ordinary glass bottles (A) at 50 °C, all samples preserved with mercury. The results (Table 3) show that, assuming a precision of ± 0.01 µmol l^{-1} for these determinations, identical concentrations of DOP + DPP are measured in all samples, whatever the storage conditions. Since phosphate increase remained below 0.015 µmol l^{-1} in the samples where the dissolution of glass was negligible (*e.g.* in Pyrex bottles E, 8 weeks at 5 °C), it may be unambiguously concluded that any additional phosphate found in the samples was leached from the glass walls. It can be seen from the experiments at 50 °C that all soda-lime glasses leach concentrations significantly greater than the background level (> 0.015 µmol l^{-1}). Bottles A can leach up to 0.20 µmol l^{-1} along with 1 000 µmol l^{-1} silicate. Considering this type of bottles, the sub-group A' (the bottles stored full of seawater up to 2 years) exhibits different behaviour in phosphate and in silicate. While the initial release of silicate was very similar at all temperatures, the phosphate leachage in two weeks was significantly lower at 5-20 °C (0.02 µmol l^{-1}) than at 50 °C (0.05-0.06 µmol l^{-1}).

As the phosphorus content of certain glasses was previously determined, it is of interest to study the phosphate increase as a function of the silicate increase. This is shown in Figure 3. Some measurements have been omitted since a white fine crystalline deposit was observed in certain bottles (all B and some A) during the third week. As there was a close relationship between erratic phosphate increases and the presence of a visible precipitate, it was assumed that coprecipitation of calcium carbonate and phosphate had occurred in these bottles. Therefore, at the end of the experiment, the precipitate, that adhered to the wall, was separated from the sample by simply discarding the water and then redissolving in 5 ml of 0.1 mol l^{-1} HCl added to the bottle in order to measure the corresponding phosphate. In addition to bottles A and B, five Pyrex bottles E, with no visible deposit, were checked as a control. It was confirmed that precipitated phosphate was found in all bottles in which crystals were observed, and only in these bottles. Consequently, in the bottles concerned, the phosphate measured in solution was assumed to be correct until the second week (no visible crystals). Then a "corrected" value was obtained for the final determination (8 weeks) by adding the precipitated to the dissolved phosphate. Intermediate determinations have been omitted.

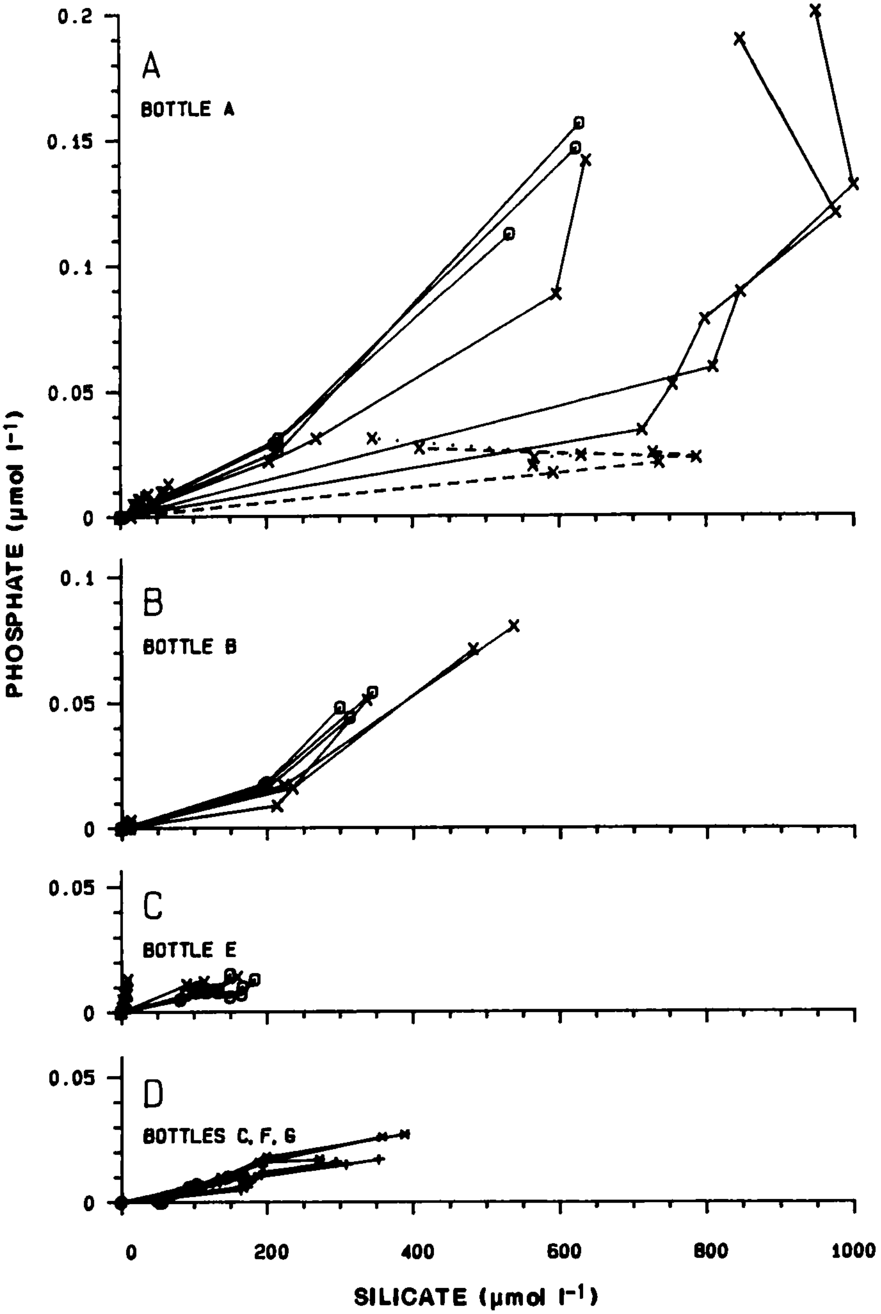


Figure 3 Phosphate concentration increase versus silicate concentration increase in seawater stored in glass bottles of various types (see table 1). Line and point symbols as in Figure 1.

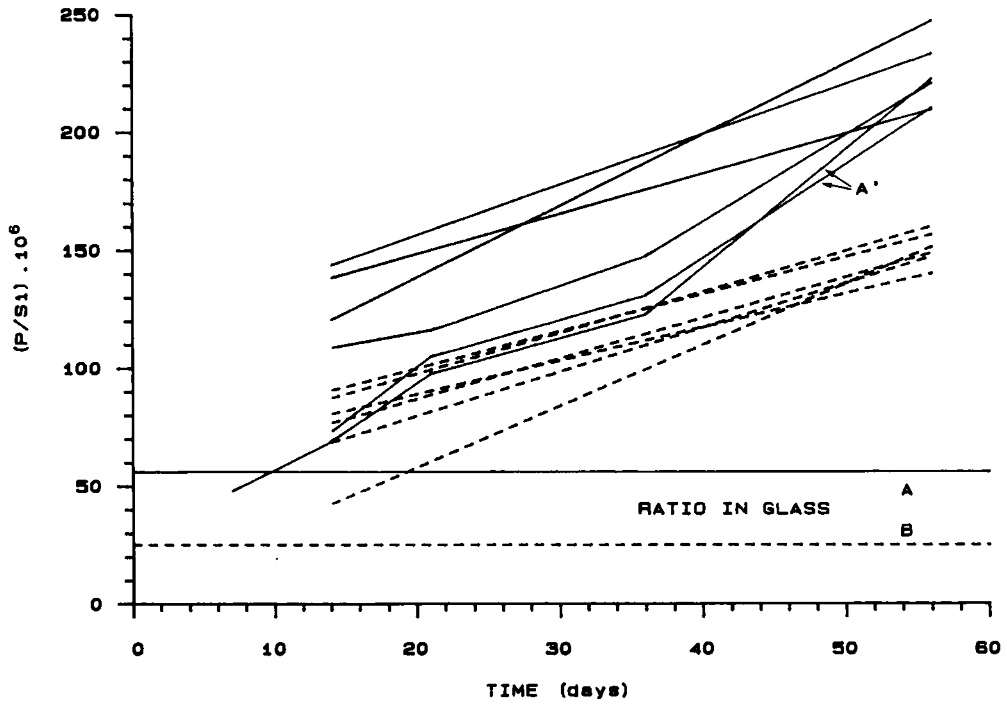


Figure 4 (P increase/Si increase) ratio in seawater stored at 50 °C in soda-lime glass bottles of types A and B (see Table 1).
Line symbols: full line = type A; dashed line = type B.
Note that curves corresponding to bottles A', kept full of seawater for years, are identified.

Figure 3 shows that the increase in phosphate is not proportional to the increase in silicate. Although the dissolution rate of glass decreases significantly, phosphate continues to increase in solution. This is well illustrated in Figure 4 by the variation of the P/Si ratio as a function of time. The first observation is that the P/Si ratio increases regularly with time consequent to the diminution of the dissolution rate of Si but not of P. Secondly, the P/Si ratio is always greater than the ratio in glass. It follows that even if the concentration of phosphorus in the glass is known, the actual leachage of phosphorus in a sample is not predictable from a knowledge of the silicate increase. The P/Si ratio in glass will provide information only on the minimum threshold of P release. As seen on Figure 4 a correction factor of two to four should be applied to the P/Si ratio in glass in order to be closer to the truth.

Table 4 Silicate dissolution from glass bottles walls during alkaline persulfate digestion of total phosphorus. Bottle reference as in Table 1. Sample: SW = seawater; DW = distilled water.

Bottle reference	*Capacity/ content ml*	*Sample*	*Number of bottles*	*Si increase mean (range) μmol l^{-1}*	
A	200/165	SW	3	123	(96-165)
B	200/165	SW	3	73	(70-77)
D	20/11	SW	7	93	(77-131)
E	50/33	SW	3	126	(39-296)
G	20/11	SW	9	150	(127-210)
G	20/11	DW	5	250	(180-280)

Glass attack during total phosphorus digestion

Compared with dissolution in seawater in the course of long periods of storage, the dissolution of glass during the alkaline digestion procedure used for total phosphorus determination appears moderate (Table 4) considering the simultaneous high temperature and initial pH conditions. Silicate concentrations never exceed 165 μmol l^{-1} Si when seawater is digested in ordinary glass bottles (A, B, D) and 300 μmol l^{-1} Si if digested in borosilicate glass bottles (E, G). Dissolution is enhanced when demineralised water is digested and silicate concentrations increase by 100 μmol l^{-1} Si on average compared with seawater. Borosilicate glass seems less resistant to the total phosphorus procedure than ordinary soda-lime glass.

The limited dissolution of glasses during the digestion procedure did not allow the determination of phosphate release since it remains in the range of uncertainty of the method for total phosphorus (± 0.01 μmol l^{-1} P). With the acidic digestion procedure (undertaken in Supelco vials, type G, only) no more than 12 ± 8 μmol l^{-1} Si was liberated into the sample. This is considered insignificant in comparison with the release under alkaline digestion conditions.

DISCUSSION

The glasses analysed in this work exhibit low but significant concentrations of phosphorus amounting up to about 0.7 μmol g^{-1}, equivalent to a P/Si ratio (by atom) of 56.10^{-6}. As the solubility of silica in water and seawater is about 2 000 μmol l^{-1} Si at pH below 9[16,17], the corresponding release of phosphate would be 0.11 μmol l^{-1}. The dissolution of silica is very slight at room temperature, illustrated by the 400-500 μmol l^{-1} Si reached in samples of seawater set aside for an intercomparison exercise and stored for times of the order of one year[11]. Nevertheless, such concentrations correspond to a dissolution of glass sufficient to produce a measurable increase in phosphate in water samples.

This hypothesis has been confirmed by a series of experiments designed to verify the simultaneous leachage of phosphate and silicate when glass dissolves in seawater. Although it cannot be claimed that all situations have been encountered, several points concerning the dissolution of glass and the related phosphate leachage have been elucidated.

As already known, seawater dissolves the walls of glass bottles at a rate controlled by temperature, but simultaneously some phosphorus contained in the glass is liberated into solution. The kinetics of dissolution controlling initial phosphate release, differ greatly from one type of glass to another: borosilicate glass dissolves more slowly than ordinary soda-lime glass. However, differences may be encountered between glasses of very similar composition.

It is important to note that the behaviour of the bottles in contact with seawater may be drastically altered depending on the previous use, storage conditions or pre-treatment of the bottles. For instance, if bottles are stored full of seawater, a rapid dissolution of silicate and phosphate takes place as soon as a new sample of low-silicate seawater is introduced. Attention must be paid to the fact that the leachage of phosphate is greater than that expected from the silicate dissolution (P/Si in solution > P/Si in glass).

A detailed explanation of the mechanisms governing the behaviour of silicate and phosphate in samples of seawater in contact with glass is beyond the scope of this work, but the results suggest the existence of multiple processes. As stated by previous authors[18] the dissolution of glass, a solid that can be considered as mixed-oxide structures, is a complex process involving many distinct reaction steps and pathways such as hydration, hydrolysis, ion exchange or condensation reactions. The different sites react separately with the solution, leading to modification of the structure of the near-surface region of the solid. An extensive altered layer of tens to hundreds angströms thickness can develop near the mineral-solution interface. This leached layer is notably depleted in cations, is amorphous[18] and comparable to a silica gel. This hypothesis has been verified for the dissolution of most silicate glasses[19]. As a consequence of this behaviour, and admitting with Krauskopf[16] that "one can speak without ambiguity of a possible "solubility equilibrium" between amorphous silica in general and silica dissolved in water", it becomes evident that the P/Si ratio in the solution in contact with glass can reach values substantially in excess compared with the ratio in the bulk glass itself. Our results are in agreement with such a mechanism. Since the processes are mainly controlled by the surface structure, it is not surprising that large differences may be noted between bottles submitted to various storage, use, or pre-treatment conditions. For example, it should be appreciated that the internal surface of a bottle kept full of seawater during a long time is extensively altered, the consequence of which is a sudden release of silicate when the contents are replaced by seawater depleted in silicate. In contrast, when bottles are kept empty, the inner surface dries up and rearranges into a new structure or is eliminated as a consequence of cracking[18] and subsequent rinsing or washing.

Consequently, the storage of water in glass bottles for phosphate determination has to be approached with caution.

Since glass dissolves more quickly in seawater than in freshwater[16] the problem is exacerbated in marine environmental studies. It should be borne in mind that the phosphorus concentration in surface seawater is generally lower than 0.5 μmol l^{-1} and seldom exceeds 0.1 μmol l^{-1} in oceanic waters, especially in oligotrophic areas (such as the Mediterranean Sea[20]). Consequently, even when samples are chemically preserved (chloroform, mercury..), the storage period should remain as short as possible. Beyond one week, contamination from the walls of glass vials may invalidate the subsequent phosphate determination, depending on the bottle type and the phosphate concentration in the sample. Increases of 0.02 μmol l^{-1} were measured in one or two weeks even when samples were stored at low temperature (20 °C, 5 °C).

In published studies of storage of seawater in glass bottles, dealing with preservation with mercury or chloroform, it appears that most of the experiments ranged from several weeks to several months [3,6,21,22]. In view of our results all the final concentrations of phosphate in these studies can be suspected to be slightly biased by a contribution from glass. Therefore, all studies involving storage of samples in glass for phosphorus determination should take due account of this effect. Checking the dissolution of silicate should probably be sufficient in most cases.

Another important instance of prolonged storage is that of reference material for intercomparison studies. In the example of ICES fourth nutrient intercomparison[11], the present work indicates that the consensus phosphate concentration in oceanic samples (1.14 μmol l^{-1}) probably contains an element of about 0.05 μmol l^{-1} leached from the bottles along with 400-500 μmol l^{-1} of silicate during prolonged storage. In this particular case the increase in phosphate had little effect on the outcome as silicate contents of the samples were approximately similar at the time of the analyses. However, any work dealing with the preparation of standards should take this process into account.

In addition to problems associated with extended storage periods there is scope for speculation on the effects of hot alkaline or acidic persulphate attack on glass and its implications for the determination of total phosphorus. Although our results indicate negligible phosphate contamination consequent to acceptable silicate levels, other methods or modifications of original procedures must undertake careful silicate dissolution controls. Indeed, pH, temperature and digestion time may influence the glass attack process. In Koroleff's alkaline procedure, for instance, the pH range is stated to be between 9.2 (initial) and 4-5 (final) while it is between 9.7 and 5-6 in the Valderrama's procedure[23]. Nevertheless, rigorously applying Koroleff's method, we obtained a final pH of 7.1 with some seawaters. Small changes in reagent concentration may generate pH drifts during the reaction and consequently enhance or decrease the dissolution of silicate (hence phosphate) into the digested samples.

In prolonged storage studies, the dissolution of silicate has to be determined by each analyst with his own bottles and procedure. Referring to the P/Si ratio determined in this work in glass and in solution, a dissolution of 100-200 μmol l^{-1} Si may probably be considered as acceptable, assuming a precision of ± 0.01 to 0.02 μmol l^{-1} for total P. Borosilicate glass, although sometimes more soluble than soda-lime glass under digestion conditions, seems preferable because of its lower phosphorus content. The use of bottles from various sources or different batches should be avoided as this may contribute additional uncertainty to results. The analyst must also satisfy himself that his blank fully takes account of any phosphate gained from the container; since blanks are usually run with deionised water instead of seawater the dissolution of silicate must also be checked for blanks.

CONCLUSION

Phosphorus, though present in glass only at low concentrations, may be brought into solution by the dissolution of the silicate matrix at various stages of the analysis of natural water samples. This dissolution may occur during prolonged storage of certain waters, notably marine samples in glass bottles, or later during the chemical processes used in the determination of total phosphorus. In some circumstances, the concentration liberated (hundredths to tenths of a micromole per litre) cannot be considered negligible compared to typical natural concentrations particularly in oligotrophic waters.

Since the behaviour of glass bottles depends on many factors, no unique rule can be stated. However, given that borosilicate glass has a lower dissolution rate and was found to contain and release a lower concentration of phosphorus than ordinary glass, the use of borosilicate glassware seems to be preferable in view of the risks identified by this work. As always, vigilance is advised in the choice and handling of materials and operating conditions for studies of phosphorus in natural waters. Samples preserved with chemicals (chloroform, mercury...) must be stored at low temperature (fridge), in order to reduce the dissolution of glass, and analysed as soon as possible. Once the samples are analysed the bottles must be washed and kept dry until the next use. Control of silicate release under normal working conditions represents good laboratory practice.

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