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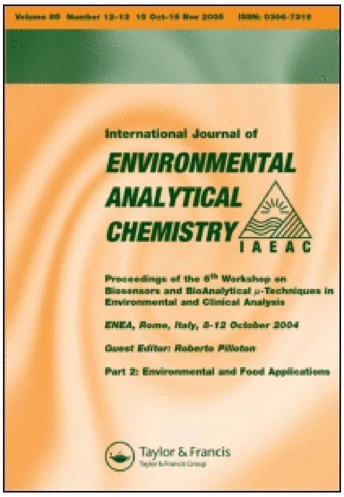

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S. Blomqvist[a b]; K. Hjellström[c d]; A. Sjösten[a]
[a] Department of Systems Ecology, Section Marine Ecology, [b] Department of Geology and Geochemistry, [c] Department of Physical, Inorganic and Structural Chemistry, Stockholm University, Stockholm, Sweden [d] Euroc Research AB, Slite, Sweden

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INTERFERENCE FROM ARSENATE, FLUORIDE AND SILICATE WHEN DETERMINING PHOSPHATE IN WATER BY THE PHOSPHOANTIMONYLMOLYBDENUM BLUE METHOD

S. BLOMQVIST[1,2,*], K. HJELLSTRÖM[3,4] and
A. SJÖSTEN[1]

[1] *Department of Systems Ecology, Section Marine Ecology,* [2] *Department of Geology and Geochemistry,* [3] *Department of Physical, Inorganic and Structural Chemistry, Stockholm University, S-106 91 Stockholm, Sweden*

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In the range of 50–500 μg PO_4-P L^{-1}, analytical procedures according to Murphy and Riley,[1] Koroleff[2] and Parsons *et al.*[3] all resulted in complete colour development of the phosphoantimonylmolybdenum blue complex within 5 min after reagent addition. Reducing the reaction temperature from +25° to +15°C slowed the formation rate of the blue complex, but not enough to be of practical importance. Arsenate (0–1.0 mg AsO_4-As L^{-1}), fluoride (0–200 mg F L^{-1}) and silicate (0–50 mg SiO_4-Si L^{-1}) affect the phosphate determination in different ways. Arsenate forms a blue complex with molybdate, but with a slower reaction rate than for the phosphate complexation. At low arsenate concentrations this interference can be reduced by timing the photometric recording according to the phosphoantimonylmolybdenum formation rate. High concentrations of fluoride slow the colour development of the phosphoantimonylmolybdenum blue complex. Silicate may affect the analytical result in two ways. Alone, after prolonged standing, a slighly increased light absorption results from a blue complex formed with molybdate, but silicate can also reduce the inhibitory effect of fluoride. High fluoride concentrations counteract the development of the blue complex between silicate and molybdate. The interfering effects of arsenate, fluoride and silicate can all be reduced by dilution of the sample prior to reagent addition.

KEY WORDS: Phosphate, interference, arsenate, fluoride, silicate, molybdenum blue, phosphoantimonylmolybdenum.

INTRODUCTION

More than 100 years ago, M. F. Osmond[4] proposed using the blue complexation between

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*Author to whom correspondence should be addressed.

[4] Present address: Euroc Research AB, Box 104, S-620 30 Slite, Sweden

phosphoric acid and molybdate as a colorimetric analytical tool. Various modifications in the analytical procedure have since been proposed, including adaptations to water samples (see reviews[5–11]). The basic chemical principle of the method is formation of a heteropoly phosphate-molybdate acid which, upon reduction, produces a blue colour, the intensity of which is proportional to the amount of orthophosphate ion incorporated into complex form. It has become the standard method for determination of phosphate concentration in water. The modifications most frequently used today are based on addition of ascorbic acid as a reducing agent in the presence of trivalent antimony, as suggested by Murphy and Riley.[1]

However, further evaluation of the Murphy and Riley[1] procedure of assaying phosphate seems warranted. In fact, only a few papers have reported rate data on the colour development of phosphoantimonylmolybdenum blue. Jones[12] presented rate measurements of a seawater sample to which 31 μg PO_4-P L^{-1} were added, To and Randall[13] reported measurements in pure water at one phosphate concentration (250 μg PO_4-P L^{-1}) and two temperatures (+5° and +22°C), while Pai *et al.*[14] measured at one phosphate concentration (155 μg PO_4-P L^{-1}) and four temperatures (+20°, +35°, +55° and +70°C) in deionized distilled water. The recommended time from addition of reagents to the photometric recording, and the time interval within which measurements ought to be made, varies in commonly used handbooks and manuals.[2–3,15–19] Moreover, many components found in water samples have been reported to interfere with the analysis, potentially biasing phosphate readings. Unfortunately, such reports often give insufficient analytical detail, making it difficult to recommend precautions in order to minimize interference effects. This applies to arsenate, fluoride and silicate, despite early attention to possible biasing interference.[4,20–23]

We report here (1) data on the reaction rate of phosphoantimonylmolybdenum complexation, involving a comparison of three commonly employed modifications[1–3] and an evaluation of the effect of room temperature variation, and (2) some experiments dealing with interference from arsenate, fluoride and silicate.

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EXPERIMENTAL

Chemicals. We used doubly distilled or deionized, reagent-grade water and chemicals of p.a. quality (E. Merck, Darmstadt, F.R.G.), i.e. ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$, L(+) ascorbic acid, $C_6H_8O_6$, potassium antimonyl tartrate, $K(SbO)C_4\ H_4\ O_6\cdot \frac{1}{2}\ H_2\ O$, potassium dihydrogen phosphate, $KH_2\ PO_4$, sodium fluoride, NaF, and sulphuric acid, H_2SO_4. Sodium fluorosilicate Na_2SiF_6 (Riedel-de Haën AG, Seelze, F.R.G.) and calcium orthoarsenate $Ca_3(AsO_4)_2$ were of purified quality.

Apparatus. Time-course measurements of phosphate and arsenate were made with a Varian Series 634 (double-beam) spectrophotometer, equipped with a Varian Recorder Model 9176, and fitted with a specially designed thermostated bath system keeping the reaction conditions in the 1-cm cuvette at a pre-selected temperature. Temperature-acclimatized water samples and reagents were mixed in Pyrex glass tubes and introduced to the cuvette within 30 sec. Other arsenate and phosphate determinations were conducted using ordinary techniques, i.e. simply mixing the sample solutions with reagents in Pyrex glass tubes and light absorbance recording by a Philips PU 8740 UV/Vis (single-beam) spectrophotometer, equipped with a Philips Plotter Printer, and carried out at room temperature (+20°C). Likewise, the solutions with fluoride and silicate were prepared in Pyrex glass tubes, but the colorimetric measurements were conducted with a Hitachi U-2000 (double-beam) spectrophotometer. Light absorbance was recorded at 880 nm throughout.

RESULTS AND DISCUSSION

The procedural modifications of Murphy and Riley,[1] Koroleff[2] and Parsons *et al.*[3] differ with respect to the recommended reagent concentration of molybdenum (5.4, 2.7 and 3.1 mM, respectively), antimony (0.068, 0.059 and 0.038 mM, respectively), ascorbic acid (4.80, 10.92 and 5.57 mM, respectively) and sulphuric acid (0.20, 0.10, 0.11 M, respectively) in the final solution. The effect of acidity on the reaction is complex, since it influences the rate as well as the amount and speciation of complexes formed.[14,24–28] We therefore compared the three procedures with respect to the time needed to yield maximum absorbance of phosphoantimonylmolybdenum blue and followed its stability by continuous time course recording. However, within the concentration range of 50–500 µg PO_4-P L^{-1}, no appreciable differences were found between the three procedures; all reached a constant absorbance level within 5 min (Figure 1a), and did not fade significantly during 1.5 h. A maximum absorbance of phosphoantimonylmolybdenum blue within 5 min during normal room temperature

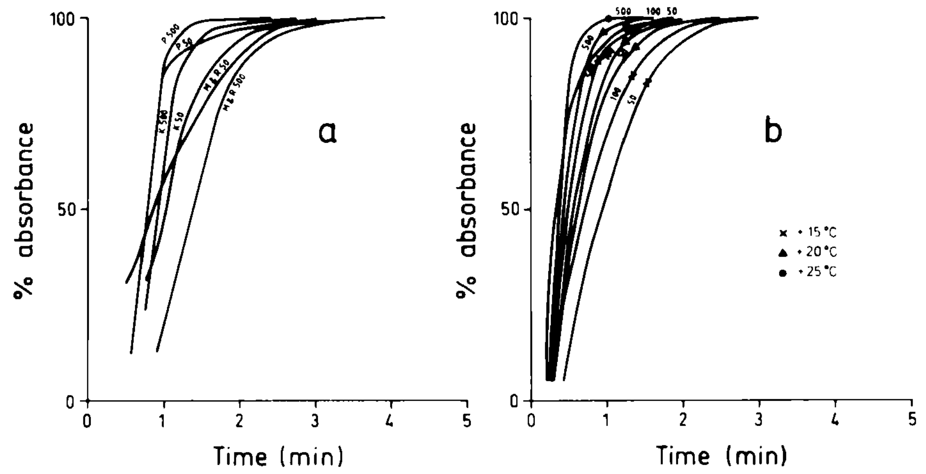

Figure 1 a Time course of formation of the phosphoantimonylmolybdenum blue complex, following procedures of Murphy and Riley[1] (M&R), Koroleff[2] (K) and Parsons *et al.*[3] (P), in water containing phosphate of a concentration of 50 and 500 µg PO_4-P L^{-1}, respectively. Reaction temperature: +20°C. **b** Time course of formation of the phosphoantimonylmolybdenum blue complex (according to Koroleff[2]) at three different reaction temperatures, +15°, +20° and +25°C of water containing phosphate in a concentration of 50, 100 and 500 µg PO_4-P L^{-1}, respectively.

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conditions accords with what is previously reported for a more narrow phosphate concentration range of 155–250 µg PO_4-P L^{-1}.[13–14] Thus, we restricted further evalutation to the modification of Koroleff.[2]

We compared the time taken to reach maximum absorbance level, at three different temperatures, +15°, +20° and +25°C, and three different phosphate concentrations, 50, 100 and 500 µg PO_4-P L^{-1}. As shown in Figure 1b, within the temperature range studied (roughly normal room temperature range), only slight differences were found. Colour development tended to be somewhat slower at lower temperatures and in solutions of lower phosphate concentrations. Caution is advised if measurements are made at temperatures below +15°C, since the time necessary to reach maximum absorbance may then be longer than shown in Figure 1b.[13]

Arsenate forms a blue molybdate complex, which absorbs light at 880 nm. However, the reaction between arsenate and molybdate (Figure 2) is slower than between phosphate and molybdate (Figure 1). For arsenate concentrations lower than considered in the present study, even longer reaction times are needed for reaching maximum absorbance.[12,26] Once maximum colour development is attained, the arsenate complex may increase the apparent absorption value considerably. Based on relations in Figure 3, the absorbance of 100 µg AsO_4-As L^{-1} corresponds to 74 µg PO_4-P L^{-1}, or an optical density ratio of the arsenate to phosphate complexes of 1.35. This is lower than a ratio of 2.6 in distilled water, calculated from data in the original paper of Murphy and Riley[1, p.35] and a ratio of about 2 in seawater, revealed from a graph presented by Jones.[12, p.20] One way to reduce the over-estimation of phosphate due to arsenate interference is to time the reading to the shorter reaction time needed for formation of the phosphoantimonylmolybdenum complex. This implies measurement after about 5 min (Figure 1), but is useful only at low or moderate arsenate concentrations and low reaction temperatures (Figure 2), provided that no high fluoride concentrations are present (see below).

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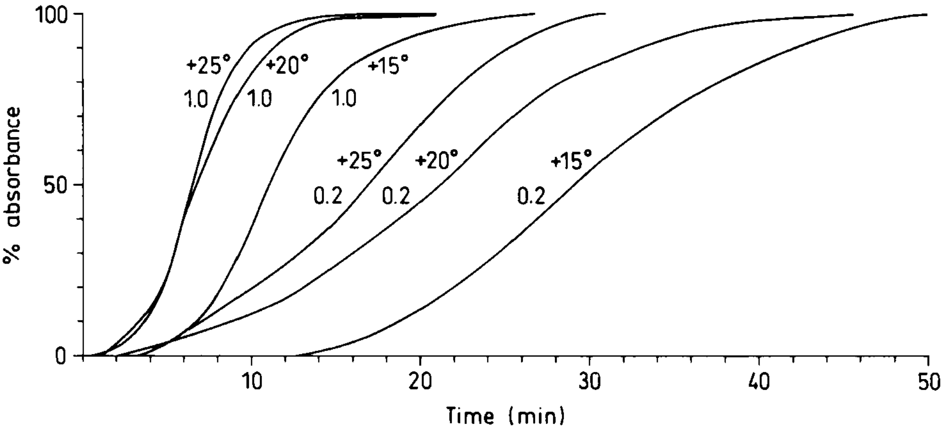

Figure 2 Time course of formation of the arsenomolybdenum blue complex (according to Koroleff[2]), at three different reaction temperatures, +15°, +20° and +25°C, in water containing arsenate in a concentration of 0.2 and 1.0 mg AsO_4-As L^{-1}, respectively.

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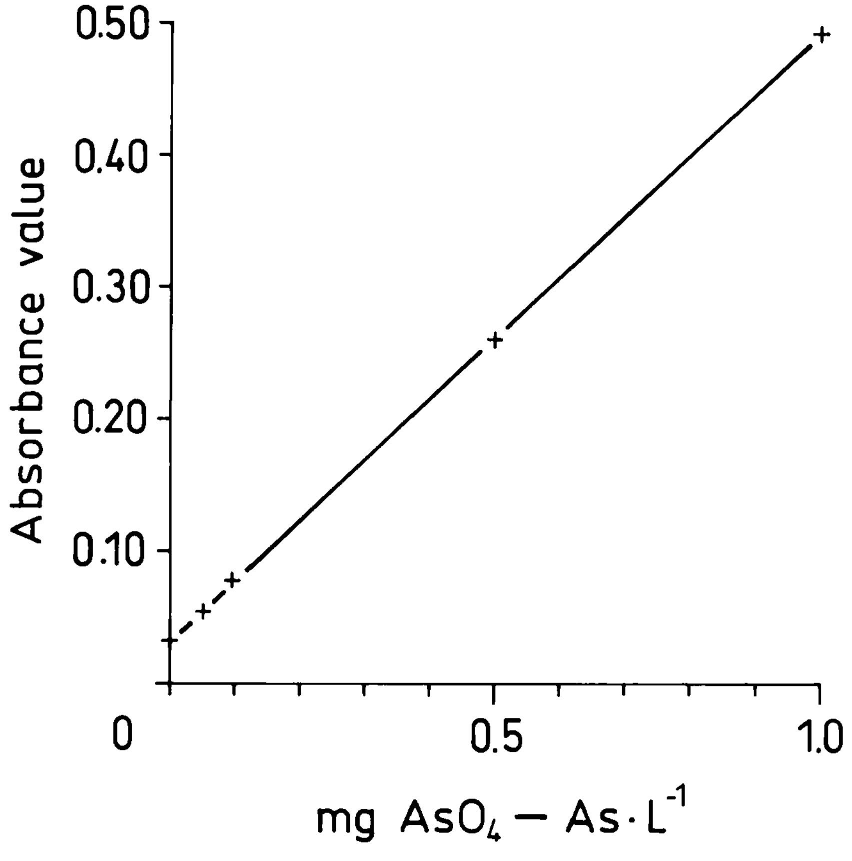

Figure 3 Apparent light absorbance as a function of varying arsenate concentration, ranging 0–1 mg AsO_4-As L^{-1}, in water solutions with a constant phosphate concentration of 50 µg PO_4-P L^{-1} (according to Koroleff[2]). Linear regression equation: $y = 0.460 \times +0.031$ (Pearson product-moment correlation coefficient $r = 0.999$, $n = 5$, $p < 0.001$). The intercept value refers to light absorbance of phosphate alone. Measurements performed at +20°C.

Arsenic typically occurs in concentrations of a few µg L^{-1}, or less, in lakes,[29–31] rivers,[29–30,32–33] coastal waters[32,34–40] and oceans.[41–43] This implies significant arsenate interference with phosphate estimates only at low phosphate concentrations. However, arsenic concentrations of over 10 µg As L^{-1}, and sometimes even higher than those studied here (Figures 2 and 3), have been reported from anthropogenically polluted areas, such as waters near mines, metal works and related activities,[35,44–51] in supernatant water of sediment incubation experiments,[52–53] in sediment pore water,[50,54–55] in lakes loaded with herbicide,[56–59] and also from some groundwater wells,[46,59–60] lakes,[61] streams and rivers,[29,37,42,45] and in waters influenced by geothermal activity.[61–66] As a rule, it seems prudent to keep in mind the risk of interference from arsenate when measuring phosphate by the molybdenum blue method.

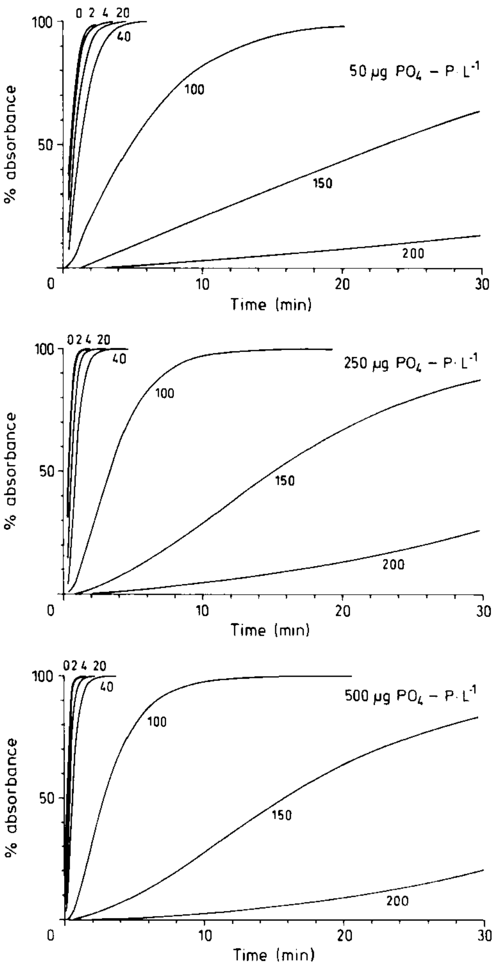

Figure 4 Time course for the formation of phosphoantimonylmolybdenum blue complex (according to Koroleff[2]) in water solutions containing three different phosphate concentrations, 50, 250 and 500 μg PO_4-P L^{-1}, respectively, and varying concentrations of fluoride (0, 2, 4, 20, 40, 100, 150 and 200 mg F L^{-1}). Measurements performed at +20°C.

The interference of fluoride contrasts to that of arsenate, since fluoride does not affect the maximum absorbance level—in other words, causes no additional blue tint, nor does it diminish the final colour intensity. However, high fluoride concentrations give rise to slower colour development of phosphoantimonylmolybdenum blue (Figure 4). Regarding Figure 4, inhibition effects of fluoride are recorded for concentrations of at least 20 mg F L^{-1}, with an enhanced effect as fluoride concentrations increases. For a solution containing 200 mg F L^{-1}, several hours are needed for complete colour development. However, if the fluoride concentration is not too high ($\leq$40 mg F L^{-1}) and the concentration of phosphate is not too low ($\geq$50 μg PO_4-P L^{-1}) a reaction time of 5 min is still sufficient for complete colour

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development. Further reaction rate studies on waters of phosphate concentrations below 50 µg PO_4-P L^{-1} are desirable.

The actual mechanism behind the fluoride inhibition remains unclear. Wavelength spectra recorded while the phosphoantimonylmolybdenum complex was being formed, with and without fluoride, as well as after full colour development, were very similar, and did not deviate from those previously reported[1,13,67] for the completed complex.[27] However, fluoride is known as a small, highly electronegative and reactive ion which readily replaces oxygen and hydroxyl groups, implying several different possible interference reactions from fluoride in the phosphoantimonylmolybdenum blue procedure, i.a. with the molybdate reagent[68] and phosphate itself.[69–70] Easy ways to reduce interference from high fluoride concentrations are simply to dilute the sample or postpone the photometric recording according to the time needed to reach the maximum absorbance level (Figure 4).

Fluoride is a major constituent of seawater, usually found in concentrations of about 1–2 mg F L^{-1} in ocean water,[71–72] and in 10-fold lower concentration in rivers and lakes,[73–74] with concentration in esturine waters being intermediate.[74–76] However, concentrations above 20 mg F L^{-1} are reported from saline lakes,[77] groundwater wells,[78–79] thermal springs,[64,80] soil extracts[81] and industrially polluted river water.[82] Even much higher fluoride concentrations (>200 mg F L^{-1}) have been reported from certain soda lakes[77] and underground brines,[78] from acid-spring waters in active volcanic areas[83] and in heavily polluted waters.[84–85]

Silicate provides an example of a component complicating the evaluation of interfering factors in the phosphate determination. In natural waters, dissolved silica occurs predominantly as protonated monomeric silicate—in other words, undissociated orthosilicic acid H_4SiO_4.[86–88] In the present study, when the reagents for phosphate analysis with the phosphoantimonylmolybdenum blue method were simply mixed with dissolved silicate, a faint, linearly and slowly formed blue tint was recorded at 880 nm. Measurements at 50 mg SiO_4-Si L^{-1} resulted, after 10 min of reaction, in an apparent light absorbance value corresponding to about 2 µg PO_4-P L^{-1}. After 30 min, the corresponding figure was about 6 µg PO_4-P L^{-1}, which is roughly similar to the absorbance value given by Koroleff.[2] However, this is considerably less than reported by Noriki,[89] and at +70°C by Pai *et al.*[14] In the study of Noriki,[89] it appears that self-reduction of molybdate ion due to a too low sulphuric acid concentration has been misinterpreted as absorbance by silicate.[14,27]

If silicate is added in combination with fluoride in the phosphate determination, the inhibition effect from fluoride is mitigated, resulting in less time needed to reach the maximum absorbance level of the phosphoantimonylmolybdenum blue complex (Figure 5). For a constant weight ratio of fluoride to silicon of four, as shown in Figure 6, the counteraction of silicate on fluoride interference is most pronounced when the fluoride concentration is extremely high (200 mg F L^{-1}). Conversely, high fluoride concentrations reduce or totally inhibit the development of the blue complex between silicate and molybdate. These findings demonstrate interaction between silicate and fluoride, probably due to equilibrium complexation.[69]

Dissolved silicate concentrations (≥5 mg SiO_4-Si L^{-1}) as high as those we have found to mitigate fluoride inhibition of phosphoantimonylmolybdenum blue have been reported in water from lakes,[77,90–96] surface drain water[97] and groundwater samples,[78,98–99] warm and cold springs,[64,96,99] streams, rivers and the low salinity zone of some estuaries.[75,79,90,93,98–100] In the

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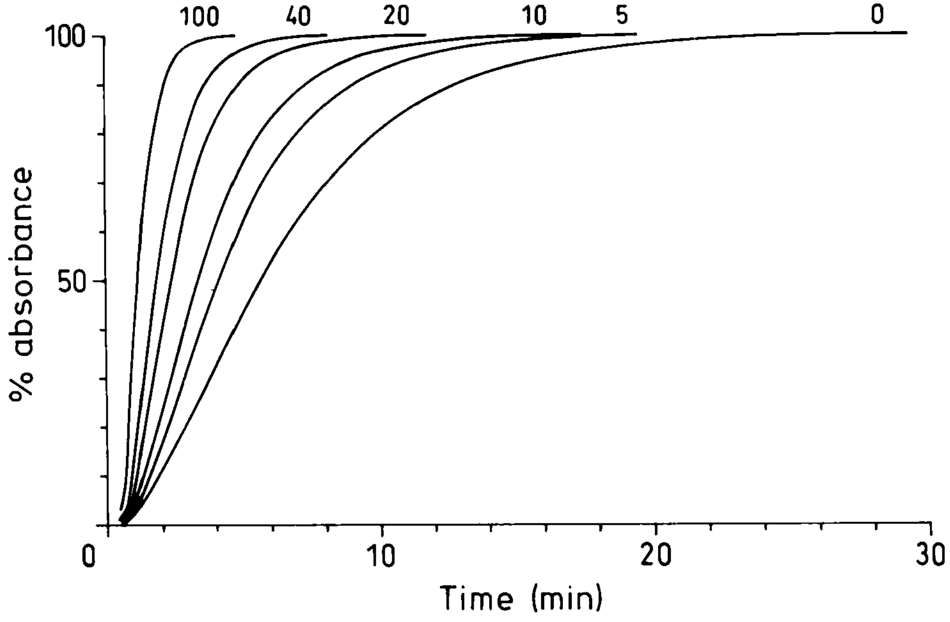

Figure 5 Time course for the formation of phosphoantimonylmolybdenum blue complex (according to Koroleff[2]) in water solutions containing constantly 250 µg PO_4-P L^{-1} and 100 and mg F L^{-1}, but varying concentrations of silicate: 0, 5, 10, 20, 40 and 100 mg SiO_4-Si L^{-1}, respectively. Measurements performed at +20°C.

true marine realm, such high silicate concentrations are not commonly found,[101-103] but have been reported from deep waters of the Bering Sea,[104-105] the Sea of Okhotsk[104] and the northern Pacific,[104-105] from hydrothermal deep-sea vents,[62,106-108] deep brine of the Red Sea,[109] and euxinic water of the Black Sea,[110-111] in supernatant water of sediment incubation experiments[112-113] and in sediment pore waters.[114-118]

Retardation of the colour development rate of the phosphomolybdenum blue complex is an interference effect previously reported for stannic ion, tungstate ion[119] and vanadate.[120] The latter two oxoanions are known to form heteropolyanions with phosphate as well as molybdate,[121-122] suggesting competitive interaction with the phosphomolybdenum blue complex formation as a possible causal explanation of slow colour development. This can be expected to be valid also for stannic ion.[123] Retardation effects such as are found for fluoride (Figure 4), or relationships describing the counteracting effect from silicate on the fluoride interference (Figures 5 and 6), seem not to have been reported before. However, already Denigès[20] noted that interference of fluoride might be counteracted by addition of silicate. A similar counteraction on the fluoride interference appears to be valid for borate[20,22-23] and a slowed phosphomolybdenum complex formation, analogous to what is found for fluoride, may be caused by hypochlorite or chlorine gas.[124] Element interactions resulting in retarded colour development provide an analytical source of error difficult to recognize, which may cause under-estimation of the true phosphate concentration. Further studies on this type of interference effects seem justified.

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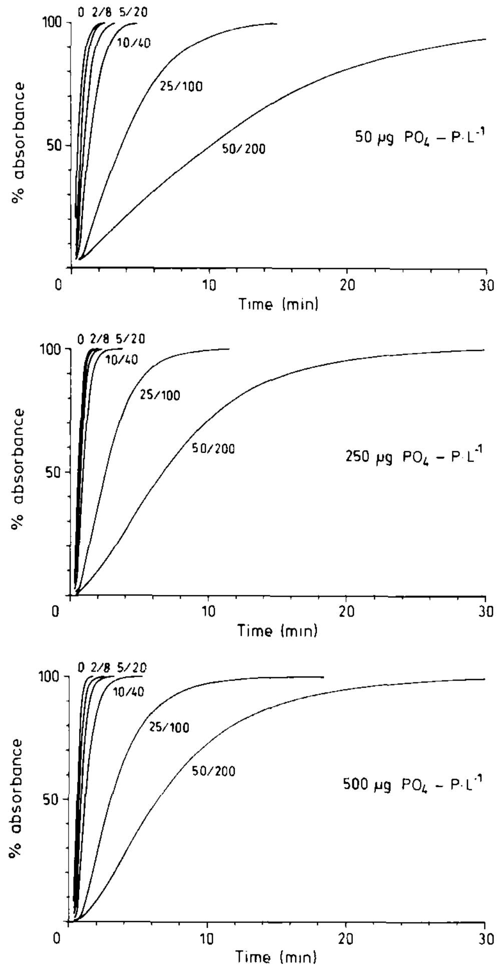

Figure 6 Time course for the formation of phosphoantimonylmolybdenum blue complex (according to Koroleff[2]) in water solutions containing three different phosphate concentrations, 50, 250 and 500 µg PO_4-P L^{-1}, respectively, and varying concentrations of fluoride (0, 8, 20, 40, 100 and 200 mg F L^{-1}) and silicate (0, 2, 5, 10, 25 and 50 mg SiO_4-Si L^{-1}), at a constant element weight ratio of four. Measurements performed at +20°C.

CONCLUSIONS

In the studied range of 50–500 µg PO_4-P L^{-1}, analytical procedures according to Murphy and Riley,[1] Koroleff[2] and Parsons *et al.*[3] all resulted in complete colour development of the phosphoantimonylmolybdenum blue complex within 5 min after reagent addition. Reducing the reaction temperature from +25° to +15°C slowed the formation rate of the blue complex, but not enough to be of practical importance. Arsenate, fluoride and silicate interfere in the analysis of phosphate in different ways.

Arsenate forms a blue complex with molybdate, albeit at a slower rate than phosphate. This interference of arsenate may cause elevated absorption values and over-estimation of the true phosphate concentration. Of course, the potential bias of this interference is highest for waters with low phosphate concentrations[56–57,125] or in waters with high arsenate to phosphate ratios.[56] The slow formation of the arsenate complex means that the interference can be minimized by recording the absorbance value as soon as the phosphoantimonylmolybdenum complex has developed fully. This effectively reduces the interference of arsenate on phosphate determinations in waters with low arsenate concentration. Still, high arsenate concentrations remain a potential source of error when determining phosphate by the molybdenum blue method.

High concentrations of fluoride (≥ 20 mg F L^{-1}) cause slower colour development of the phosphoantimonylmolybdenum blue complex formation, but do not diminish the final colour intensity. The inhibitory effect may be caused either by competitive interaction between fluoride and phosphate for a common factor, or by a direct reaction between fluoride and phosphate.

Silicate may affect the analytical procedure in two ways. Alone, after prolonged standing, silicate can cause slightly increased light absorption, due to a blue complex formed with molybdate. High fluoride concentrations, however, reduce or totally inhibit this complexation. Conversely, silicate counteracts the inhibitory effect of fluoride in the phosphoantimonylmolybdenum complex formation, and may thereby indirectly affect the determination of phosphate.

Element interactions resulting in varying rates of colour development may be treacherous sources of analytical error. In particular, slowed formation rates of the phosphoantimonylmolybdenum complex can easily cause serious under-estimation of the true phosphate concentration. Therefore, intermittent checking of the rate of colour development, to ensure full expression, may be a useful precaution in spectrophotometric analysis, particularly when new types of samples are analyzed. An easy way to reduce interference by arsenate, fluoride as well as silicate is to simply dilute the sample prior to addition of reagents, provided that phosphate concentrations are sufficiently high.

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