

On the colorimetric measurement of aqueous Si in the presence of organic ligands and common pH buffering agents

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ABSTRACT

The effects of the presence of ten organic ligands and common pH buffering agents — acetate, oxalate, tartrate, citrate, phthalate, EDTA, carbonate, TRIS, phosphate and borate — on aqueous Si concentration measurements made using the common molybdate blue method were quantified. The concentrations of these additives ranged from 0.01 to 0.1 mol/kg in the measured aqueous solutions. Whereas measured Si concentrations were not affected by the presence of up to 0.1 mol/kg acetate, hydrogen phthalate or TRIS, the presence of 0.1 mol/kg of all other selected additives altered substantially the measured Si concentrations using the molybdate blue method. For example the presence of 0.1 mol/kg of citrate, EDTA, and hydrogen phosphate decreased the ratio of measured to true Si concentrations to ~0.05. These variations are interpreted to stem from the formation of competing aqueous complexes in the aqueous phase limiting the formation of the characteristically blue SiMo₁₂O₄⁰ complex.

KEYWORDS: Si concentration measurements, molybdate blue, organic ligands, pH buffers.

Introduction

THE automated spectroscopic determination of Si concentration in aqueous solutions via the molybdate blue method is standard in chemistry and geochemistry (Dove, 1999; Welch and Ullman, 2000; Icopini et al., 2005; Oelkers et al., 2008; Declercq et al., 2013). Such analyses, however, may be influenced by a large number of factors including ionic strength (Fanning and Pilson, 1973), salinity (Froelich and Pilson, 1978), the presence of nitrate and ammonia (Stewart and Elliott, 1996), organic ligands (Wolf and Baker, 1990; He et al., 1998; Neal et al., 2000), iron (Mullin and Riley, 1955; Coradin et al., 2004), sugars, gelatin, hydroxylated polymers (Iler, 1979) and degree of polymerization (Coradin et al., 2004). These studies demonstrate that the composition of the aqueous solution can influence significantly the measured Si concentrations. Nevertheless, such effects have yet to be quantified for many of the pH buffering agents and organic ligands commonly used in experimental low-temperature geochemistry. In an attempt to better quantify such effects, the presence of ten common pH buffering agents and organic ligands¹ (Table 1), on Si measurements was investigated. The purpose of this

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¹ The term 'pH buffering agents and organic ligands' is used to describe the additives considered in this study as the anions acetate, carbonate, citrate, phthalate, phosphate and borate are commonly used to buffer the pH of aqueous solutions used in low-temperature geochemical experiments

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Table 1. Name, chemical formula, dissociation constants at 25°C, and origin of all chemical products used in the present study. The pKa values are given for the associated acid-anion hydrolysis constants and derived from Lide (1997).

Name and distributor	Chemical formula	pKa values
Oxalic acid (Prolabo)	C ₂ H ₂ O ₄	1.23; 4.19
Sodium tartrate (Prolabo)	$Na_2C_4H_4O_6\cdot 2H_2O$	2.98; 4.34
Ammonium tartrate	$C_2H_7NO_2$	4.76
Sodium citrate tribasic dehydrate (Sigma Aldrich)	C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O	3.14; 4.77; 6.39
EDTA (Merck)	C ₁₀ H ₁₄ N ₂ Na ₂ O ₈ ·2H ₂ O	2; 2.7; 6.2; 10.3
Sodium carbonate (Merck)	Na ₂ CO ₃	6.35; 10.33
Potassium hydrogen phthalate (Acros organics)	$C_8H_5KO_4$	2.98; 5.28
Tris(hydroxymethyl)aminomethane TRIS (Merck)	$C_4H_{11}NO_3$	8.1
Sodium dihydrogen phosphate (Sigma Aldrich)	NaH ₂ PO ₄ ·2H ₂ O	2.16; 7.21; 12.32
Sodium tetraborate decahydrate (Acros organics)	$Na_{2}B_{4}O_{7}\cdot 10H_{2}O$	9.23; 12.74; 13.80

communication is to report the results of these measurements illuminating potential ambiguities in laboratory-measured aqueous Si concentrations. The measurement of aqueous Si concentrations by the molybdate blue method takes advantage of the reaction

$$7Si(OH)_4 + 12H_6Mo_7O_{24}.4H_2O + 126H_2O \leftrightharpoons 7H_8Si(Mo_2O_7)_6.28H_2O$$
 (1)

in which dissolved Si reacts with molybdate at acidic conditions to form yellow beta-molybdosilicic acid (silicomolybdate). The heteropolyanion formed by this reaction can be reduced producing the blue Mo(V) complex following reaction 2 (Debiemme-Chouvy and Quennoy, 2004).

$${\rm H_2SiMo^{VI}}_{10}{\rm Mo^{V}}_2{\rm O^{4-}_{40}} + 2{\rm e^{-}} + 2{\rm H^{+}} \rightarrow {\rm H_4SiMo^{VI}_8Mo^{V}_4O^{4-}_{40}}$$

It follows from reactions 1 and 2 that any other reaction forming stable aqueous complexes with Si or Mo will influence the concentration of the molybdate blue complex, and thus the spectrophotometric measurement of aqueous Si concentration. The degree to which this is the case for numerous common pH buffering agents and aqueous organic ligands is explored in detail below.

Materials and methods

A common application of the molybdate blue method, as described by Tréguer and Le Corre (1975), uses sulfuric acid as acidifying agent, and oxalic acid to avoid interference with phosphate by destruction of the molybdatophosphate complex, which occurs *via* ligand exchange

between oxalate and molybdate, to produce phosphate and molybdo-oxalate (Schwartz, 1942; Galhardo and Masini, 2000). Ascorbic acid is used as a reducing agent and ammonium molybdate as the source of H₆Mo₇O₂₄.4H₂O. The resulting aqueous solution is analysed for absorbance at 660 nm, and the absorbance is assumed to be proportional to aqueous dissolved Si concentration.

All aqueous Si measurements in the current study were performed using a Bran & Luebbe technicon analyser III with a Seal XY-2 autosampler and an auto analyser II mixing unit. Reagent-grade sulfuric, oxalic and ascorbic acid, and ammonium molybdate were added to the analysed solution in proportions prescribed by Tréguer and Le Corre (1975) (Table 2). The ammonium molybdate solution was first mixed at a flow rate of 0.8 ml/min with the sample at a flow rate of 0.32 ml/min. Thereafter oxalic acid and then ascorbic acid were mixed into this aqueous sample ammonium molybdate at a flow rate of 0.23 ml/min. The whole mixing procedure from sample uptake to absorbance measurement took 8 min. The pH of the merged solutions before entering the spectrometer was between 1.42 and 1.54, consistent with the ideal pH range for the formation of the heteropoly blue complex (Govett, 1961; Truesdale and Smith, 1975; Coradin et al., 2004).

Aqueous calibration solutions of 2.5, 5, 7.5 and 10 ppm total Si were created by diluting a 1000 ppm Merck-CertiPUR silicon standard solution with deionized water (18.2 M Ω). Once calibrated, the Si concentrations of aqueous solutions containing selected pH buffering

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Table 2. Name, source and concentration of all chemical products used for colorimetric analysis. All solutions were prepared by mixing the indicated amount of the chemical products with deionized water in a conical flask and dissolved by shaking the mixture for several minutes. Solution 3 was stored in a lightproof flask immediately after preparation and was considered stable for at least 1 week.

	Name and source	g/l
Solution 1	Oxalic acid dihydrate (Prolabo)	59.3
Solution 2	L(+)-Ascorbic acid (Merck) Acetone (Prolabo) Aerosol 22 (Sigma Aldrich)	4.2 9.6 0.5
Solution 3	Ammoniumheptamolybdate tetrahydrate (Merck) Sulfuric acid (1 N)	10 103.2

agents or organic ligands were measured. Analysed solutions were created by adding known quantities of pH buffering agents or organic ligands to these Si calibration solutions. A Si-free blank solution of each pH buffering agent and organic ligand was analysed to check for absorbance at 660 nm. The concentrations of the pH buffering agents and organic ligands of these analysed solutions ranged from 0 to 0.1 mol/kg. Although natural solutions rarely contain 0.1 mol/kg of organic ligands, such concentrations are not uncommon in laboratory experiments.

Results

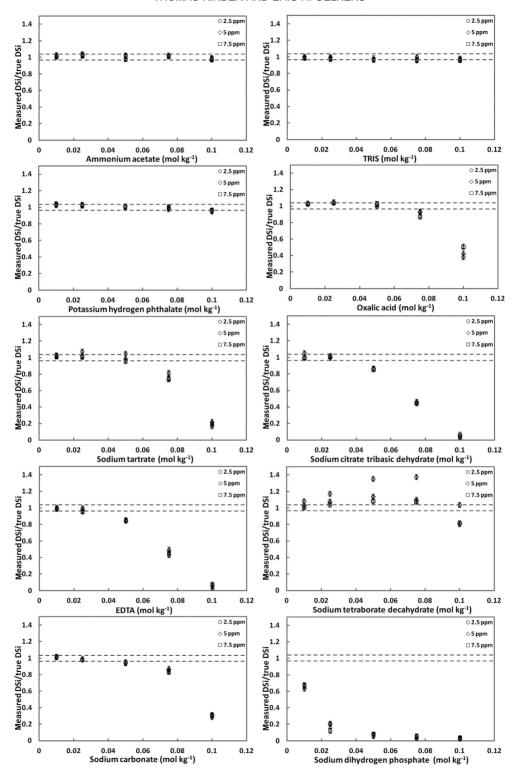
The results of all measurements are summarized in Fig. 1 and displayed as the ratio of Si concentration measured in the aqueous solutions using the molybdate blue method divided by its true concentration. As such this ratio is equivalent to the fraction decrease or increase in solution absorbance at 660 nm induced by the presence of the aqueous additive. The measured Si concentrations for the solutions containing up to 0.1 mol/kg TRIS, potassium hydrogen phthalate, and ammonium acetate were within $\pm 3\%$ of their true value (Fig. 1): note that 3% is two times the standard deviation of the calibration standards based on six replicates. Measured aqueous Si concentrations appear to decrease linearly but slightly with increasing potassium hydrogen phtalathe concentration, with a strong linear correlation ($R^2 = 0.99$) and a decrease in measured Si concentrations of 0.09%/mmol. All other tested aqueous salts affected significantly the Si concentrations measured. The ratio of measured to true Si concentrations decreased from ~1 to <0.03 with

increasing citrate and EDTA concentration from 0.025 to 0.1 mol/kg. The presence of oxalate and tartrate decreased measured Si concentrations to a lesser degree. The ratio of measured to true Si concentrations decreased from ~ 1 to ~0.3 with increasing oxalate and tartrate concentrations from 0.05 to 0.1 mol/kg. Sodium tetraborate decahydrate showed a distinct behaviour: the ratio of measured to true Si concentration depends on the Si concentration; the presence of low concentrations of this salt increased the Si concentrations measured. This contrasts with the other investigated additives where the decrease of measured concentration was independent of the aqueous silica concentration. Despite these effects, measured aqueous Si concentrations are equal, within uncertainty, to their corresponding true Si concentration in all solutions containing <0.025 mol/kg pH buffering agents or organic ligand with the exception of tetraborate and phosphate, which influenced measured Si concentrations at the lowest concentration tested (0.01 mol/kg).

Discussion

As the molybdate blue method determines aqueous Si concentration from light absorbance at a wavelength of 660 nm by silicomolybdate, the effect of various salts on measured Si concentrations probably stems from a competition among various dissolved species for aqueous Si or aqueous molybdate. A number of previous studies have focused on such complexing. For example, the effect of sodium dihydrogen phosphate on measured aqueous Si concentrations could stem from the formation of a phosphomolybdate complex, as suggested by Foulger (1927). Similarly, Zhang et al. (2013) reported significant

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complexation between aqueous citrate and molybdate at pH ranging from 1 to 2. On the other hand, Pokrovski and Schott (1998) reported only weak complex formation between aqueous Si and aqueous carboxylates and phenols. With very few exceptions - such as the aqueous Si-catechol complex – being reported so far, the likely major aqueous Si complexes forming in the aqueous solutions considered in this study contain Si in four-fold coordination. The likelihood that the effect of dissolved organic salts on measured Si rates stems from aqueous organic complexation is consistent with the observation that the recovery of P in the spectrophotometric measurements is related to the binding energy of the organic acids (Wei et al., 2009). Those authors also noted that if phosphate is added directly to the stock solutions containing organic acids, the Mo⁶⁺ may be bound to the organic ligands instead of forming the aqueous molybdate blue complex. In the present study there is a qualitative correlation between the maximum negative charge of the dissociated organic complexes and the effect of the organic salt on measured Si concentrations. The effect of the presence of 0.1 mol/kg of additive on measured Si concentrations is strongest for EDTA and citrate, which have a charge when completely dissociated of -4 and -3, weaker for tartrate, phthalate, and oxalate which have charge, when completely dissociated, of -2, and barely perceptible for acetate and TRIS which have a charge when completely dissociated of -1 (Fig. 1).

Other factors can influence the quantity of molybdate available in solution to complex with the aqueous Si. The EDTA forms chelate complexes in acid solutions with molybdate with a Mo:EDTA ratio of 2:1. (Scadden, 1960). The same has been reported for Mo:citrate with a ratio of 2:1 in a pH range of 2–3 (Samotus *et al.*, 1991). In general there are a number of complexes that can form between molybdate and organic acids, all of which can compete with Si for the molybdenum blue complex. Cruywagen *et al.* (1995) reported the formation of dinuclear and tetranuclear citrate-molybdate aqueous complexes at a pH of ~1.5. Aqueous maleate molybdate complexation was reported by Cruywagen *et al.*

(1997). Such complexation will also influence the formation of the aqueous Si-molybdate complex commonly used for total aqueous Si analyses.

Conclusions

The results summarized above illustrate the limitations of the molybdate blue method for determining aqueous Si concentrations in the presence of common pH buffers and organic ligands. For the most part, the presence of not more than 0.025 mol/kg of common organic solutes has little influence on Si concentration measured by the molybdate blue method. The presence of these organic additives, however, may have significant effects at higher concentrations. These effects appear to increase with the absolute charge of the completely dissociated organic anion, and may also be influenced by the coordination environment of the corresponding Mo-acid complex. These results suggest, therefore, that this analytical method probably does not provide accurate Si measurements in such solutions, and other methods such as optical mass spectrometry are likely to be more suitable.

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Fig. 1 (facing page). Ratio of measured to true reactive aqueous silica content (DSi) with increasing molarity of the added salt indicated. Dashed lines denote the largest standard deviation of ± 0.06 ppm (n=3) calculated as % deviation from the 2.5 ppm calibration standard (i.e. $\pm 2.5\%$).

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