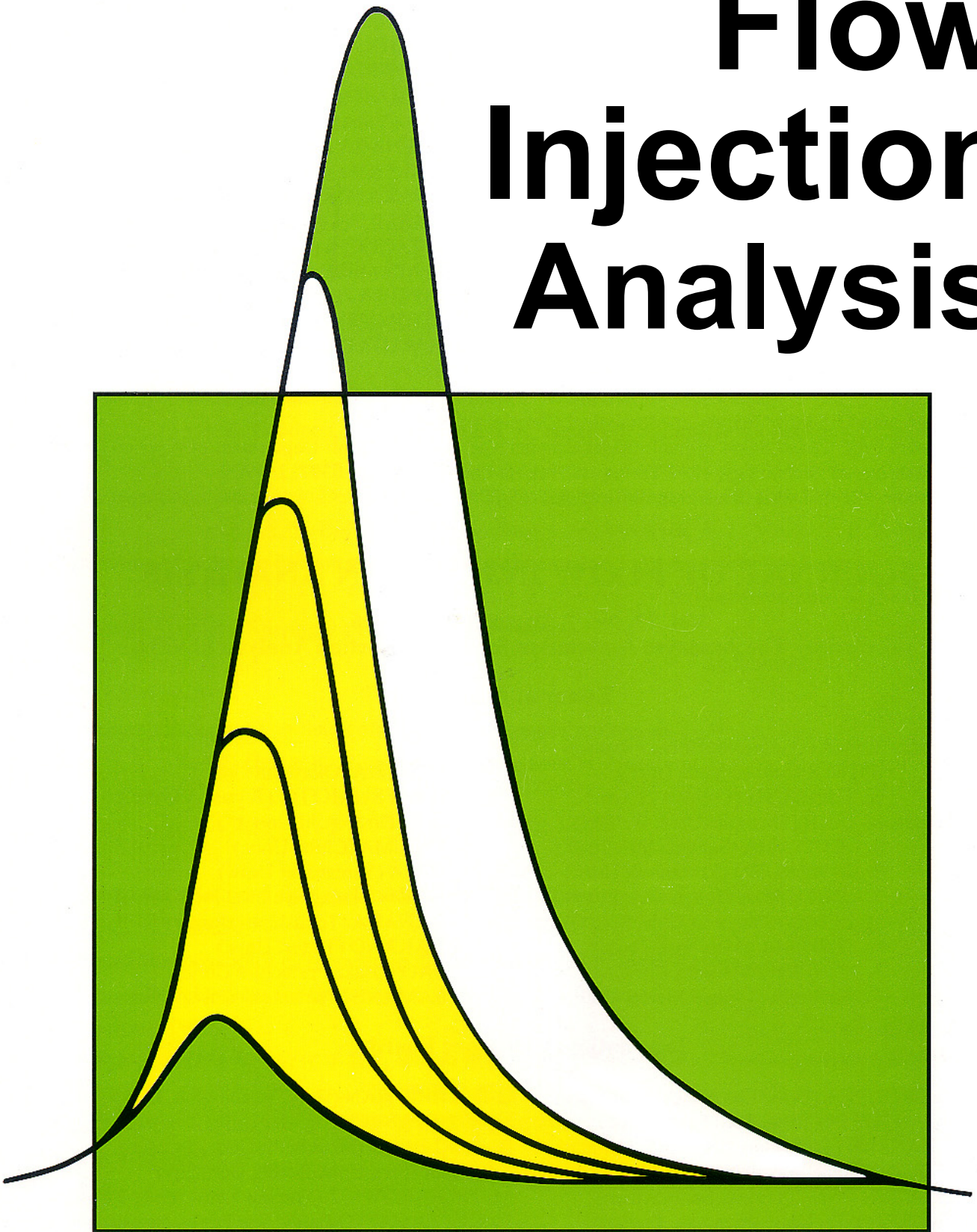


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Determination of Silicate in Anthropogenically Impacted Natural Waters using Flow Injection Spectrophotometry

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Abstract

An optimised flow injection (FI) method suitable for the determination of silicate in the presence of high concentrations of arsenate ($216 \mu\text{g As L}^{-1}$) in anthropogenically impacted natural waters is presented. The proposed method has a practical limit of detection of $10 \mu\text{g Si L}^{-1}$ and typical RSDs of $\approx 1.5\%$ ($n = 3$) and a sample throughput of 40 samples h^{-1} . Strategies are presented for the removal of matrix interferences. The manifold incorporates a thiosulfate stream to remove arsenate (AsO_4^{3-}) by reduction to arsenite (AsO_3^{3-}) and two micro-columns containing a chelating resin (iminodiacetate) to remove metal ions and an anion exchange resin (Dowex 1X8, 200–400 mesh, Cl^- form) to remove phosphate. The chelating column successfully removed matrix cations; Cu(II) at 0.1 mg L^{-1} , Ni(II), Co(II), Fe(II) and Fe(III) at 1.0 mg L^{-1} and Mn(II), Zn(II) and Pb(II) at 10 mg L^{-1} . The anion exchange column effectively removed phosphate interference by complexing up to 1.5 mg P L^{-1} and had no effect on the silicate response. A linear calibration was obtained with the optimised manifold in the range $10 - 1000 \mu\text{g Si L}^{-1}$ ($R^2 = 0.998$). This method was applied to the determination of Si in the Tamar Estuary, an area of historical mining activity, and the results compared well with those from a segmented flow analyser standard method with spectrophotometric detection ($P = 0.05$; $t_{\text{cal}} = 1.44$ and $t_{\text{crit}} = 2.14$).

Keywords Flow injection analysis, silicate, arsenate, phosphate, anthropogenically impacted natural waters

1. Introduction

The main source of silicon in natural waters is the weathering of silicate and aluminosilicate rocks and soil/sediment in runoff waters. Silicon is an essential nutrient for diatoms in natural waters and can be the limiting nutrient in surface waters during spring/summer blooms [1]. In addition to biological removal, variable inputs from silicon rich groundwaters and silting affect dissolved silicon concentrations. Silicate concentrations in UK surface waters range from below the detection limit up to 19 mg Si L^{-1} [1], with $0.02 - 2.5 \text{ mg Si L}^{-1}$ reported for the Tamar catchment [2].

Given the influence of silicon (primarily as silicate) on water quality it is surprising that there are very few reported flow injection methods for its determination. Narusawa [3] reported a spectrophotometric flow injection (FI) method for the determination of silicate, phosphate and arsenate that incorporated an anion exchange column for separation. The detection limit for Si was $1 \mu\text{M}$ at 80°C . Galhardo and Masini [4] used sequential injection analysis with spectrophotometric detection for the determination of silicate and phosphate. Oxalic acid was used to mask phosphate interference and the detection limit for SiO_3^{2-} was 1 mg L^{-1} . Grudpan et al. [5] used a stopped flow FI technique with spectrophotometric detection for the simultaneous determination of silicate and phosphate but no detection limit was reported for silicate. A more sensitive FI method, based on the oxidation of luminol in the presence of the silicomolybdenum blue complex, with chemiluminescence detection, was reported by Yaqoob et

al. [6]. The practical limit of detection was $0.35 \mu\text{g Si L}^{-1}$ and the throughput was 80 h^{-1} .

The main interferences in the spectrophotometric determination of silicate in natural waters using the molybdenum blue reaction are phosphate and arsenate. Trace metals such as copper(II) can also interfere due to direct absorbance from inorganic complexes. In nutrient rich and anthropogenically impacted waters (draining catchments with a history of mining and mineral processing such as the Tamar Valley in SW England [7]) these matrix interferences need to be removed prior to derivatisation with molybdate. The aim of this paper was therefore to develop a simple but robust FI method for the spectrophotometric determination of silicate in anthropogenically impacted natural waters containing up to $216 \mu\text{g As L}^{-1}$ (as arsenate) and 1.5 mg P L^{-1} (as phosphate). A thiosulfate stream was incorporated to reduce As(V) to As(III) and two micro-columns containing iminodiacetate and a strong anion exchanger were used to remove trace metals and phosphate respectively.

2. Experimental

2.1. Reagents

All reagents were analytical grade and prepared using ultrapure water (UPW; Elga, $18.2 \text{ m}\Omega \text{ cm}^{-1}$). Ammonium heptamolybdate, sulphuric acid, ascorbic acid, phosphate standard solution (Spectrosol 1000 mg P L^{-1}) and antimonyl potassium (+)tartrate (all BDH), sodium metasilicate and sodium arsenate heptahydrate (Sigma),

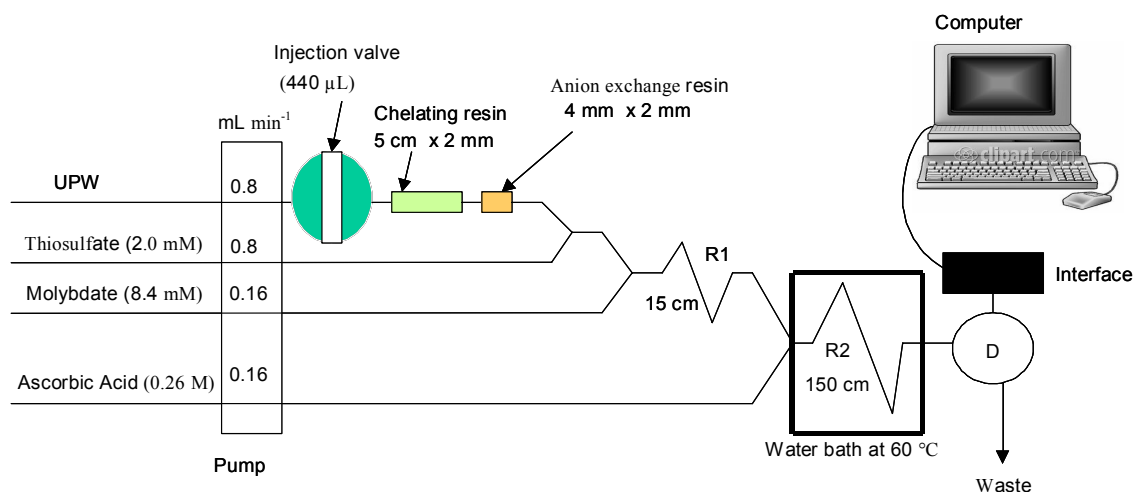


Fig. 1 Optimised four line FI manifold incorporating a thiosulfate stream for the determination of Si in the presence of $>300 \mu\text{g As L}^{-1}$ in natural waters. Detector wavelength 800 nm, reaction coil temperature 60 °C.

sodium thiosulfate (Fisher) and low nutrient seawater (LNS, salinity 35, Ocean Scientific, UK) were used as received. In order to minimise contamination, all glassware and high-density polyethylene (HDPE) storage bottles for reagent solutions were acid cleaned following a standard procedure [8]. All reagents and standards were prepared on the day of use in UPW from stock solutions which were stored in the dark, unless otherwise stated. Silicon standards ($0.4 - 2.0 \text{ mg SiO}_2 \text{ L}^{-1}$) were prepared from a 1000 mg L^{-1} stock of sodium metasilicate ($\text{Na}_2\text{O}_3\text{Si}\cdot 9\text{H}_2\text{O}$), phosphate standards ($0.1 - 0.5 \text{ mg P L}^{-1}$) were prepared from a 1000 mg L^{-1} stock of potassium hydrogen phosphate and arsenic standards ($0.05 - 1.0 \text{ mg As L}^{-1}$) were prepared from a 50 mg L^{-1} stock of sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$) in 2% HNO_3 . The ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) reagent (8.4 mM) containing antimonyl potassium tartrate ($\text{KSbO}\cdot\text{C}_4\text{H}_4\text{O}_6$) (1.5 mM) was prepared by dilution of a 0.1 M stock with appropriate volumes of UPW and sulfuric acid (2.0 M stock). The ascorbic acid reagent (0.26 M) was prepared daily by dissolving 4.6 g in 100 mL of UPW. The sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$) reagent (2.0 mM) was prepared fresh as required in UPW. Salinity matrices in the salinity range 10-30 were prepared by mixing appropriate volumes of LNS and UPW. A divinylbenzene strong anion exchanger (Dowex 1X8 200 – 400 mesh, Cl^- form) and an iminodiacetate chelating resin (Chelex 100) immobilized on 1 % cross-linked polystyrene (50-100 dry mesh sodium form) were used to prepare the micro-columns.

2.2. Instrumentation and procedures

The optimised four line FI manifold (Fig. 1) incorporated 0.75 mm i.d. PTFE tubing, a peristaltic pump (Gilson Minipuls 2, Villiers le Bel, France) and a Rheodyne six-port injection valve. The peristaltic pump was used to propel the carrier and thiosulfate streams at 0.80 mL min^{-1} and the two reagent streams at 0.16 mL min^{-1} . The rotary injection valve was used to inject 440 μL of sample into the carrier stream. Sample and carrier mixed at a T-piece with the thiosulfate stream where As(V) was reduced to As(III). This then mixed with the molybdate reagent at another T-piece and finally with the ascorbic acid reductant in a water

bath at 60 °C. The mixture was then pumped into a uv/visible/nir (320 – 2500 nm) spectrophotometer (PU8620, Philips, Cambridge, England) equipped with a 30 μL flow cell (178.011-OS optical glass, 10 mm path length, Hellma UK, Southend on Sea, England) and the absorbance monitored at 800 nm. Detector output was automatically recorded using an in-house LabVIEW™ software programme.

A uv-visible spectrophotometer (Hewlett Packard HP84553) was used to obtain an absorbance spectrum of the silicomolybdenum blue complex formed using the manifold described in Fig.1 in order to determine the wavelength of maximum absorbance for the FI manifold. Water samples collected from a transect of the Tamar Estuary on 29th April 2004 were filtered in situ using a 0.45 μm cellulose acetate filter, 47 mm diameter (Whatman) and stored in acid washed HDPE containers. Samples were analysed within 24 h and, when possible, stored at 4 °C prior to analysis. If samples needed to be stored for longer periods they were frozen at $-20 \text{ }^\circ\text{C}$. Phosphate was determined using a segmented flow analyser method with spectrophotometric detection [9]. Total arsenic was determined using hydride generation atomic absorption spectrometry (HGAAS) for saline samples and ICP-MS for freshwater samples.

3. Results and Discussion

3.1. Optimisation of variables

Key experimental variables were investigated using the FI manifold shown in Fig. 1 but with the two micro-columns and the thiosulfate stream removed. The formation of the silicomolybdenum blue complex is favoured at higher temperatures as shown in Fig. 2 but the optimum for this manifold was 60 °C because at 70 °C and above doublet peaks were observed and interferences increased. The pH of the reaction is a critical parameter and Fig. 3A shows that a $[\text{H}^+]$ of 0.62 M in the molybdate reagent gave the best signal-to-blank ratio. Fig. 3B shows that complex formation increased linearly with increasing molybdate concentration. However above 8.4 mM molybdate the blank signal increased significantly due to

self-reduction [25]. The optimised H^+ (0.62 M) and molybdate (8.4 mM) concentrations gave a $[H^+]:[molybdate]$ ratio of 74 and a final reaction pH, after merging with the carrier stream, of 1.2, which compares well with the optimum range for molybdenum blue complex formation reported for batch methods [10].

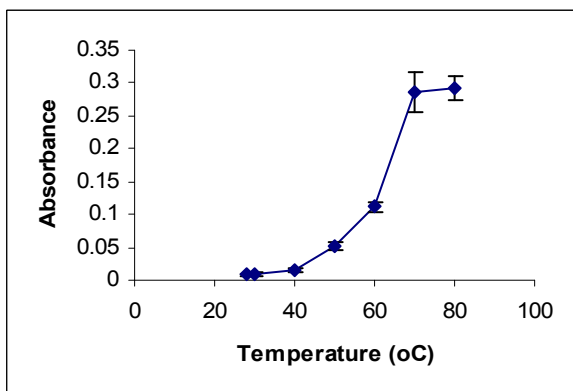


Fig. 2 Effect of temperature on silicate determination using $47 \mu\text{g Si L}^{-1}$. Error bars indicate $\pm 3s$ ($n = 3$).

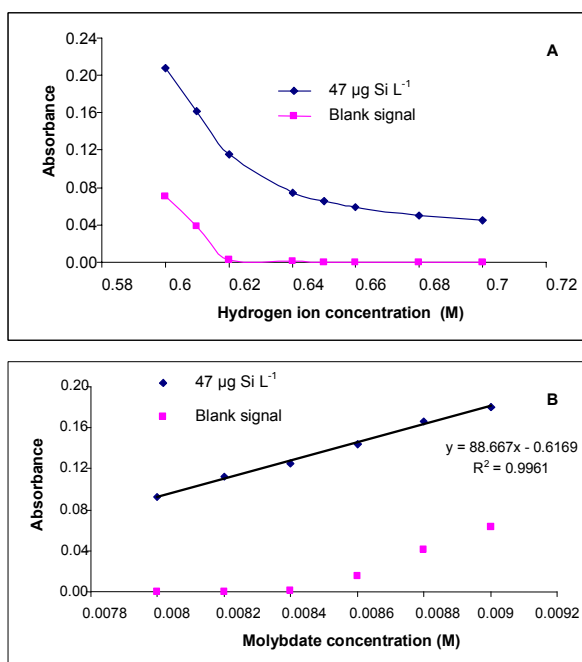


Fig. 3 (A) Effect of hydrogen ion concentration on the determination of silicate using $47 \mu\text{g Si L}^{-1}$, ($n = 3$). High blank signal at low $[H^+]$ and suppressed response at high $[H^+]$ were observed. (B) Effect of molybdate concentration on the determination of silicate using $47 \mu\text{g Si L}^{-1}$ and 0.62 M $[H^+]$.

3.2. Interferences

Figure 4 shows the effect of a range of potential anionic interferences of the determination of silicate. These data were obtained using the reported FI manifold except that the two micro-columns and the thiosulfate stream were removed. The results confirm that phosphate and arsenate are the only significant anionic interferences in

freshwater systems. In estuarine samples (salinity >2) chloride would also interfere but this is overcome by matrix matching the carrier stream by mixing UPW with an appropriate volume of low nutrient seawater and pumping for 5 min to equilibrate the system before sample injection.

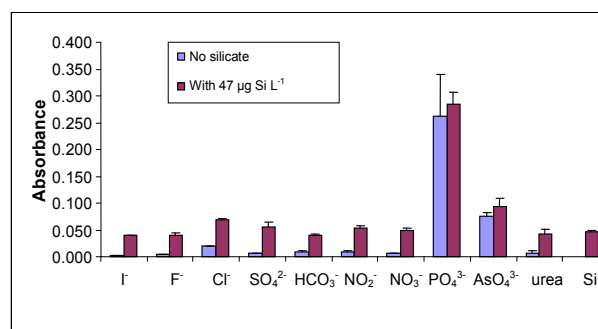


Fig. 4 Effect of anions on the determination of silicate using the FI manifold with the two micro-columns and the thiosulfate stream removed. Error bars indicate $\pm 3s$ ($n = 3$). The anion concentrations used were (mg L^{-1}), I^- (1), F^- (1), Cl^- (2,000), SO_4^{2-} (500), HCO_3^- (100), NO_2^- (1), NO_3^- (30), PO_4^{3-} (0.1), AsO_4^{3-} (0.05) and urea (1). For comparison the silicate response ($47 \mu\text{g Si L}^{-1}$) is also shown.

Oxalic acid is commonly used to mask interferences from phosphate by promoting ligand exchange between silicate and phosphate in the complex [4] but was not suitable in this manifold (over the range 0.0005–0.1 M) because it also suppressed the response for silicate and hence degraded the detection limit. An anion exchange micro-column (4 mm length \times 2.0 mm i.d.) containing 50 mg of a strongly basic resin was therefore incorporated in the FI manifold [6] and was highly effective in masking phosphate without suppressing the silicate ($47 \mu\text{g Si L}^{-1}$) response due to the higher affinity of the resin for phosphate. Thirty phosphate standards covering the range 330 - 1500 $\mu\text{g P L}^{-1}$ were injected onto the column and no response was observed (signals < 0.003 absorbance units). The micro-column was therefore used for all future experiments.

Fig. 4 also shows that arsenate gives a positive interference using the standard FI manifold. A thiosulfate stream was therefore added to the manifold and the effect of injecting an arsenate standard ($216 \mu\text{g As L}^{-1}$) was observed at various thiosulfate concentrations (0.5 – 10 mM). Concentrations >2 mM had an increasingly deleterious effect on the baseline but 2 mM gave a steady baseline and only a 0.002 absorbance units signal for $216 \mu\text{g As L}^{-1}$, with negligible effect on the silicate response.

Some metal ions, particularly Cu(II), Ni(II) and Cr(III) can interfere with molybdenum blue formation [10] so a micro-column (5 mm length \times 2.0 mm i.d.) containing iminodiacetate chelating resin was also incorporated in the FI manifold. Highly elevated freshwater concentrations of various cations were then injected into the manifold, both with and without silicate ($47 \mu\text{g Si L}^{-1}$) present and the results are shown in Fig. 5. Only Cu(II) at 0.1 mg L^{-1} gave any significant interference but this is in excess of the copper concentration found in most natural waters (all Tamar Estuary samples analysed in this study were $< 20 \mu\text{g Cu L}^{-1}$).

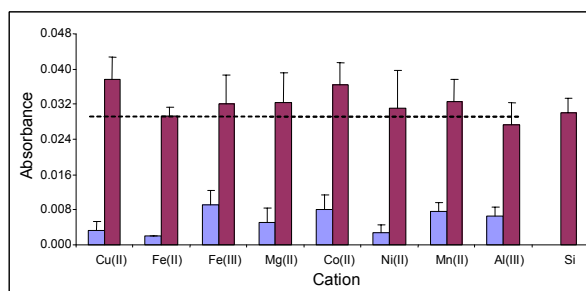


Fig 5 Cationic interferences on the determination of silicate using the optimised FI manifold incorporating a chelating resin micro-column. The cations used were (mg L⁻¹); Mg(II) (100), Mn(II) (10), Cu(II) (0.1), Zn(II) (10), Pb(II) (10), Al(III) (10), Ni(II) (1), Co(II) (1), Fe(II) (1) and Fe(III) 1. The data show the response in the absence of silicate (light bars) and in the presence of 47 µg Si L⁻¹ (dark bars). The dashed line represents the response for 47 µg Si L⁻¹ in the absence of any cations.

3.3. Analytical performance

A linear range of 10 - 1000 µg Si L⁻¹ ($R^2 = 0.9984$) was obtained using the manifold shown in Fig. 1 and the equation of the line was y (absorbance units) = 0.0005 x (µg Si L⁻¹) + 0.0276. The limit of detection was 10 µg Si L⁻¹ and RSDs were in the range 1.0 – 2.7 % ($n = 3$). The throughput was 40 h⁻¹ for standards and freshwater samples.

3.4. Application of the FI method to the determination of silicate in natural waters

The Tamar Estuary, fed by the rivers Tamar, Lynher and Tavy, is situated in SW England and flows into the Western English Channel. The Tamar River provides the main input of fresh water and the catchment is heavily impacted by historical mining activity.

Water samples from various locations in the Tamar Estuary were collected as grab samples on 29th April 2004 and analysed using the proposed method for silicate. A segmented flow analyser method with spectrophotometric detection was used as a reference method and was shown to be free of interference from phosphate and arsenate. The results for silicate (mg Si L⁻¹) are presented in Table 1, with phosphate (µg P L⁻¹) and total arsenic (µg As L⁻¹) data shown for comparative purposes. Relative standard deviations were all < 5% for three replicates and a paired t-test ($p = 0.05$) showed that the results from the two methods were not significantly different ($t_{\text{calc}} = 1.44$ and $t_{\text{crit}} = 2.14$).

Phosphate concentrations were typical of those reported for the Tamar Estuary [11] and were an order of magnitude lower than the highest concentration used to validate the method (1.5 mg P L⁻¹). The highest total arsenic concentration observed during the campaign was 35 µg As L⁻¹, which is indicative of an impacted environment but nearly tenfold lower than the concentration investigated during the interference study.

Table 1 Comparison of the FI method with a segmented flow analyser (Skalar) reference method for the determination of silicate (mg Si L⁻¹) in Tamar Estuary samples.

Location	Salinity	Si (Skalar)	Si (FI)	P	As
Weir Quay	28	0.5	0.4	94	18
Tamar Bridge	30	0.4	0.4	94	16
Neal Point	29	0.4	0.4	70	23
Weir Quay	11	0.6	0.5	104	19
Halton Quay	14	1.1	1.2	105	14
Southward Fm.	8	1.2	1.2	101	16
Calstock	0	1.3	1.2	108	33
Rumleigh Fm.	0	1.2	1.2	99	13
Morwellham	0	2.0	2.0	151	16
Weir Head	0	1.2	1.3	88	4
Morwellham	0	1.2	1.2	85	15
Rumleigh Fm.	0	1.3	1.2	144	38
Calstock	0	1.3	1.3	94	14
Southward Fm.	8	1.2	1.0	108	18
Halton Quay	19	1.1	1.1	107	13
Weir Quay	29	0.5	0.4	85	20

4. Conclusions

A FI spectrophotometric method for the determination of silicate in natural waters has been developed and provides reliable results in the presence of high concentrations of phosphate and arsenate. Arsenate was masked by on-line reduction with thiosulfate, phosphate was removed by a micro-column containing strong anion exchange resin and cations were removed by a micro-column containing an iminodiacetate chelating resin. In addition the FI method was optimised at a very low (47 µg Si L⁻¹) silicate concentration compared with typical freshwater concentrations (0.4 – 2.0 mg Si L⁻¹) which emphasises the suitability of the method for silicate depleted waters.

The proposed FI manifold therefore offers the advantages of relatively easy field deployment, rapid response time and reliable performance in silicate depleted waters. Silicate concentrations in anthropogenically impacted Tamar Estuary samples obtained using the optimised FI method showed good agreement with a laboratory segmented flow analyser reference method and confirmed the potential of the method for field deployment.

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