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Energy-dispersive X-ray spectrometry combined with directly suspended droplet microextraction for determination of dissolved silicate in surface water *via* silicomolybdenum blue complex

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A B S T R A C T

Energy-dispersive X-ray fluorescence spectrometry (EDXRF) is a well-established analytical technique successfully applied with good precision and accuracy to determination of many elements. However, in the case of elements of low atomic number, such as silicon, direct determination is hampered due to low fluorescence yield and relatively low energy easily absorbed by sample matrix. An indirect method for determining surface water silicate is thus proposed. The method is based on silicate determination *via* molybdenum present in silicomolybdenum blue complex. Determination follows directly suspended droplet microextraction. Optimum conditions for both microextraction and EDXRF measurement were studied. A good ratio of silicon to molybdenum (1–41) and a sensitive K_α line of molybdenum make it possible to determine low concentrations of silicate. Under optimized conditions, good linearity, up to 3 $\mu g\,mL^{-1}$ ($r=0.9990$), and good detection limit (6 $ng\,mL^{-1}$) were achieved. The total RSD for the EDXRF determination of silicate following DSDME was 6.7%. Taking into account all steps preceding the determination and the uncertainty of XRF measurements, the proposed method can be recognized as precise. The enrichment factor was 140. The developed method was used to determine dissolved silicate content in surface water samples. The accuracy and repeatability of the proposed procedure were checked by standard addition method and compared to the results obtained using ICP-OES technique. The recovery (92.2–96%) was satisfactory and indicates usefulness of the developed procedure.

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1. Introduction

Determination of trace amounts of silicate in water samples is presently of special concern in such applications as semiconductors, metallurgical products, industrial and purified waters as well as production of pure reagents or biomedical samples. Considering low concentration of silicate in water, reliable and high-quality analytical techniques and procedures are strongly desired.

Different analytical techniques have been proposed so far to determine silicate, including spectrophotometry [1–5], atomic absorption spectrometry (AAS) [6–8], inductively coupled plasma atomic emission spectrometry (ICP-OES) [6,9–10], and inductively coupled plasma mass spectrometry (ICP-MS) [6,11–12], ion chromatography (IC) [13–17] or capillary electrophoresis (CE) [18]. The interest in sensitive methods of silicate determination is evident since many of the reported methods have drawbacks or suffer from interference, *e.g.* (in ICP-MS) from polyatomic ions produced by nitrogen, oxygen, hydrogen and carbon or (in ICP-OES), due to the influence of acid digestion mixtures when Si and other silicate-bound elements are dissolved. In some cases, the required instruments are expensive and their day-to-day maintenance cost is high. Furthermore, direct determination of silicate in water samples is usually hampered due to its low concentration and various types of inherent interferences. Thus, a preconcentration step is often required prior to measurement in order to improve detection limits and to remove matrix effects.

Energy dispersive X-ray fluorescence spectrometry (EDXRF) is a well-established instrumental technique which has a truly multi-element character and can be successfully applied to determine several elements with good precision and accuracy. However, direct EDXRF analysis of liquid samples is difficult due to the behavior of liquid samples during XRF analysis (under X-ray irradiation solution heating and formation of bubbles occur) and due to high X-ray scatter background resulting in essential errors such as a poor signal-to-noise ratio. Furthermore, typical detection limits of conventional direct XRF analysis with 30 min counting time are in the $mg\,L^{-1}$ range which is not satisfactory for environmental analysis [19]. Moreover, in the case of elements of low atomic number such as silicon, direct determination is hampered due to low fluorescence yield and relatively low energy easily absorbed by sample matrix. Therefore, EDXRF determination of trace elements in liquid samples usually requires a preconcentration step.

The use of preconcentration usually improves detection limit, increases sensitivity and accuracy of results by several orders but, on the other hand, increases time required for analysis.

A great progress in the application of EDXRF technique for trace analysis of liquid samples was made by introducing to laboratory practice the liquid–liquid microextraction (LLME). As a preconcentration step, LLME offers short extraction time, ease of operation, low cost, and high enrichment factor. Moreover, it eliminates, or significantly reduces, the use of chemicals, in particular organic solvents. From EDXRF perspective, small volume of organic phase-containing enriched analyte can be easily evaporated to obtain a solid thin target suitable for XRF analysis. Compared to spectroscopic techniques usually combined with LLME, in EDXRF there is no need to dilute extractant phase prior to measurement, so the obtained enrichment factors are significantly higher [20–26].

In this paper, a method of EDXRF determination of silicate dissolved in surface water is described. The proposed procedure takes advantage of directly suspended droplet microextraction (DSDME) of silicomolybdenum blue complex into isoamyl alcohol. The enriched extractant phase separated from water sample is then deposited onto a Millipore filter and the K_α line of molybdenum is recorded by EDXRF. This technique allows preconcentrating the analyte as well as measuring an efficient X-ray fluorescence emitter (41:1 ratio to silicon). The proposed method offers high sensitivity of silicate determination, low consumption of both sample and organic solvent, simplicity of sample preparation, and low operating costs. To the best of my knowledge, DSDME as a step that allows preconcentrating trace amounts of silicate has not been used in combination with any spectroscopic technique, nor with XRF determination of silicon in the form of silicate (via silicomolybdenum blue complex). However, the original pattern for the strategy adapted in this paper for the detection of Si was previously succesfully applied for phosphate determination in water samples [27].

2. Experimental

2.1. Reagents and materials

All reagents were of analytical grade. Deionized water from a Milli-Q system was used for solution preparation. A stock standard solution of silicon (1 mg mL^{-1}) was purchased from Merck. Working standard solutions were prepared daily by suitable dilution of the stock solution. Other reagents used in the developed procedure were: 5% (m/v) hexaammonium heptamolybdate tetrahydrate solution (POCh), 2% hydrazine sulfate (m/v) solution (POCh), 2% (m/v) oxalic acid solution (POCh), 1 mol L^{-1} sulfuric acid solution (POCh), 1-butanol (POCh), 1-hexanol (Acros), isoamyl alcohol (POCh) and methyl isobutyl ketone (Fluka). The pH levels were adjusted with 0.1 and 0.01 mol L^{-1} H$_2$SO$_4$ solutions.

2.2. Instrumentation

The measurements were performed using a laboratory-constructed EDXRF spectrometer. The air-cooled side window Rh target X-ray tube of ca. 100 μm nominal focal spot size (XTF 5011/75, Oxford Instruments, USA) supplied by an XLG high-voltage generator (Spellman, USA) were used as excitation sources. The X-ray tube was operated at 45 kV and 600 μA. The counting time was 300 s. X-ray spectra emitted by the sample were collected using a thermoelectrically cooled Si-PIN detector (XR-100CR Amptek, Bedford, MA, USA) with a 145 eV resolution at 5.9 KeV that was coupled to a multichannel analyzer (PX4 Amptek, Bedford, MA, USA). The spectrometer is described in detail in Ref. 28. The deconvolution of X-ray spectra was performed using XRF-FP Amptek software.

Measurements were also carried out using SpecroFMS16a spectrometer with excitation in the ICP plasma (Spectro Analytical Instruments) and application of the following operating parameters: plasma power – 1.4 kW, coolant gas – Ar, 12 L min^{-1}, auxiliary gas – Ar, 1 L min^{-1}, nebulizer gas – Ar, 1 L min^{-1}, nebulizer pressure – 3.2 bar, nebulizer-cross-flow type, sample uptake rate – 2 mL min^{-1}, wavelength – 251.611 nm.

pH measurements were performed using pH-meter CP-315 (Elmetron) with a combination glass electrode.

2.3. DSDME procedure

An aliquot (5 mL) of the solution, containing less than 15 μg of Si, was placed in a polypropylene vial. Then, 200 μL of 5% ammonium molybdate was added and pH of the sample was adjusted to 1.3 using 0.1 mol L^{-1} H$_2$SO$_4$. The sample was sonicated and heated (80 °C) in an ultrasonic bath for 40 min. After cooling, 1.2 mL of 1 mol L^{-1} H$_2$SO$_4$, 1 mL of 2% hydrazine sulfate (m/v), and 250 μL of isoamyl alcohol were added. The sample was shaken for 5 min and centrifuged for 10 min at 4000 rpm. Next, 20 μL of the organic phase was deposited (using a microsyringe) in 3 portions onto a 5-mm diameter Millipore 390 filter with intermittent drying of the filter. The blank sample was prepared in the same
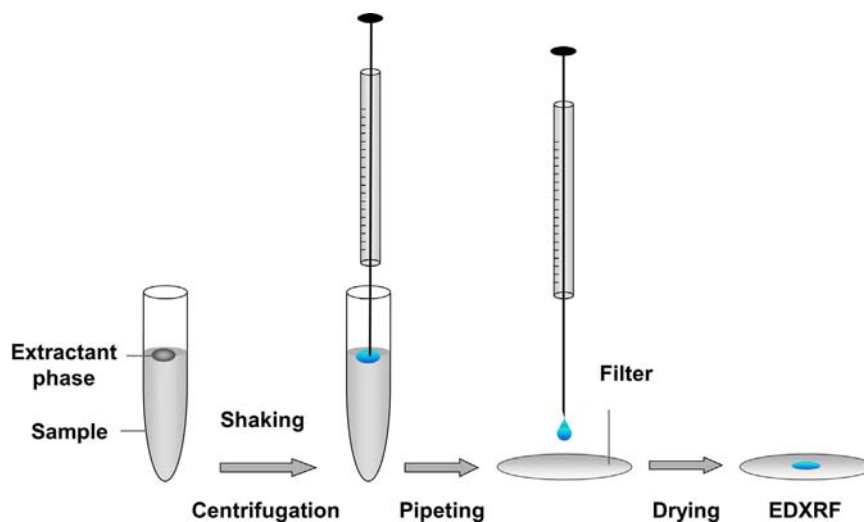

Fig. 1. DSDME procedure applied prior to EDXRF measurements.

way as described above, but 5 mL of high-purity water was added instead of silicate solution. The analytical procedure is shown in Fig. 1.

3. Results and discussion

EDXRF spectrum of a sample containing 10 μg of silicon is shown in Fig. 2. As can be seen, K_α line of silicon is not sensitive enough to be used for determining trace amounts of silicate due to low energy (1.74 keV), usually absorbed by sample matrix, as well as low fluorescence yield ($\omega_{Si}=0.05$). In such cases, to improve the detection limit, indirect EDXRF determination *via* more efficient X-ray fluorescence emitters is usually proposed. In this study, determination of silicon *via* K_α line of molybdenum present in the silicomolybdenum blue complex was performed. As emitter, molybdenum has excellent sensitivity compared to silicon, resulting from high fluorescent yield ($\omega_{Mo}=0.77$). Moreover, molybdenum is strongly excited by characteristic radiation of the rhodium target X-ray tube, owing to a very small distance of rhodium K_α and K_β lines (20.20 and 22.71 keV, respectively) from the absorption edges of molybdenum (20.00 keV). Furthermore, favorable weight ratio between silicon and molybdenum in the silicomolybdenum blue complex (1:41) makes the proposed methodology very sensitive.

The proposed method of EDXRF determination of dissolved silicate is based on the formation of silicomolybdenum blue complex and its extraction into a microvolume of an organic solvent. The following complex formation reactions apply:

$$SiO_4^{4-} + 12MoO_4^{2-} + 28H^+ \rightarrow H_4SiMo_{12}O_{40} + 12H_2O \quad (1)$$

$$H_4SiO_4(MoO_3)_{12} \xrightarrow{\text{reduction}} \text{silicomolybdenum blue} \quad (2)$$

The first reaction, formation of 12-molybdosilicate heteropoly acid (HPA), is a rate-limiting step in silicate determination. It depends on some experimental parameters such as pH, sonication time, temperature and concentration of ammonium molybdate. The second reaction, reduction of HPA to silicomolybdenum blue complex and its microextraction, is faster and depends on the concentration of sulfuric acid and hydrazine sulfate, as well as organic solvent type and volume, and extraction time. All parameters influencing the formation of silicomolybdenum blue complex were optimized independently and in all cases three replicate measurements were carried out. Optimization studies were performed with 10 μg of silicon aqueous standard.
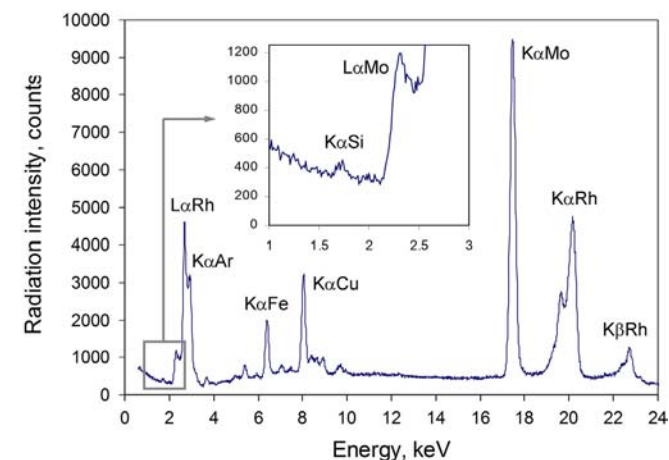

Fig. 2. EDXRF spectrum of a sample containing 10 μg of silicon.

3.1. Optimization of the HPA formation

Initial studies showed that EDXRF determination of silicates *via* silicomolybdenum blue complex strongly depends on the formation reaction of HPA. It is well known that this reaction occurs slowly. According to literature data, to speed up the complex formation, sample heating has been usually employed. Ultrasound can also facilitate the formation of heteropolyacids [29]. Therefore, influence of both sonication time and temperature on the formation of HPA was tested.

The effect of sonication time (5–60 min. range, 60 °C) was studied using solutions of fixed pH, analyte and reagents' concentration. As shown in Fig. 3a, extending sonication time up to 40 min brings an increase of the analytical signal resulting from faster achievement of equilibrium state during HPA formation. Above 40 min, radiation intensity of the complex remained fairly constant. Thus, a sonication time of 40 min was selected for further studies.

The effect of temperature (20–90 °C, 40 min sonication) was also studied using solutions of fixed pH, analyte and reagents' concentration. As shown in Fig. 3b, temperature elevation up to 80 °C increases significantly the analytical signal as a result of speeding up HPA formation reaction. Above 80 °C the radiation intensity of the complex remained fairly constant. Hence, a temperature of 80 °C was selected for further studies.

HPA formation reaction strongly depends also on pH and molybdate concentration. Thus, influence of these two parameters on the measured analytical signals was studied.

The effect of pH value (1–1.5) on the fluorescent radiation intensity of the HPA complex is shown in Fig. 3c. Sensitivity of the reaction increases with rising pH up to 1.3. Above this pH, analytical signal decreases with decreased concentration of the acid. The highest and constant radiation intensity of the complex was obtained for pH 1.3 and this value was chosen for further experiments.

The effect of ammonium molybdate concentration (6.5×10^{-4}–1.8×10^{-3} mol L^{-1}) on the radiation intensity of the complex was also studied and the results of experiments are shown in Fig. 3d. They indicate that the addition of molybdate gives rise to an increased analytical signal, up to 8.1×10^{-4} mol L^{-1}. Therefore, further experiments were performed with 8.1×10^{-4} mol L^{-1} ammonium molybdate in the sample.

3.2. Optimization of silicomolybdenum blue complex formation and microextraction

3.2.1. Selection of organic solvent type and volume

The criteria of solvent selection in DSDME include high enrichment factor, low volatility, low water solubility and density lower than that of water. Taking into account silicomolybdenum blue complex solubility in oxygen solvents, four of them having different physicochemical properties were tested. They included 1-butanol, 1-hexanol, isoamyl alcohol and MIBK (water solubility 63.2 g L^{-1} [30], 5.9 mg L^{-1} [31], 26.7 g L^{-1} [32] and 19 mg L^{-1} [33] at 25 °C, respectively). Extraction efficiency of the studied solvents decreased in the following order: isoamyl alcohol > 1-butanol > MBIK > 1-hexanol (in the case of 1-hexanol the extraction process did not occur). The highest extraction efficiency was achieved using isoamyl alcohol and this solvent was selected for further studies as extractant. Moreover, it forms a stable and well-defined drop after centrifugation which facilitates uptake of the enrichment extractant phase separated from the water sample.

The impact of isoamyl alcohol volume used (200–300 μL) on the extraction efficiency of the complex was also studied (Fig. 4a). At volumes lower than 200 μL the drop did not form due to high solubility of isoamyl alcohol in water. It was noted that the enrichment factor at equilibrium increases with decreasing solvent
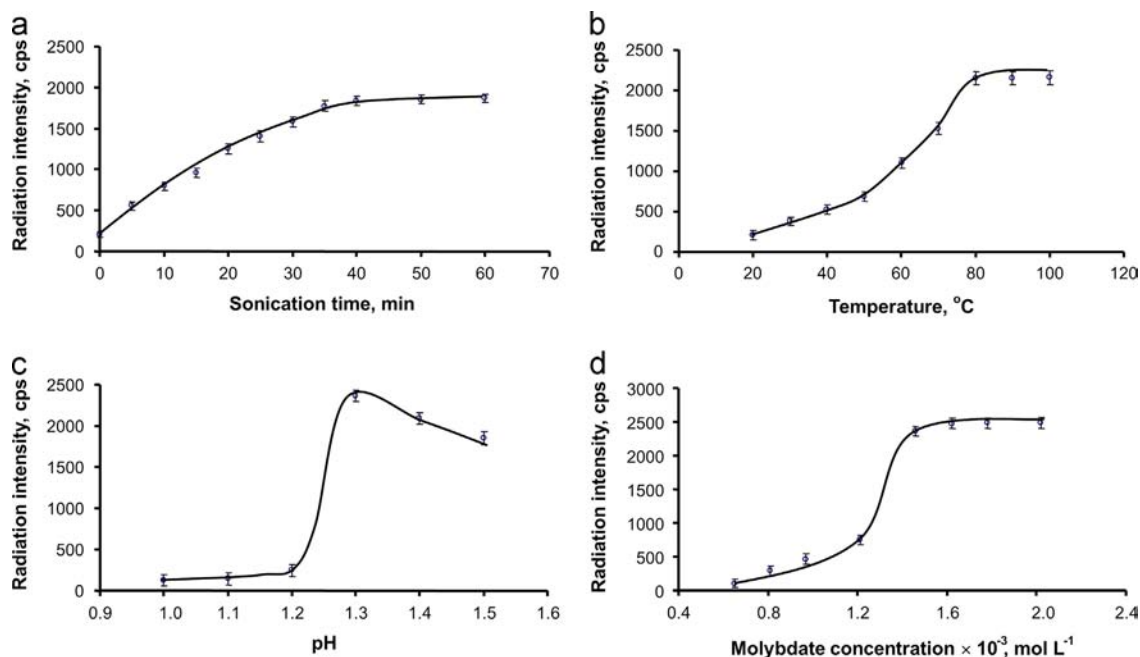
Fig. 3. The influence of: (a) sonication time; (b) temperature; (c) pH, and (d) molybdate concentration on radiation intensity of the molybdenum blue complex by the proposed procedure. Error bars represent standard deviation for $N=3$.

Fig. 4. The influence of (a) isoamyl alcohol volume; (b) extraction time; (c) H_2SO_4 concentration, and (d) hydrazine sulfate concentration on radiation intensity of the molybdenum blue complex by the proposed procedure. Error bars represent standard deviation for $N=3$.
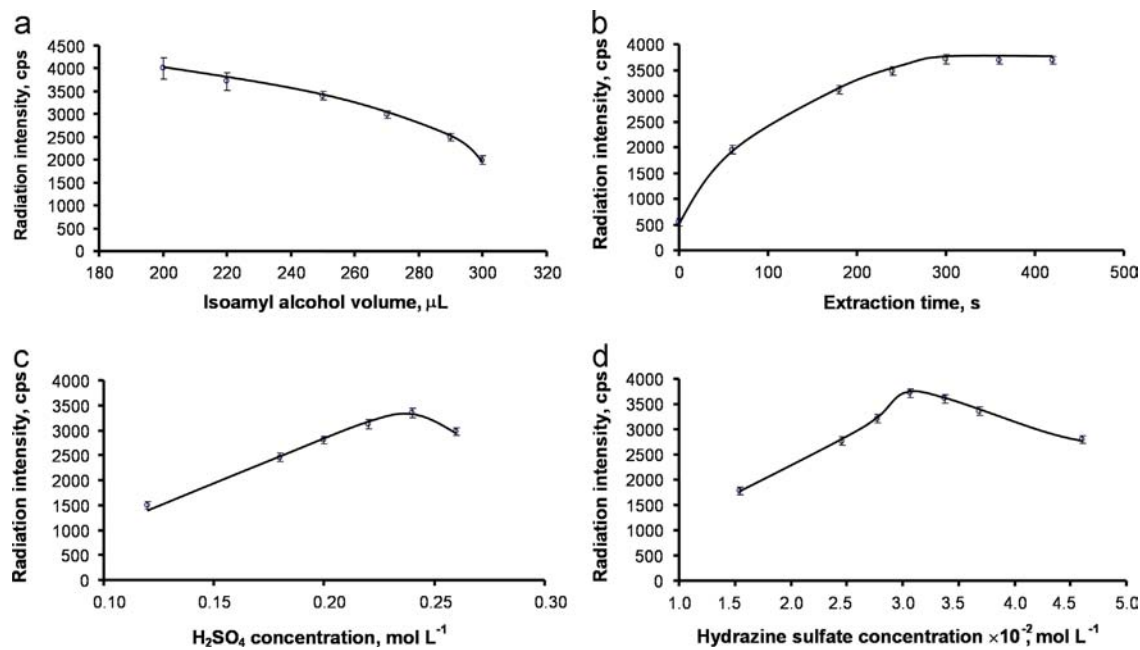
volume, but the time to achieve equilibrium state is longer. Moreover, using solvent volumes lower than 250 μL brings about higher blank values and worse repeatability, due to smaller drop and difficulty in uptaking the organic phase into a microsyringe. Accordingly, a 250 μL volume of isoamyl alcohol was selected as the most suitable. After the extraction process, volume of the organic phase was 35 ± 3 μL. For EDXRF determination, 20 μL of the enrichment extractant phase was used.

3.2.2. Extraction time

Mass transfer within the droplet is a limiting step of microextraction kinetics. If the process is only driven by molecular diffusion, time required to approach the equilibrium state is long. Owing to sample mixing, both molecular diffusion and convective mass transfer occur in a droplet and equilibrium state is achieved faster. In classical DSDME, to intensify mass transfer the sample is vortexed. However, in this study shaking of the sample was employed. Due to strong dispersion of the organic phase following mechanical shaking, it was necessary to centrifuge the sample to obtain a well-defined drop of the enrichment extractant phase. The effect of shaking time length on the extraction efficiency was checked (0–420 s). As shown in Fig. 4b, longer shaking time (up to 300 s) increases analytical signal as a result of enhanced mass transfer. At times longer than 300 s radiation intensity of the complex remained fairly constant. Shaking time of 300 s was thus selected for further studies.

3.2.3. Effect of sulfuric acid concentration

The reduction of 12-molybdosilicate heteropoly acid to a blue complex strongly depends on the concentration of sulfuric acid, due to the possibility of self-reduction of the molybdate (non-phosphate sensitized reduction) under low acidity conditions [34]. The effect of sulfuric acid concentration (1.2×10^{-1}–2.6×10^{-1} mol L^{-1}) on the radiation intensity of the complex was studied. As shown in Fig. 4c, sensitivity of the reaction increased with higher concentrations of sulfuric acid, up to 2.4×10^{-1} mol L^{-1}. Above this concentration the analytical signal decreased. The highest and constant radiation intensity of the complex was obtained for 2.4×10^{-1} mol L^{-1} value and this concentration was selected for further experiments.

3.2.4. Effect of reductor concentration

The type and concentration of reductor both influence the kinetics of HPA reduction and the stability of molybdenum blue complex. Ascorbic acid [2,4,5,16,35,36], tin(II) chloride [37] and 1-amino-2 naphtol-4-sulfonic acid [38] are the most common reductants used in determining silicate concentration in natural waters. Ascorbic acid has a major disadvantage of developing color slowly [37]. The addition of antimony to ascorbic acid increases the rate of HPA reduction [39]. When using tin(II) chloride, unstability of the silicomolybdenum blue complex has been observed. On the other hand, this compound offers a much faster reaction rate than ascorbic acid [37]. In the present study hydrazine sulfate was employed for reduction of 12-molybdosilicate heteropoly acid. The reductor action is temperature-independent; a stable blue complex is formed and the reaction kinetics is satisfactory. The effect of hydrazine sulfate concentration (1.5×10^{-2}–4.6×10^{-2} mol L^{-1}) on radiation intensity of the blue complex was studied and the results of experiments are presented in Fig. 4d. The obtained results indicate that the addition of reductant up to 3.1×10^{-2} mol L^{-1} increases the analytical signal. Above this concentration radiation intensity of the complex remained fairly constant. Therefore, 3.1×10^{-2} mol L^{-1} hydrazine sulfate concentration in the sample was selected for further studies.

3.3. Interferences

Phosphate is the major potential interferent when determining silicate in surface waters due to the fact that both have similar reaction chemistries with molybdate in acidic solution. Ground waters rarely contain more than 0.1 mg L^{-1} phosphorus unless they have passed through soil containing phosphate or have been polluted by organic matter [40]. Thus, the effect of phosphate content on determination of silicate by the proposed method was investigated. The obtained results show that, at optimal conditions, phosphate does not affect silicate determination if the former is present in quantities equal or lower than that of silicate. Above 1:1 ratio the radiation intensity of phosphate is increased compared to the results obtained for standard solution of silicate. To avoid interference of phosphate on determination of silicate, a selective masking with oxalate was used. Oxalic acid suppresses interference from phosphate by decomposing molybdophosphate without affecting the molybdosilicate formation [41]. The studies showed that 0.009 mol L^{-1} oxalic acid is sufficient to eliminate the effect of 8-fold weight excess of phosphate over silicate. The studied phosphate content is far higher than normal phosphate content in surface waters.

3.4. Analytical characteristics of the method

In order to construct a calibration curve, reference samples containing varying concentrations of silicate were prepared under conditions optimized for both extraction and measurement steps.

The calibration plot was linear in the 0.06–3 µg mL^{-1} range of silicate ion. The obtained regression coefficient was 0.9990. A nonlinearity observed above 3 µg mL^{-1} can be explained by self-absorption effects which increase with increasing thickness of the dried residue.

The detection limit (DL) calculated from the equation: $DL = (3/K)(B/t)^{1/2}$ [where k is the sensitivity in counts s^{-1} µg^{-1}; B is the background count rate in counts s^{-1}; and t is the counting time], was 6 ng mL^{-1}.

To assess precision of the method seven replicates of samples containing 0.2 µg of silicon (in the form of silicate) were examined. Total precision of a DSDME–EDXRF determination is dependent on several errors that occur at: the extraction step ($s_{extraction}$), deposition of the organic phase onto the carrier ($s_{deposition}$), positioning of the sample in the spectrometer chamber ($s_{positioning}$), and during measurement ($s_{measurement}$). $s_{measurement}$ was calculated based on repeated (7 times) measurements of the same sample without removing it from the spectrometer chamber; $s_{positioning}$ was calculated by measuring the same sample removed every time from the chamber and recentered before the measurement. Total standard deviation was obtained by measuring 7 replicates prepared under conditions optimized for preconcentration procedure. For calculating $s_{deposition}$, a sample was prepared containing reagent volumes 10-fold higher than those described in DSDME procedure. After extraction, 7 replicates were prepared by using each time 20 µL of the same organic phase. $s_{extraction}$ was calculated from the equation:

$$s_{total} = \sqrt{s_{extraction}^2 + s_{deposition}^2 + s_{positioning}^2 + s_{measurement}^2}$$

As can be seen in Table 1 the extraction step and the deposition of organic phase onto the carrier have considerably greater influence on total uncertainty than factors associated with measurements. Nevertheless, the total precision of DSDME combined with EDXRF spectrometry was 6.7%. For concentrations higher than 0.2 µg mL^{-1}, total precision of the proposed procedure did not exceed 4%. Taking into account all steps preceding the determination and the uncertainty of XRF measurements, the proposed procedure can be recognized as precise.

The enrichment factor calculated as a ratio of the sample volume to the volume of the organic phase (after extraction process) was found to be approximately 140.

Detailed analytical information concerning the developed procedure is shown in Table 1.

3.5. Determination of dissolved silicate in surface water

Reliability of the recommended procedure was examined by determining silicate in different kinds of water samples collected from the Upper Silesia region in Poland. Water samples before analysis were filtered through a Millipore cellulose acetate membrane (0.45 µm) and stored at 4 °C. The accuracy of the method

Table 1
Analytical characteristics of DSDME–EDXRF procedure for determination of silicate in water samples.

Parameter	Analytical feature
Linear range, µg mL^{-1}	0.06–3
Correlation coefficient, R	0.9990
Detection limit, ng mL^{-1}	6
RSD$_{total}$, % ($n=7$)	6.7
RSD$_{measurement}$, % ($n=7$)	0.5
RSD$_{positioning}$, % ($n=7$)	0.9
RSD$_{deposition}$, % ($n=7$)	4.8
RSD$_{exctraction}$, % ($n=7$)	6.2
Enrichment factor	140

Table 2
Analysis of surface water samples and samples spiked with silicate standard solution.

Sample	Added Si, $\mu g \cdot 5\ mL^{-1}$	Determined Si, $\mu g \cdot 5\ mL^{-1}$	Recovery, (%)	ICP-OES, $\mu g \cdot 5\ mL^{-1}$	Relative difference, (%)
Water I	0	0.223 ± 0.008	92.8	0.219 ± 0.006	-1.8
	0.2	0.407 ± 0.009	–	–	–
Water II	0	1.78 ± 0.09	94.1	1.74 ± 0.05	-2.3
	1	2.72 ± 0.08	–	–	–
Water III	0	10.9 ± 0.7	98.0	11.1 ± 0.3	1.8
	5	15.7 ± 0.6	–	–	–
Water IV	0	5.2 ± 0.3	95.4	5.3 ± 0.2	1.9
	2	7.1 ± 0.3	–	–	–
Water V	0	12.8 ± 0.7	94.5	13.0 ± 0.4	1.5
	5	17.5 ± 0.7	–	–	–

was verified by analyzing samples spiked with a known amount of Si standard solution, and by using ICP-OES technique. As illustrated in Table 2, recoveries of the added standard solution are good, between 92.2% and 96%, and there is no significant difference between the results obtained by the developed procedure and reference ICP-OES technique. Thus, the proposed method is indeed capable of measuring dissolved silicate in surface water samples.

4. Conclusion

An indirect method was developed for determining nanoscale levels of silicate by DSDME combined with EDXRF. The main benefits of the proposed procedure include wide linear range, low detection limit, good precision, high enrichment factor achieved for 5-mL samples along with minimized use of organic solvent and low cost. The proposed DSDME–EDXRF combination significantly broadens the scope of XRF application to liquid samples and belongs to eco-friendly procedures, in accordance with green chemistry rules.

References

[1] N. Nakatani, W. Masuda, D. Kozaki, R. Goto, N. Nakagoshi, M. Mori, K. Hasebe, K. Tanaka, Anal. Sci. 25 (2009) 379–383.
[2] A. Afkhami, M. Abbasi-Tarighat, Anal. Sci. 24 (2008) 779–783.
[3] O.A. Zaporozhets, J.P. Bas, I.A. Kachan, L.S. Zinko, V.I. Davydov, Talanta 90 (2012) 85–90.
[4] J. Ma, R.H. Byrne, Talanta 88 (2012) 484–489.
[5] A.V. Bulatov, A.A. Tsapko, L.N. Moskvin, J. Anal. Chem. 64 (2009) 580–584.
[6] M.P. Verma, E. Tello, F. Sandoval, R. Tovar, J.L. Martinez, Geothermics 31 (2002) 677–686.
[7] M. Burguera, J.L. Burguera, P. Carrero, C. Rondón, Talanta 58 (2002) 1157–1166.
[8] M.C. Giacomelli, O. Largiuni, G. Piccardi, Anal. Chim. Acta 396 (1999) 285–292.
[9] K. Fujiwara, E.P.H. Wagner, B.W. Smith, J.D. Winefordner, Anal. Lett. 29 (1996) 1985–1992.
[10] A. Lopez Molinero, L. Martinez, A. Villareal, J.R. Castillo, Talanta 45 (1998) 1211–1217.
[11] A. Hioki, J.W.H. Lam, J.W. McLaren, Anal. Chem. 69 (1997) 21–24.
[12] P. Klemens, K.G. Heumann, Fresenius J. Anal. Chem. 371 (2001) 758–763.
[13] H.-B. Li, F. Chen, J. Chromatogr. A 874 (2000) 143–147.
[14] Q. Xu, C. Xu, W. Zhang, Y.P. Wang, L.T. Jin, H. Haraguchi, A. Itoh, K. Tanaka, Chromatographia 53 (2001) 81–84.
[15] Y. Yokoyama, T. Danno, M. Haginoya, Y. Yaso, H. Sato, Talanta 79 (2009) 308–313.
[16] N. Nakatani, D. Kozaki, W. Masuda, N. Nakagoshi, K. Hasebe, M. Mori, K. Tanaka, Anal. Chim. Acta 619 (2008) 110–114.
[17] M. Ikedo, M. Mori, K. Kurachi, W. Hu, K. Tanaka, Anal. Sci. 22 (2006) 117–121.
[18] E. Santoyo, R. García, A. Aparicio, S.P. Verma, M.P. Verma, J. Chromatogr. A 1071 (2005) 197–204.
[19] E. Marguí, R. Van Grieken, C. Fontàs, M. Hidalgo, I. Queralt, Appl. Spectrosc. Rev. 45 (2010) 179–205.
[20] K. Kocot, B. Zawisza, R. Sitko, Spectrochim. Acta B 73 (2012) 79–83.
[21] R. Sitko, K. Kocot, B. Zawisza, B. Feist, K. Pytlakowska, J. Anal. At. Spectrom. 26 (2011) 1979–1985.
[22] K. Pytlakowska, R. Sitko, Anal. Methods 5 (2013) 6192–6199.
[23] E. Marguí, I. Queralt, M. Hidalgo, J. Anal. At. Spectrom. 28 (2013) 266–273.
[24] E. Marguí, G.H. Floor, M. Hidalgo, P. Kregsamer, G. Román-Ross, C. Streli, I. Queralt, Anal. Chem. 82 (2010) 7744–7751.
[25] E. Marguí, M. Sagué, I. Queralt, M. Hidalgo, Anal. Chim. Acta 786 (2013) 8–15.
[26] G.H. Floor, E. Marguí, I. Queralt, P. Kregsamer, C. Streli, G. Román-Ross, Chem. Geol. 352 (2013) 19–26.
[27] K. Pytlakowska, R. Sitko, J. Anal. At. Spectrom. 27 (2012) 460–465.
[28] R. Sitko, B. Zawisza, E. Malicka, Spectrochim. Acta B 64 (2009) 436–441.
[29] F. Priego Capote, M.D. Luque de Castro, Anal. Bioanal. Chem. 387 (2007) 249–257.
[30] ⟨http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?sid=162296000&loc=es_rss#x27⟩.
[31] ⟨http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?sid=163803210&loc=es_rss#x27⟩.
[32] ⟨http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?sid=134974567&loc=es_rss#x27⟩.
[33] ⟨http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?sid=124489935&loc=es_rss#x27⟩.
[34] L. Drummond, W. Maher, Anal. Chim. Acta 302 (1995) 69–74.
[35] A.Y. El-Sayed, Y.Z. Hussein, M.A. Mohammed, Analyst 126 (2001) 1810–1815.
[36] K. Grudpan, P. Ampan, Y. Udnan, S. Jayasvati, S. Lapanantnoppakhun, J. Jakmunee, G.D. Christian, J. Ruzicka, Talanta 58 (2002) 1319–1326.
[37] J. Thomsen, K.S. Johnson, R.L. Petty, Anal. Chem. 55 (1983) 2378–2382.
[38] A.Y. El-Sayed, Y.Z. Hussein, M.A. Mohammed, Anal. Sci. 17 (2001) 1461–1464.
[39] C.X. Galhardo, J.C. Masini, Anal. Chim. Acta 417 (2000) 191–200.
[40] Water Quality Monitoring-A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes, UNEP/WHO, 1996.
[41] A.K. Pettersson, B. Karlberg, Anal. Chim. Acta 378 (1999) 183–189.