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Field sampling, speciation and determination of dissolved iron (II) and iron (III) in waters

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A simple and rapid field sampling procedure was developed for the speciation of dissolved Fe(II) and Fe(III) in waters. The determination of iron species was possible by selective batch solid phase extraction of Fe(III) using chelating resin Chelex-100 in H^+ form, sample acidity range of pH 1.5–2.5, elution with 0.03 mol L^{-1} NH_4-EDTA, and detection of Fe(III) by flame or electrothermal atomic absorption spectrometry (ETAAS). The concentration of Fe(II) was determined in the solution above the resin by direct ETAAS or after adsorption on Chelex-100 in NH_4^+ form without the need for preoxidation of Fe(II) to Fe(III). Water samples were collected *in situ* and filtered by passing them through a syringe filter (0.45 μm). The batch procedure was performed at the field and then, the tubes containing the resins with the loaded analytes were returned to the laboratory where the iron species were eluted and determined. Field sampling prevents changes in the oxidation state of iron. The effect of humic acid was also investigated. The results obtained indicated that the method was not affected by the presence of up to 0.01% humic acid. The limit of detection (3*s*) was 0.8 μg L^{-1} Fe (ETAAS detection). The relative standard deviation (n=10) ranged from 2% at the 1 mg L^{-1} Fe up to 20% at the 1 μg L^{-1} Fe(III) level. Recoveries of spiked Fe(II) and Fe(III) in river, lake, tap and groundwater samples ranged from 93 to 105%.

Key words: Iron speciation, Chelex-100, ETAAS, Humic acids, Water analysis

INTRODUCTION

Iron has an essential role for many metabolic functions and is one of the most important elements in environmental and biological systems. In fresh waters, iron is also an important nutrient for phytoplankton and other organisms. It is known that the biological activity in certain ocean regions is affected by iron [1]. Iron is not normally considered a toxic element, but it becomes toxic when accumulated, especially when present as free ion [2–4]. The question about the comparative toxicity of ferrous and ferric ions has not been clarified. In general, Fe(II) is considered to be more toxic than Fe(III) because it may cause cell degeneration [5–7]. The probable mechanism of this process involves iron catalysed auto-oxidation reactions, which generate hydroxyl-free radicals. The environmental and biological effects of iron depend on its oxidation state, solubility and the degree of complex formation. The ratio between the oxidation states Fe(III)/Fe(II) in waters depends on redox, light and flow conditions, pH, and the amount and type of dissolved organic matter. The main fraction of dissolved iron(III) is strongly complexed by organic ligands [8–10] as humic acids or organic substances produced by phytoplankton [11] or bacteria [12]. This organic complexation prevents the formation of insoluble oxyhydroxides. Iron(II) is thermodynamically unstable and is rapidly oxidized to iron(III). This oxidation is accelerated by some micro-organisms, trace metals, phosphate and fluoride ions and particles, including autocatalysis by fresh Fe oxides. However, dissolved or colloidal organic ligands, sulfate, nitrate and chloride ions may stabilize Fe(II) and retard its oxidation [13]. Further, Fe(III) complexed with organic compounds can be readily photoreduced by UV light to Fe(II) [14]. Accurate and precise measurements of iron redox species are important in the study of aqueous environmental chemistry and oceanic biogeochemistry. It will be beneficial to clarify the role of the two oxidation states of this element, and the essentiality and toxicity of both Fe(II) and Fe(III). Critical reviews of historical and current analytical methods for the determination of

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total dissolved iron and iron speciation in waters were presented by Pehkonen [15], Achterberg et al. [16] and Pohl and Prusisz [17]. Very low concentrations of iron species in non polluted waters and high reactivity of iron species poses a major challenge for redox speciation measurements. The ideal analytical strategy would be the direct *in situ* determination of Fe(III) and Fe(II) with minimal manipulation, use of minimal reagent amounts and minimal laboratory or research equipment. Flow injection techniques using resin-based column chromatography were developed to fulfill most of these requirements [17, 18]. A main drawback of these methods is that the selective complexing agents used can shift the iron redox speciation [17, 19, 20] and the necessity of preliminary oxidation or reduction of iron species. Some of the procedures require adjustment of pH higher than 4 [18] which changes the concentration of labile iron species. In addition, the flow injection systems are laboratory made and commercially not available constructions. Atomic absorption spectrometry and inductively coupled plasma mass spectrometry techniques applied for dissolved iron speciation require laboratory performance [21, 22]. In this case, the risk of changing of the oxidation state of iron during sample preservation and transportation always exists [23]. On the other hand, methods for *in situ* field sampling of several elements, allowing the final species determination in the laboratory, have been already published [22–25]. In this paper, the analytical potential of Chelex-100 resin in H^+ form for solid phase extraction separation/preconcentration of dissolved iron species and their *in situ* field sampling using batch process is investigated. The method involves final elution of Fe(III) species from the Chelex-100 in the laboratory using NH_4-EDTA as eluent and final detection of iron species using flame or electrothermal atomic absorption spectrometry.

EXPERIMENTAL

Instrumentation. The flame AAS technique used was AA400 (Perkin-Elmer) in an air acetylene flame. The light source was a hollow cathode lamp for Fe, wavelength 283.3 nm. The instrumental parameters were set up to obtain maximum signal to noise ratio. The ETAAS measurements were carried out using a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace. The spectral bandpass was 0.2 nm. Pyrolytic coated graphite tubes were used as atomiser. Autosampler AS-60 was used for injections of 20 μL sample solutions into the graphite tube. Only peak areas were used for quantification. The graphite furnace operating parameters for modifier-free ETAAS measurements of Fe were: drying at 120 ºC, pretreatment at 1100 ºC, atomization at 2100 ºC, cleaning at 2500 ºC.

Reagents and materials. All reagents used were of analytical reagent grade. Milli-Q water was used throughout. The stock standard solution of 1 g L^{-1} Fe(III) was prepared from Titrisol (Merck, Darmstadt, Germany) in 0.5 mol L^{-1} hydrochloric acid (p.a. Merck). The standard solution of 1g L^{-1} Fe(II) was prepared by dissolving 3.5111 g of ferrous ammonium sulfate hexahydrate (Sigma-Aldrich) in 500 mL of 0.5 mol L^{-1} HCl. The exact concentration of Fe(II) in the stock solution was checked by titration with standardized potassium permanganate. Working standard solutions for calibration were prepared by appropriate stepwise dilution of their stock solutions just before use. The hydrochloric acid was preliminary purified by isothermal distillation. Ethylenediaminetetraacetic acid diammonium salt (NH_4-EDTA) was prepared from EDTA-disodium salt (p.a. Merck) after precipitation as ethylenediaminetetraacetic acid with 6 mol L^{-1} HCl and subsequent dissolution of the precipitate in NH_4OH (p.a. Merck, additionally purified by isothermal distillation). Humic acid was supplied by Fluka, Switzerland. The chelating resin Chelex-100 (50–100 mesh, sodium form, Bio-Rad, UK) was previously NH_4-EDTA and water washed. The resin was converted to the H^+ form by stirring with 0.02 mol L^{-1} HCl for 20 min, followed by several water washes (till neutral reaction). Sterile polyethylene centrifuge tubes (15 and 50 mL), pasteur pipettes and syringe filters (0.45 μm) were NH_4-EDTA and Milli-Q water washed before use.

Water samples. For laboratory experiments and method development distilled water, river water from the local river (Perlovska), local tap water and groundwater (collected from 12.8 m depth) were used. River and ground waters were filtered through 0.45 μm pore size Millipore cellulose acetate membrane filters. The optimized procedure was further applied for *in situ* sampling/separation of dissolved Fe(II) and Fe(III) species (free ions and their labile complexes) in several rivers in Bulgaria (Danube, Iskar, Mariza, Ropotamo, Veleka, Struma, Mesta, Vladajska) and in lake Pancharevo situated near to Sofia city. The standard reference materials, SLRS-5 (river water) and a mineral water sample (Devin: pH 9.5, 62 mg L^{-1} Na^+, 18 mg L^{-1} SO_4^{2-}, 4 mg L^{-1} F^-, 2.3 mg L^{-1} Cl^-) from national proficiency testing procedure were

analysed to check the accuracy of the developed method for determination of total iron in water.

Procedure for iron speciation. The sample was acidified with 6 mol L^{-1} HCl to pH 2–2.5. The polyethylene centrifuge tube (15 mL) was rinsed with about 2 mL of the sample. Then 14 mL of the sample and 0.5 g of the sorbent Chelex-100 in H^+ form were placed in the tube. The tube was closed and the sample with the resin was shaken manually for 2 min. During this process, Fe(III) was removed from the water sample onto the chelating resin, Fe(II) remained in the aqueous solution above the resin. This aqueous solution was transferred to a second 15 mL polypropylene centrifuge tube using pasteur pipettes. For elution of the sorbed Fe(III) 3 mL of 0.03 mol L^{-1} NH_4-EDTA were added to the chelating resin, the tube was closed and the resin with the eluent was shaken manually for 3 min. The concentration of eluted Fe(III) was determined by flame AAS or ETAAS. Three blank samples were prepared in parallel. The concentration of Fe(II) can be determined direct or after the same preconcentration/elution procedure as for Fe(III), using the chelating resin Chelex-100 in ammonium form.

For preconcentration and determination of total dissolved iron a second aliquot (14 mL) of the same sample (acidified to pH 2–2.5) was placed in a new pre-rinsed polyethylene centrifuge tube. Then 0.5 g of the sorbent Chelex-100 in NH_4^+ form was placed in the tube. The tube was closed and the sample with the resin was shaken manually for 2 min. During this process both Fe(II)+Fe(III) were retained by the resin. The aqueous phase above the resin was removed using pasteur pipettes. The sorbent with the loaded total iron was two times water washed. Then 3 mL of 0.03 mol L^{-1} NH_4-EDTA were added to the sorbent, the tube was closed and the resin with the eluent was shaken manually for 3 min. The concentration of eluted Fe(II) + Fe(III) was determined by flame AAS or ETAAS. Two blank samples were prepared in parallel.

RESULTS AND DISCUSSION

Optimization of the batch procedure. The most important factor which affects the speciation, preconcentration and determination of iron species was the acidity of the samples. The range of pH investigated was between 1 and 8. The recovery values obtained using the proposed method for the Fe(II) and Fe(III) species as a function of pH are shown in Fig. 1. The results showed that the sorption of Fe(III) onto the Chelex-100 in H^+ form

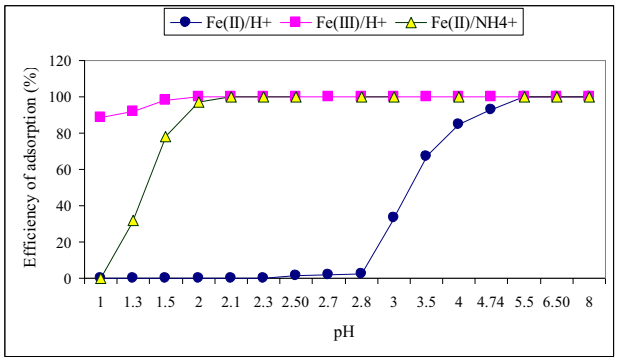

Fig.1. Influence of pH on adsorption of iron species on Chelex-100 in H^+ form (sample volume 10 mL, 5 mg L^{-1} Fe(II, III), contact time 5 min).

was quantitative between pH values of 1.5 and 8. In the pH range 1.5–2.5 the ferrous ions were not retained on the sorbent at all. This means that at pH 1.5–2.5 the Chelex-100 in H^+ form selectively retains Fe(III), making possible to quantitatively separate Fe(II) and Fe(III). The reason for this high selectivity is the big difference in the stability of chelate complexes formed between iron species and ligands containing iminodiacetic functional groups. The high recovery values for Fe(III) even at low pH values using Chelex-100 in H^+ form can be explained with the high conditional formation constant (β′) of Fe(III)-IDA complex at pH 2 (log β′= 10.7–11.1) [26, 27]. Chemosorption for Fe(II) under this conditions is not possible (log β′ (Fe(II)-IDA) < 0.6). Retention on Chelex-100 in H^+ form due to ion exchange is also not possible in acidic media because the equilibrium

$$\text{-R-N-(CH}_2\text{COOH)}_2 + \text{Fe(II)} \leftrightarrow \text{-R-N-(CH}_2\text{COOFe/2)}_2 + 2\text{H}^+$$
(Chelex-100 in H^+ form)

is shifted to the left and the protons on the sorbent functional groups cannot be exchanged with iron ions at pH 1.5–2.5. These are the reasons for the non-adsorptivity of Fe(II) ions which allows the subsequent quantitative separation of Fe(II) and Fe(III). The sorption recoveries obtained for both iron species at pH values between 2 and 2.5 were higher than 95% when the chelating resin Chelex-100 was in its ammonium form (Fig. 1). This allows to achieve quantitative separation using the chelating resin Chelex-100 in H^+ form for selective sorption of Fe(III) at pH 1.5–2.5 and in NH_4^+ form for sorption of total Fe(III)+Fe(II) at pH 2–2.5. The proposed procedure allows to estimate the content of the free Fe(II) and Fe(III) species released in this acidic medium and their labile complexes with inorganic or organic ligands.

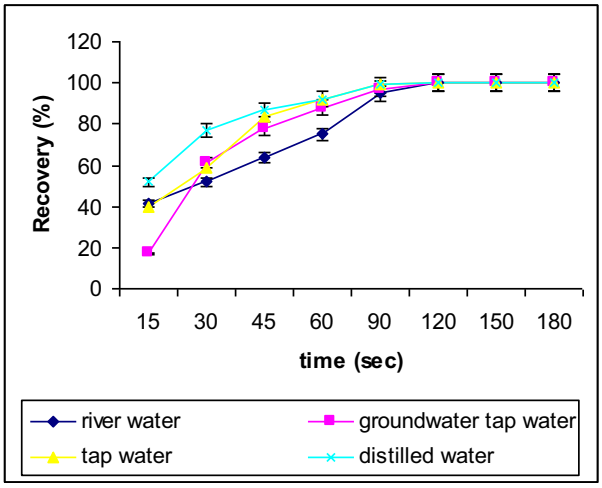

Fig.2. Kinetics of adsorption of Fe(III) on Chelex-100 in H^+ form (sample volume 10 mL, 5 mg L^{-1} Fe(III), pH 1.8–2.2).

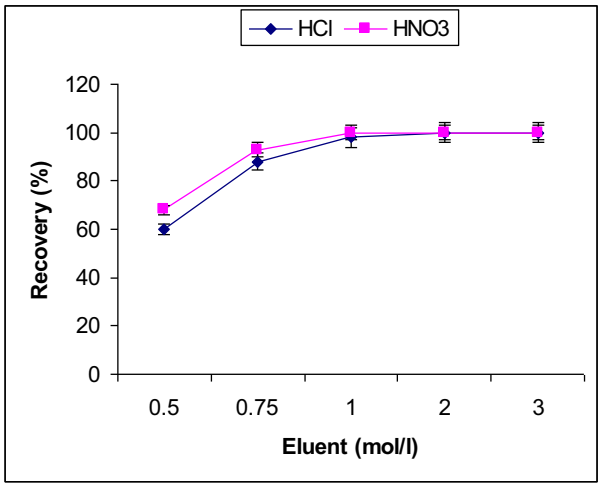

Fig. 3. Recoveries for elution of Fe(III) from Chelex-100 by the use of different concentrations of HCl and HNO_3 (volume of eluent 3 mL, elution time 5 min).

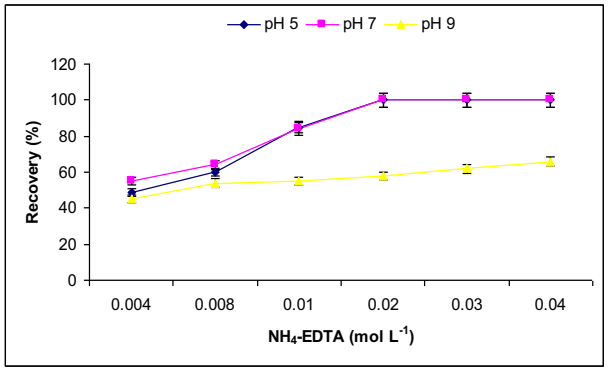

Fig. 4. Recoveries for elution of Fe(III) from Chelex-100 by the use of different concentrations of NH_4–EDTA (volume of eluent 3 mL, elution time 5 min).

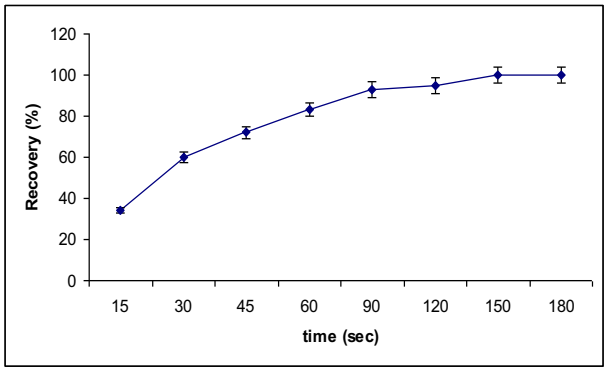

Fig. 5. Recoveries for elution of Fe(III) from Chelex-100 by the use of 3 mL of 0.03 mol L^{-1} NH_4–EDTA at pH 5 as a function of elution time.

To optimize the adsorption procedure, the kinetics of the retention of Fe(III) was investigated using 5 mg L^{-1} Fe(III) spikes in distilled, river, tap and groundwater. The contact time was varied between 15 sec and 5 min. The concentration of the non-sorbed Fe was measured in the aqueous layer above the Chelex-100 resin using flame AAS. The results are presented in Fig. 2. Obviously independent of the sample type, 2 min shaking time are sufficient for quantitative sorption of Fe(III). The experiment was repeated with spike concentrations of 100 μg L^{-1} Fe(III) to distilled water and ETAAS measurement of the concentration of the non-retained Fe. The same sorption behavior of Fe(III) was registered. Hence, 2 min sorption time can be considered as optimal.

Important step in the optimization of a solid phase extraction procedure is the choice of appropriate eluent. Quantitative elution of iron adsorbed on Chelex-100 was achieved with 3 mL of 1–3 mol L^{-1} HCl or HNO_3 or with 3 mL of 0.02–0.05 mol L^{-1} NH_4-EDTA (pH 5–7), as can be seen from Figs. 3 and 4. The use of NH_4-EDTA as eluent is preferable because in this case the same resin can be reused at least ten times for separation/preconcentration purposes. Hydrochloric and nitric acids destroy the resin and it cannot be used again. In addition, the ammonium salt of EDTA does not cause any interference during the analytical measurement by AAS. In all further experiments 0.03 mol L^{-1} NH_4-EDTA was used as eluent. The results for the kinetics of elution are presented in Fig. 5. Three minutes elution time were accepted as optimal.

It was found that the sorption recovery depends on the sample volume. In the investigated concentration range 0.1–5 mg L^{-1} the retention of Fe(III) is quantitative up to 14 ml sample for all studied waters. For 20 ml sample volume the recoveries varied between 74 and 80% in dependence on the water type. When the procedure was performed with 25 ml sample, the recoveries were between 60 and 65%.

Table 1. Efficiency of sorption (%) of Fe(III) in dependence on the water temperature (10 mL sample (pH 2), 2 min contact time; number of parallel determinations n=2–3

Temperature (°C)	Chelex-100 in H^+ form 5 mg L^{-1} Fe(III)	0.5 mg L^{-1} Fe(III)	0.05 mg L^{-1} Fe(III)	Chelex-100 in NH_4^+ form 0.5 mg L^{-1} Fe(III)	0.05 mg L^{-1} Fe(III)
6 ± 2	72 ± 5	78 ± 5	82 ± 6	95 ± 3	96 ± 3
10 ± 2	88 ± 2	92 ± 4	91 ± 5	98 ± 2	97 ± 1
14 ± 2	95 ± 3	96 ± 2	96 ± 3	98 ± 3	97 ± 3
16 ± 2	98 ± 4	97 ± 2	98 ± 3	97 ± 2	99 ± 1
20 ± 2	99 ± 2	100 ± 1	99 ± 1	99 ± 2	98 ± 3

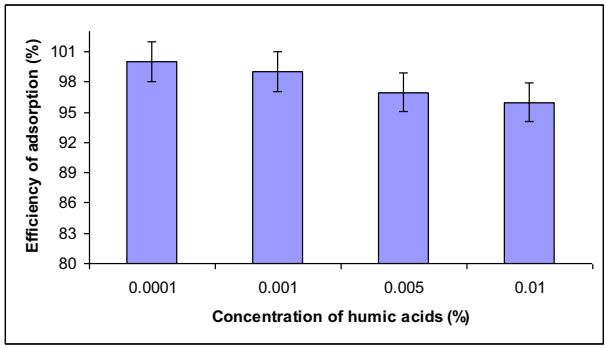

Fig. 6. Efficiency of adsorption of 5 mg L^{-1} Fe(III) on Chelex-100 in H^+ form (sample volume 10 mL, contact time 2 min).

For an in situ experiment it was also important to investigate the influence of the water temperature on the sorption of Fe(III). The results from these investigations are presented in Table 1. The effect of the water temperature on the adsorption efficiency depends on the chelating resin form and does not depend on the iron concentration in the range 0.05–5 mg L^{-1} Fe. At pH 2 the Chelex-100 in H^+ form is sufficiently effective at temperatures above 10°C. The chelating resin in NH_4^+ form is not so temperature sensitive. The DGT devices for passive sampling contain Chelex-100 chelating resin beads in ammonium or sodium form and at pH values of the natural waters the low temperatures are not expected to hinder the adsorption of free ions.

The effect of humic acid. Humic acids form relatively stable complexes with metal ions in natural systems. This was the reason to investigate their effect on the sorption of Fe(III) on Chelex-100 in H^+ form. The concentration range studied was 0.0001–0.01% humic acid, the pH range was 1.5–2.5. The results obtained (Fig. 6) indicated that the quantitative retention of Fe(III) is not affected by the presence of up to 0.01% humic acid.

Preconcentration of other ions. It was expected that other ions which could be quantitatively retained by Chelex-100 in H^+ form at low pH values, are ions producing complexes with EDTA with very high formation constants. Experiments were conducted to investigate the sorption of Bi(III), Tl(III), Sb(III), Sb(V), Sn(II) and Sn(IV) on Chelex-100 in H^+ form at pH 2 using batch procedure for 2 min contact time, i.e. at the optimal conditions for retention of Fe(III) and separation from Fe(II). The results showed that Bi(III), Tl(III), Sb(III) and Sn(II) were totally retained on the sorbent (> 97% retention). The sorption degree of Sn(IV) was around 82% and that of Sb(V) – around 34%. At the same experimental conditions Cu(II) was totally sorbed, while 60% of Pb(II), 40% of Ni, 25% of Cd, 20% of Co and Mn were sorbed. The adsorption of Fe(III) was not interfered by the presence of up to 1 mg L^{-1} Bi(III)+Tl(III)+Sb(III,V)+Sn(IV) as well as of up to 10 mg L^{-1} Cu(II) and of 20 mg L^{-1} Cd(II)+Co(II)+Ni(II)+Mn(II)+Pb(II). Tin(II) could change the oxidation state of iron by reducing the concentration of Fe(III) species if present in concentrations equal or higher to that of iron.

Analytical performance. Quantification has been performed based on calibration using aqueous standards for Fe(III) prepared in 0.3 mol L^{-1} HNO_3. The correlation coefficient R^2 of the calibration curves was 0.9996 for flame AAS (number of points 5) and 0.9991 for ETAAS (number of points 7). The detection limit was 0.8 μg L^{-1} Fe (ETAAS detection) and was evaluated as the concentration corresponding to three times the standard deviation of ten replicate measurements of a blank sample. The accurate determination of trace iron species requires low and reproducible blanks. The procedural blank based on 10 mL sample volume was (2.6±0.4) ng (analysis of five separate aliquots), provided: i) pre-cleaning of tubes, pipettes and syringe filters with 0.01 mol L^{-1} EDTA, followed by several Milli-Q water washes; ii) use of sterile disposable polyethylene centrifuge tubes; iii) preliminary check (ETAAS) for Fe content of the Milli-Q water and of all reagents and sorbents used. The relative standard deviation (n=10) ranged from 2% at the 1 mg L^{-1} Fe up to 20% at the 1 μg L^{-1} Fe(III) level.

To examine potential interference effects and to prove the accuracy of the proposed method in case of real samples, spike experiments were performed with river water, tap water and groundwater. The

Table 2. Determination of iron species in waters (mean ± *s*, number of parallel determinations *n* = 3)

Samples	Added (μg L^{-1})		Found (μg L^{-1})		Mean recovery (%)	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
SLRS-5*	0	0	< 0.8	101±3		101.0
Mineral water**	0	0	< 0.8	9.3±0.6		93.0
River water	0	0	19±1	57±3		
	20	50	37±3	108±6	94.9	100.9
	50	20	65±4	80±3	94.2	103.9
Tap water	0	0	< 0.8	39±3		
	10	50	10.5±0.8	88±7	105.0	98.9
Lake water	0	0	< 0.8	11±1		
	10	10	10.2±0.8	20 ± 2	102.0	95.2
	20	0	18.9±1.3	10.7±0.8	94.5	
Groundwater	0	0	57±4	29±2		
	50	50	111±5	72±6	103.7	91.1

*certified value: (100 ± 2) μg L^{-1} Fe
**accepted value: 10 μg L^{-1} Fe

Table 3. Iron species in waters (*n*–number of parallel determinations).

Sample	Fe_{total} (direct ETAAS) (μg L-1)	Fe(III)	Fe(II) (separation/ preconcentration)* (μg L-1)	$Fe_{tot.}$ calculated / measured	Fe(III)/ Fe_{total} (%)
River Danube (n=3)	23 ± 2	17 ± 2	7 ± 1	1.04	72 ± 4
River Iskar (n=3)	34 ± 2	27 ± 2	6.8 ± 0.8	0.99	79 ± 5
River Mesta (n=3)	84 ± 3	60 ± 3	25 ± 2	1.01	71 ± 5
River Struma (n=3)	16 ± 1	11 ± 1	4.3 ± 0.7	0.96	67 ± 4
River Maritsa (n=3)	21 ± 1	13 ± 2	6.4 ± 0.8	0.97	62 ± 3
River Ropotamo(n=2)	182 ± 8	126 ± 6	58 ± 2	1.01	69 ± 3
River Veleka (n=3)	12 ± 1	7.7 ± 0.8	4.3 ± 0.6	1.02	64 ± 4
River Perlovska (n=5)	76 ± 2	57 ± 3	19 ± 2	1.00	75 ± 3
River Vladajska (n=4)	56 ± 2	43 ± 3	14 ± 1	1.02	77 ± 4
Tap water (n=5)	39 ± 2	40 ± 3	< 0.8	1.03	> 98
Lake water (n=3)	11 ± 1	10.6 ±0.8	< 0.8	0.96	> 98
Groundwater (n=4)	83 ± 6	29 ± 2	57 ± 4	1.04	34 ± 5

* Inorganic Fe(III) and Fe(II) species measured after separation/preconcentration on Chelex-100 in H^+ (for quantification of Fe(III) species) and NH_4^+ form (for quantification of Fe(II) species) at pH 2.

river water reference material SLRS-5 was 10 fold diluted and analysed according to the described procedure. Mineral water sample from national proficiency testing experiment was analysed according to the described procedure. All results of the accuracy tests are summarized in Table 2. The evaluated recoveries for Fe(II) and Fe(III) were in the range 93–105%, i.e. within the accepted range (90–110%) for the examined concentration levels [28]. In addition, the accuracy of the proposed procedure was validated by comparing the sum of the concentrations of individual iron species with that of total iron concentration. The ratio between the sum of the values for Fe(II) and Fe(III) determined individually and total iron concentration measured by direct ETAAS or after preconcentration (*Procedure for iron speciation*) was in the range 0.96–1.04 (Table 3).

The main advantages of the described batch procedure consist in: simplicity; possibility to

separate the species within 10–15 minutes after sampling thus preventing any redox changes due to transportation and storage [23]; use of commercially available chelating resin; possibility to determine both inorganic iron species separately at the same sample pH value using the chelating resin either in H^+ form or in ammonium form; separation/preconcentration without preliminary oxidation or reduction of analytes; no use of complexing agents. The chelating resin itself is not expected to change the iron redox state because it is known that aminocarboxylic acids are used to preserve the elements oxidation state due to fast formation of stable complexes. At pH 2 (applied for separation /preconcentration in the proposed procedure) it could be expected that all iron species in the studied water exist as free hydrated ions or labile iron complexes. At the pH values of most environmental waters (pH around 6 for tap water and pH > 7 for river and lake water) iron exists in form of stable complexes with some naturally occurring ligands as humic acids and fluorides. These complexes almost completely dissociate at pH 2. In this way, with the described procedure we determine the oxidation state of iron included in stable complexes with naturally existing ligands. At pH 2 the chelating resin gel swells, but this does not present any problem for batch procedure performance.

In situ field sampling, separation/preconcentration and sample analysis.

The sampling and speciation steps were performed off-line and *in situ* on the field. The sampling was performed on the coast of the river and the lake. The samples were taken using disposable syringes (20 mL). The syringes were at least three times rinsed with the examined sample. After sampling the sample was filtered through 0.45 μm syringe filter and the filtrate was collected in a 50 mL polyethylene centrifuge tube. To 50 mL of filtrate 100 μL of 6 mol L^{-1} HCl was added by Eppendorf pipette to adjust pH around 2 and then two aliquots of 14 mL were analysed for iron species as described in

Procedure for iron speciation.

The results obtained for the distribution of iron species in environmental waters are given in Table 4. Inorganic Fe(II) species and their labile complexes were not detected in tap and lake waters. These results agree with the results of Yan et al.[21] for tap water and disagree with the data reported by Pehlivan and Kara (27% Fe(II) in tap water) [22]. The tap water in Sofia is used as drinking water and is usually chemically treated before use, which explains the absence of Fe(II) species in our case. In river waters the Fe(III) species and their labile complexes were found as the predominant iron oxidation form representing 64–78 % of total iron concentration. Similar results for river waters were reported by Yan et al. (69% Fe(III)) [21], Pehlivan and Kara (74% Fe(III)) [22] and Bağ et al. (67% Fe(III)) [29]. In groundwater, the Fe(II) species represented 59–66 % of the total iron.

CONCLUSION

The batch solid phase extraction procedure using chelating resin Chelex-100 in hydrogen form as sorbent allows *in situ* field sampling and separation/preconcentration of dissolved Fe(II) and Fe(III) in waters. The developed method is simple, fast, reliable and cost effective. The use of the chelating resin in both H^+ form (for Fe(III)) and ammonium form (for Fe(II) or total iron) allows to separate/preconcentrate the iron species at the same sample acidity without preliminary oxidation or reduction. The contents of inorganic Fe(II) and Fe(III) species can be determined separately. The separation/preconcentration proceeds at pH of 2–2.5, which ensures high degree of dissociation of iron-natural ligands complexes. The method was used for the speciation of iron in river, tap, ground and lake waters with satisfactory precision and accuracy. It was found that the predominant form in all waters except groundwater is Fe(III).

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ПОЛЕВО ПРОБОВЗЕМАНЕ, ОПРЕДЕЛЯНЕ НА РАЗТВОРЕНИТЕ ХИМИЧНИ ФОРМИ НА ЖЕЛЯЗО (II) И ЖЕЛЯЗО (III) ВЪВ ВОДИ

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(Резюме)

Разработена е проста и бърза процедура за определяне на разтворените химични форми на Fe(II) и Fe(III) във води. Определянето на химичните форми на желязо е възможно след селективна твърдофазна екстракция на Fe(III) върху хелатираща смола Chelex-100 в H^+ форма, киселинност на пробата в областта pH 1.5–2.5, елуиране с 0.03 mol L^{-1} NH_4-EDTA и определяне на Fe(III) с пламъкова или електротермична атомноабсорбционна спектрометрия (ETAAS). Концентрацията на Fe(II) в разтвора над сорбента се определя директно с или след сорбция върху Chelex-100 в NH_4^+ форма без необходимост от предварително окисление на Fe(II) до Fe(III). Взетите за изследване водни проби се филтруват на място през филтър спринцовки (0.45 μm). Сорбционната процедура се провежда при полеви условия и епруветките със сорбираните проби се пренасят до лабораторията, където формите на желязото се елуират и определят. Полевото пробовземане предотвратява промени в окислителното състояние на желязото. Установено е, че присъствието на хуминови киселини във водните проби до 0.01% не оказва влияние върху метода. Границата на откриване (3*s*) е 0.8 μg L^{-1} Fe (ETAAS). Относителното стандартно отклонение (n=10) е от 2% за съдържания около 1 mg L^{-1} Fe до 20% за съдържания около 1 μg L^{-1} Fe(III). Извличането на Fe(II) и Fe(III) от речна, езерна, питейна и подпочвена вода е в рамките на 93 –105%.