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Determination of iron in complex matrices by ion chromatography with UV–Vis, thermal lens and amperometric detection using post-column reagents

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Abstract

The advantages of thermal lens spectrometry (TLS) and amperometry in comparison to UV–Vis spectrophotometry were tested for Fe^{3+} and Fe^{2+} detection after their ion chromatographic separation. Iron species were separated on Dionex IonPac CS5A analytical column as anions using a PDCA-based eluent. Non-specific [4-(2-pyridylazo)resorcinol] as well as specific (1,10-phenanthroline in combination with Fe^{3+} reducing agent-ascorbic acid) as post-column reagent were tested. Lower detection limits were obtained when selective and colourless post-column reagents were used in combination with TLS detection (25 $\mu g\ l^{-1}$ for Fe^{3+} and 5 $\mu g\ l^{-1}$ for Fe^{2+}). Electrochemical detection was also used in some experiments because of its wide linear concentration range and selectivity based on the selection of the applied potential. All three detection systems were tested for the detection of Fe^{3+} and Fe^{2+} (in synthetic samples) and Fe^{3+} (in real samples) in the presence of high concentrations of Cu^{2+} and Mn^{2+}. Electrochemical detection was found to be the most suitable among the detection systems used for Fe^{3+} detection in samples with high Cu^{2+} concentration due to the possibility of elimination of Cu^{2+} interference by post-column copper masking.

Keywords: Thermal lens spectrometry; Amperometry; Iron; 1,10-Phenanthroline

1. Introduction

The detection of heavy metal ions after the ion chromatographic separation has been most often performed using UV–Vis spectrophotometry after post-column derivatisation of metal ions using different metallochromic reagents [1–13]. The most frequently used reagent mentioned in the literature is 4-(2-pyridylazo)resorcinol (PAR). Because of its low selectivity, other techniques were applied in the case of co-elution of heavy metals, as, for example, post-column addition of a masking agent [14] or coupled-column chromatography [15]. Selectivity of UV–Vis detection of certain heavy metals was increased also by using selective post-column metallochromic reagents, such as acidic arsenazo III for lanthanides [14], 1,5-diphenylcarbazide (DPC) for Cr^{6+} and/or Cr^{3+} after its oxidation to Cr^{6+} [1,16–18], 1,10-phenanthroline for Fe^{2+} and/or Fe^{3+} after its reduction to Fe^{2+} [1,19,20] or dimethylglyoxime for Ni^{2+} [20]. In some cases, the capability of other detection

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methods like electrochemical detection [12,13], atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES) [21–23], inductively coupled plasma (ICP) AES [24,25], ICP mass spectrometry (MS) [26,27], can also be successfully exploited for the selective detection of individual heavy metals.

The aim of this work was the determination of the most suitable conditions for the detection of Fe^{3+} and Fe^{2+} in the presence of increased concentrations of Cu^{2+} and Mn^{2+}, respectively. The advantages and disadvantages of UV–Vis spectrophotometry, thermal lens spectrometry (TLS) [28,29] and amperometry with selective and non-selective post-column reagent were tested. The findings were successfully applied to the determination of total iron in real samples (copper alloys, manganese ores and ancient copper jewelery).

2. Experimental

2.1. Reagents

All the reagents used in this study (if not separately specified) were of analytical-reagent grade (Merck, Darmstadt, Germany). The eluent solution was prepared by the dilution of 200 ml of the Dionex MetPac PDCA eluent concentrate [35 m*M* pyridine-2,6-dicarboxylic acid (PDCA), 330 m*M* KOH, 28 m*M* K_2SO_4, 370 m*M* HCOOH] to 1 l with 18 mΩ cm^{-1} water. The PAR reagent (0.5 m*M*) was prepared by the dissolution of 53.8 mg of PAR in 500 ml of Dionex MetPac PAR post-column reagent diluent (1 *M* 2-dimethylaminoethanol, 0.5 *M* ammonium hydroxide, 0.3 *M* Na_2CO_3). The 1,10-phenanthroline reagent was prepared by dissolving 1.26 g of 1,10-phenanthroline (Kemika, Zagreb, Croatia) in 100 ml of acetate buffer (3.24 *M* CH_3COONH_4, 3.67 *M* CH_3COOH, pH=5.1) and diluting to 500 ml with 18 MΩ cm^{-1} water. The post-column electrolyte solution for electrochemical detection (0.5 *M* KCl) was prepared by dissolving 18.64 g of KCl in 500 ml 18 MΩ cm^{-1} water. Standard solutions of Cu^{2+} (20 g l^{-1}), Mn^{2+} (10 g l^{-1}), Fe^{2+} (1 g l^{-1}) and Fe^{3+} (1 g l^{-1}) were prepared by dissolving 7.8582 g $CuSO_4 \cdot 5H_2O$, 3.6024 g $MnCl_2 \cdot 4H_2O$, 702.2 mg $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and 484.0 mg $FeCl_3 \cdot 6H_2O$ in 100 ml 18 MΩ cm^{-1} water, respectively. A Millipore (Bedford, MA, USA) system was used for water purification.

2.2. Apparatus

The ion chromatography (IC) system was composed of a Dionex IonPac CG5A guard column and a Dionex IonPac CS5A analytical column (Sunnyvale, CA, USA), which were coupled either to a UV–Vis spectrophotometer (Spectra-Physics SpectraSYSTEM UV2000, Fremont, CA, USA), to a thermal lens spectrometer (for details see Fig. 1) or to the electrochemical detector Metrohm 656 (Herisau, Switzerland) consisting of a wall-jet cell (a glassy carbon working electrode, an Ag/AgCl reference electrode and an Au counter electrode) with a potentiostat Iskra MA 5410 (Ljubljana, Slovenia). Sample injection loop was 50 μl, the flow-rates of the PDCA-based eluent and post-column reagents were 1.2 ml min^{-1} and 0.65 ml min^{-1}, respectively. Post-column reagent addition system comprised a Dionex Reagent Delivery Module with a Dionex Ionpac Membrane Reactor. For comparison, the samples were also analyzed by ICP-AES system (Thermo Jarell Ash AtomScan 25; Franklin, MA, USA).

2.3. Sample preparation

Model solutions were prepared from stock standard solutions of Fe^{3+} and Fe^{2+} with addition of appropriate amounts of stock standard solutions of Cu^{2+} and Mn^{2+}. The real samples [SRM materials British Chemical Standards B.C.S. No. 179/1 (high tensile brass), No. 176/1- (manganese ore), No. 180/1 (cupro-nickel alloy) and a fragment of a bracelet dated 800 B.C. divided into sample A (non-metallic) and sample B (metallic) material were weighed (50–100 mg) in a 50-ml glass beaker. Afterwards 5 ml of concentrated HNO_3 and 5 ml of concentrated HCl were added. After the dissolution the samples were quantitatively transferred into volumetric flasks and diluted to 100 ml.

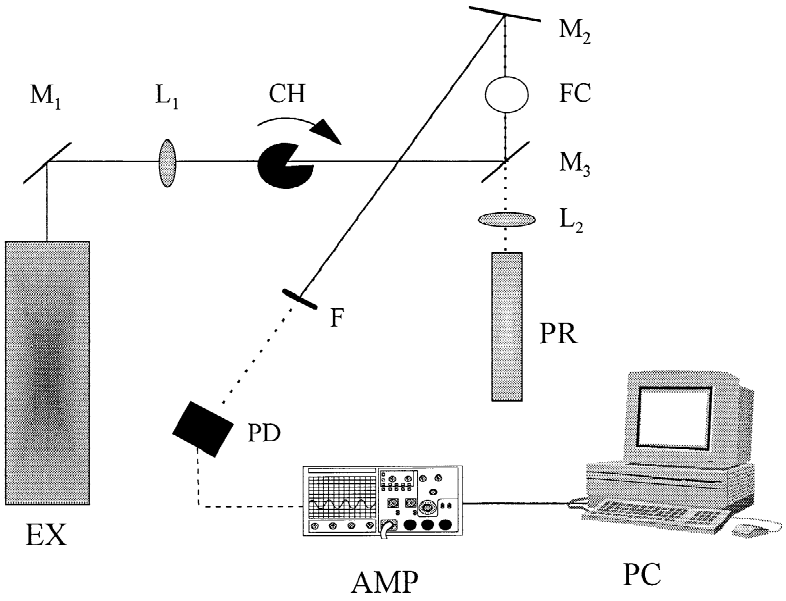

Fig. 1. A scheme of the TLS set-up [EX: excitation argon-ion laser at 514 nm (P=150 mW), PR: probe He–Ne laser, CH: mechanical chopper (n=75 Hz), PD: silicon photo-diode, FC: flow-through cell, AMP: lock-in amplifier (t_S=3 s), PC: personal computer, M_1, M_2: mirrors, M_3: dichroic mirror, L_1, L_2: lenses, F: filter).

3. Results and discussion

3.1. UV–Vis spectrophotometry

Initially UV–Vis spectrophotometry was used for the determination of the detection limits for Fe^{3+} and Fe^{2+} by using PAR as a non-selective post-column reagent. The detection limits for Fe^{3+} and Fe^{2+}, obtained from the calibration curves, were 340 μg l^{-1} and 120 μg l^{-1}, respectively. Because of co-elution the detection of Fe^{3+} in samples containing more than 0.3 g l^{-1} of Cu^{2+} (Fig. 2a) and the detection of Fe^{2+} in samples containing more than 0.5 g l^{-1} of Mn^{2+} (Fig. 2b) was not possible. Thus, the detection of Fe^{3+} and Fe^{2+} in samples with high concentrations of Cu^{2+} and Mn^{2+}, respectively, demands the use of either a specific reagent or a specific detection technique.

At first, 1,10-phenanthroline as selective post-column reagent for Fe^{2+} detection was investigated. The formation of red colored $Fe(o\text{-}Ph)_3^{2+}$ (maximum molar absorptivity of 11 100 l·mol·cm^{-1} at 508 nm [20], our measurement 10 970 l·mol·cm^{-1}) from Fe^{2+}–PDCA after the addition of 1,10-phenanthroline was checked in a batch experiment. The red colored complex formed instantly. During that experiment it was observed, that the solution of Fe^{2+}–PDCA itself was slightly red colored. The investigation of the Fe^{2+}–PDCA complex showed a maximum molar absorptivity of 850 l·mol·cm^{-1} at 480 nm. Manganese does not form colored complexes with PDCA and consequently the detection of Fe^{2+} in solutions with high concentration of Mn^{2+} can be performed also without any post-column reagent as shown in Fig. 3. The detection limit for Fe^{2+} without any post-column reagent was found to be 1.8 mg l^{-1}.

A hump-like peak in front of the Fe^{2+} peak, representing the change of the refractive index of the effluent Δn, is the consequence of the elution of the Mn^{2+}–PDCA complex. Fe^{2+} can be still determined in the presence of up to approx. 1 g l^{-1} of Mn^{2+}. At higher Mn^{2+} concentration (2 g l^{-1}) Fe^{2+} peak evaluation was rendered difficult (curve V in Fig. 3).

Similar chromatographic behavior of Fe^{2+} (shortening of the retention time, peak broadening) in presence of increased Mn^{2+} concentrations was also observed when selective post-column reagent (1,10-phenanthroline) was used. The decrease in retention

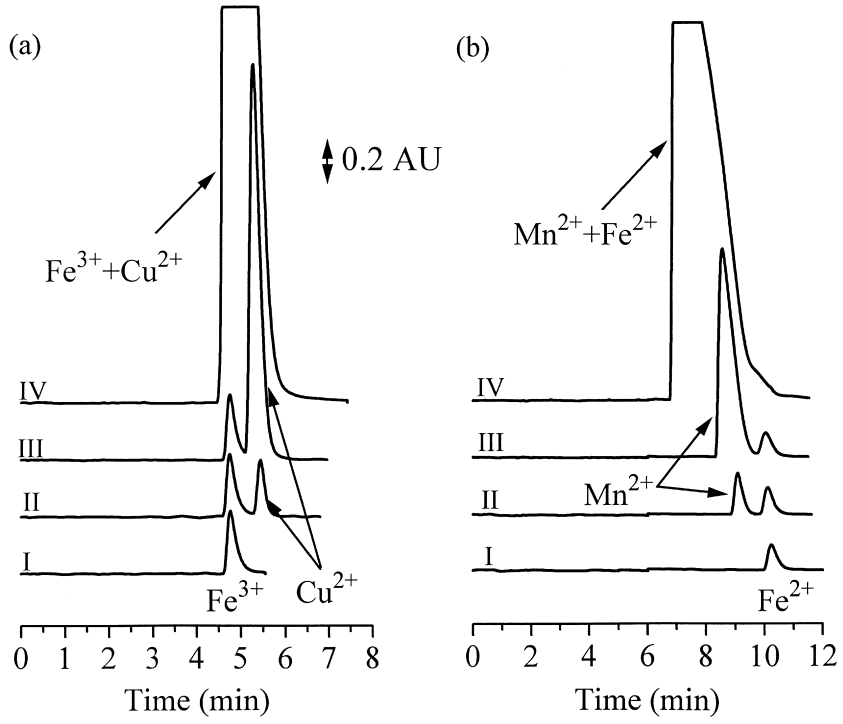

Fig. 2. Chromatograms of samples containing (a) 5 mg l^{-1} of Fe^{3+} and increasing concentrations of Cu^{2+} (I: 0 g l^{-1}, II: 5 mg l^{-1}, III: 50 mg l^{-1} and IV: 500 mg l^{-1}); (b) 5 mg l^{-1} of Fe^{2+} and increased concentrations of Mn^{2+} (I: 0 gl^{-1}, II: 5 mg l^{-1}, III: 50 mg l^{-1} and IV: 500 mg l^{-1}). Chromatographic conditions: see Section 2.2; detector: UV–Vis spectrophotometer at λ=530 nm; post-column reagent: PAR.

time and Fe^{2+} peak broadening (Fig. 3) is thus the consequence of increased concentration of Mn^{2+}. The parameters influencing the decrease in retention times and peak broadening are currently being investigated. By the analogy to the influence of the matrix components on the retention behavior of some anions [30], it is expected that the self-elution effect of the matrix metal component represents one of the main reasons for the observed phenomenon.

A slightly modified IC set-up, enabling the addition of the reducing agent (ascorbic acid) to the column effluent to reduce Fe^{3+} to Fe^{2+}, was used for the simultaneous determination of both iron species. The detection limits for Fe^{3+} and Fe^{2+}, obtained using UV–Vis detection, were 87 μg l^{-1} and 45 μg l^{-1}, respectively, thus representing an improvement compared to the detection limits obtained with PAR. As already mentioned, when samples with Mn^{2+} concentrations were analysed, no Mn^{2+} interference, apart from its influence on the Fe^{2+} peak shapes and retention time, was observed. Contrary to that, Cu^{2+} interfered with the determination of Fe^{3+}, because it formed a colored complex with 1,10-phenanthroline.

3.2. Thermal lens spectrometry

In next experiments more sensitive thermal lens detection technique was used both with unmodified and modified IC set-up. The detection limits for Fe^{3+} and Fe^{2+} obtained with TLS using PAR as the post-column reagent were found to be 55 μg l^{-1} and 20 μg l^{-1}, respectively, whereas the detection limits for Fe^{3+} and Fe^{2+} obtained with ascorbic acid and 1,10-phenanthroline as post-column reagents were lower (25 μg l^{-1} and 5 μg l^{-1}, respectively). Compared to the detection limits obtained with UV–Vis detection, both sets of detection limits represent a marked improvement. This is mainly the consequence of higher sensitivity of TLS compared to UV–Vis and additionally, of lower background absorption and lower noise in case of colourless ascorbic acid and 1,10-phenanthroline.

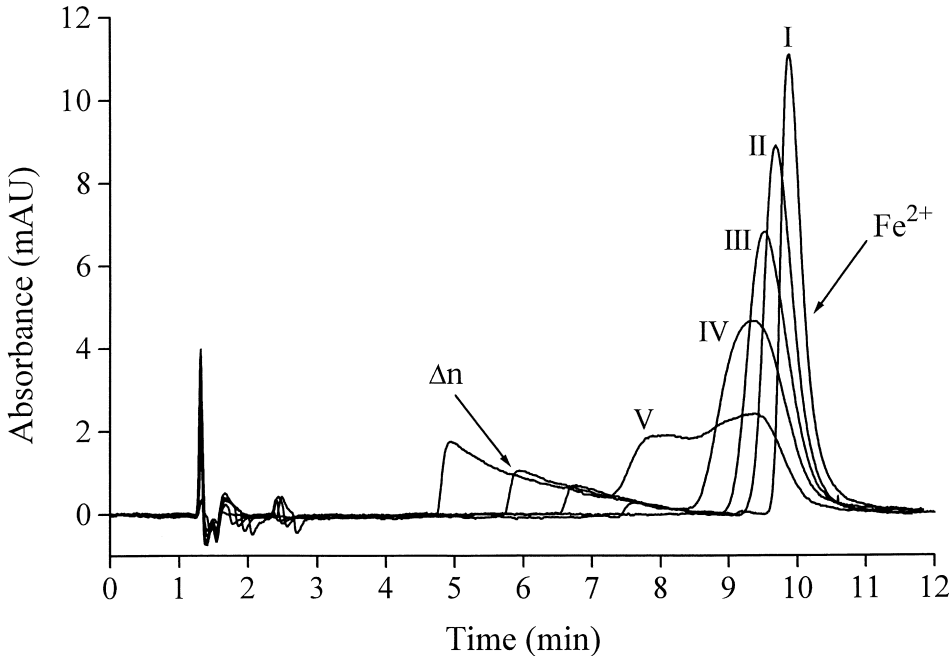

Fig. 3. Chromatograms of samples containing 5 mg l^{-1} of Fe^{2+} and increased concentrations of Mn^{2+} (I: 0 mg l^{-1}, II: 200 mg l^{-1}, III: 500 mg l^{-1}, IV: 1000 mg l^{-1} and V: 2000 mg l^{-1}). Chromatographic conditions: see Section 2.2; detector: UV–Vis spectrophotometer at λ=480 nm.

An example of simultaneous TLS detection of both iron species in the samples without any matrix component and in presence of both Cu^{2+} and Mn^{2+} using the modified IC set-up is shown in Fig. 4. Similar effects of increased concentrations of Cu^{2+} and Mn^{2+}, observed with UV–Vis detection, can also be seen in the case of TLS detection.

3.3. Amperometry

Amperometry was applied for the detection of iron species because of its much wider linear concentration range and selectivity, which can be obtained by controlling the applied potential. Sufficient electrical conductivity of the solution, constant ionic strength and stable and reproducible amperometric signal were ensured by post-column addition of KCl solution. The optimal KCl concentration (0.5 *M*) and the optimal potentials for the reduction of Fe^{3+}–PDCA (−100 mV vs. Ag/AgCl) and the oxidation of Fe^{2+}–PDCA (+550 mV vs. Ag/AgCl) were determined by using an appropriate FIA system. The eluent solution was used as a carrier. KCl solution was added to the carrier solution after the injection of the sample through a T-shaped cross. The mixing reactor was a 750 μl knitted mixing coil (PTFE tubing, I.D.=0.5 mm). The detection limits for Fe^{3+} and Fe^{2+} (in a synthetic solution) obtained under optimal experimental conditions were 95 μg l^{-1} and 75 μg l^{-1}, respectively.

Amperometry was also used for the detection of Fe^{3+} and Fe^{2+} in samples with high concentrations of Cu^{2+} and Mn^{2+}. Mn^{2+} species were found to be electroinactive at the applied potential at which Fe^{2+} was detected, therefore no additional peak could be observed. However, a strong distortion of Fe^{2+} peak, as in the case of UV–Vis detection and TLS detection, was observed at Mn^{2+} concentrations above 1 g l^{-1}.

A decrease in retention time of Fe^{3+} accompanied by peak broadening was observed also at increased Cu^{2+} concentration. However, at concentrations of Cu^{2+} above 3 g l^{-1} a large peak (Fig. 5a), which became bigger with the increase in Cu^{2+} concentration, appeared. This peak overlapped with the Fe^{3+} peak at Cu^{2+} concentrations above 5 g l^{-1}.

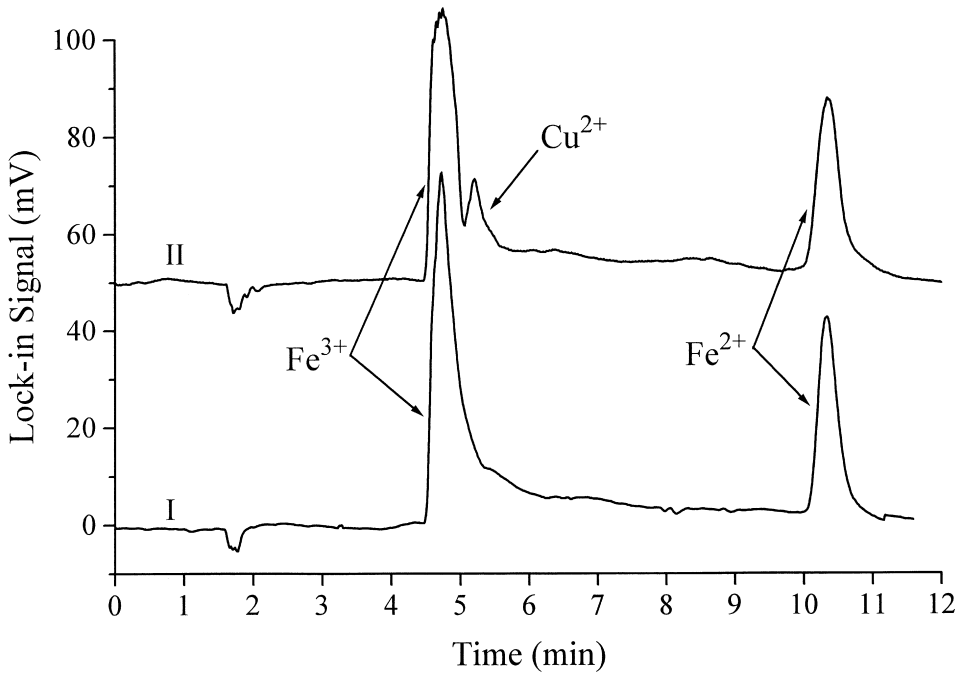

Fig. 4. Chromatograms of a sample (2 mg l^{-1} Fe^{3+} and 2 mg l^{-1} Fe^{2+}) containing no interferring metals (curve I) and with 0.1 g l^{-1} Cu^{2+} and 0.1 g l^{-1} Mn^{2+} added (curve II). Chromatographic conditions: see Section 2.2; detector: TLS; post-column reagents: ascorbic acid and 1,10-phenanthroline added successively.

By comparing chromatograms obtained by amperometric detection (solid line, Fig. 5b) and UV–Vis detection after post-column reaction with PAR (dashed line, Fig. 5b), it was assumed that the aforementioned peak originated from copper species. This assumption was verified using a fraction collection technique (peak fraction between 2.9 and 3.3 min, Fig. 5b) and consequent ICP-AES analysis of that fraction, which confirmed the presence of high concentration of copper.

The explanation for the appearance of copper peak above a certain Cu^{2+} concentration can be offered by taking into account the chromatographic separation mechanism. In case of PDCA-based eluent the metals are separated as anionic metal–PDCA complexes. Consequently, the amount of PDCA in the eluent must be high enough so as to complex the injected metals. In case of Cu^{2+} concentration above approx. 3 g l^{-1}, a part of the injected Cu^{2+} can not be complexed due to the insufficient amount of the complexing agent (PDCA) in the mobile phase. The batch voltammetric measurements of the excess Cu^{2+} in the eluent confirmed that uncomplexed Cu^{2+} was electroactive at −100 mV vs. Ag/AgCl. Therefore, a conversion of electroactive Cu^{2+} into Cu^{2+}–PDCA should result in the elimination of the copper peak. The conversion was experimentally carried out by post-column addition of PDCA. In order to simplify the experimental set-up and to retain peak broadening at the same level, PDCA was added into KCl post-column reagent in the concentration range equal to that in the eluent. The delay time between the addition of PDCA and detection was long enough to enable almost quantitative complexation of Cu^{2+}, resulting in the elimination of Cu^{2+} peak.

3.4. Determination of Fe in real samples

Amperometry was used for the detection of iron because of its advantages over UV–Vis and TLS detection. However, only total iron content of the selected real samples is reported. The concentrations obtained by IC and certified values are given in Table 1.

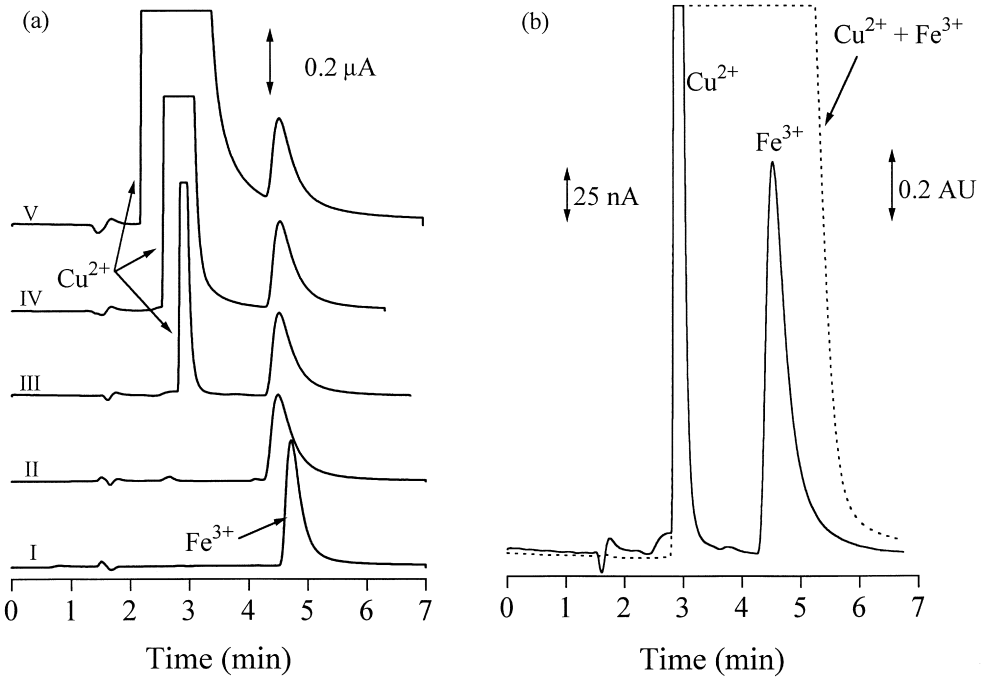

Fig. 5. Chromatograms of samples containing (a) 5 mg l^{-1} of Fe^{3+} and increased concentrations of Cu^{2+} (I: 0 g l^{-1}, II: 1 g l^{-1}, III: 3 g l^{-1}, IV: 5 g l^{-1} and V: 10 g l^{-1}) obtained with electrochemical detection and (b) of a sample with 5 mg l^{-1} of Fe^{3+} and 3 g l^{-1} of Cu^{2+} using electrochemical detection (solid line) and UV–Vis spectrophotometry (dashed line). Chromatographic conditions: see Section 2.2.

IC analysis and certified values for total iron content at the 95% significance level do not differ. A series of experiments was also carried out by spiking the samples of standard reference materials with an iron standard solution prior to the acid digestion step for the determination of recovery rates. These were in the range from 93.3% to 99.4%. The iron content determined by IC was also in a good agreement with the values obtained by ICP-AES. The parallel ICP-AES analysis of the sample of archaeological origin confirmed the assumption of the presence of two different materials, namely sample A was actually found to have low metal content, whereas sample B comprised mostly (75.1%) of copper. Both samples contained also trace amounts of iron (sample A, 0.39% and sample B, 0.01%). The concentration of Fe^{3+} in sample B was below the detection limit of the ion chromatographic separation and amperometric detection, what is partly due to very high copper concentration.

Table 1
The concentrations of Fe in the standard reference materials and in the archaeological sample

Sample	IC	c.v.
B.C.S. No. 179/1	1.35±0.05 (N=3)	1.34±0.01 (N=8)
B.C.S. No. 176/1	4.7±0.3 (N=3)	5.2±0.1 (N=8)
B.C.S. No. 180/1	0.72±0.06 (N=3)	0.82±0.02 (N=9)
Sample A	0.39±0.04 (N=3)	–
Sample B	<DL	–

c.v.=Certified value, DL=detection limit.

4. Conclusions

The application of various detection techniques (UV–Vis spectrophotometry, TLS and amperometry) with different metallochromic post-column reagents for IC determination of Fe^{3+} and Fe^{2+} were studied. The lowest detection limits for Fe^{3+} and Fe^{2+} were obtained by using TLS detection, when colourless ascorbic acid and 1,10-phenanthroline were used as a post-column reagent (5 μg l^{-1} for Fe^{2+} and 25 μg l^{-1} for Fe^{3+}). The usefulness of UV–Vis and TLS

detection is limited for the detection of Fe^{3+} co-eluting with Cu^{2+}, because of Cu^{2+} forming colored complexes with PAR and with 1,10-phenanthroline. Nevertheless, 1,10-phenanthroline proved to be advantageous for Fe^{2+} determination in the case of samples containing high concentrations of Mn^{2+}.

Amperometric detection was found to be the most suitable among the detection techniques used in this study for the detection of Fe^{3+} species in samples having high Cu^{2+} concentration. It was found that the selectivity of amperometric detection of Fe^{3+}, when co-eluted with Cu^{2+}, could additionally be enhanced by post-column masking of Cu^{2+} with the addition of PDCA.

In the routine work, IC with amperometric detection was applied to the determination of total iron in selected samples. The values for total iron content were in good agreement with the values obtained by ICP-AES analysis and also with the certified values. High recovery rates for iron were also obtained (93.3–99.4%).

Acknowledgements

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