A simple flow injection spectrophotometric determination method for iron(III) based on O-acetylsalicylhydroxamic acid complexation

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A simple and rapid flow-injection spectrophotometric method for the determination of iron(III) and total iron is proposed. The method is based on the reaction between iron(III) and O-acetylsalicylhydroxamic acid (AcSHA) in a 2 % methanol solution resulting in an intense violet complex with strong absorption at 475 nm. Optimum conditions for the determination of iron(III) and the interfering ions were tested. The relative standard deviation for the determination of 5 µg L\(^{-1}\) iron(III) was 0.85 % (n = 10), and the limit of detection (blank signal plus three times the standard deviation of the blank) was 0.5 µg L\(^{-1}\), both based on the injection volumes of 20 µL. The method was successfully applied in the determination of iron(III) and total iron in water and ore samples. The method was verified by analysing a certified reference material Zn/Al/Cu 43XZ3F and also by the AAS method.

Keywords: flow-injection analysis, iron(III), O-acetylsalicylhydroxamic acid

Introduction

Iron is the fourth most abundant element in the earth’s crust. In general, the main source of iron in natural waters is from the weathering and leaching of rocks and soils (Dojlido & Best, 1993). Iron(II) is normally less present in river water (Sangi et al., 2004) and iron(III) can precipitate rapidly forming hydrous iron oxide and hydroxides which absorb other trace metals. Thus, iron ion controls the mobility, bioavailability and toxicity of other trace metals in the natural water system (Wirat, 2008; Lunvongsra et al., 2006). Therefore, simple and low cost methods for the determination of iron are needed to predict the fate and mobility of metals in natural waters.

Flow-injection analysis, as a rapid and precise technique, has found wide application in the determination of iron in several sample matrices (Bowie et al., 1998; Hirata et al., 1999; Qin et al., 1998; Kass & Ivaska, 2002; Saitoh et al., 1998; Weeks & Bruland, 2002; Giokas et al., 2002; Themelis et al., 2001; Bagheri et al., 2000; Pascual-Reguera et al., 1997; Teshima et al., 1996). Spectrophotometric detection based on the measurement of absorbance at a characteristic wavelength of the complex formed by a chelating agent and iron has been mainly applied (Kass & Ivaska, 2002; Saitoh et al., 1998; Weeks & Bruland, 2002; Giokas et al., 2002; Themelis et al., 2001; Bagheri et al., 2000; Pascual-Reguera et al., 1997; Teshima et al., 1996; Tesfaldet et al., 2004; Udnan et al., 2004; Morelli, 1983; Pojanagaron et al., 2002; van Staden & Kluever, 2002). 1,10-phenanthroline and salicylic acid are the most reported chelating agents applied for the determination of iron(III) and total iron after oxidation to iron(III) (Tesfaldet et al., 2004; Udnan et al., 2004). A number of other chelating agents that have been reported for the spectrophotometric and/or flow-injection spectrophotometric determination of iron(III) and total iron include 2-thiobarbituric acid (Morelli, 1983), norfloxacin (Pojanagaron et al., 2002) tiron (van Staden & Kluever, 2002) DMF (Asan et al., 2003), tetracycline (Sultan et al., 1992) and chlortetracycline (Wirat, 2008). Flow-injection spectrophotometric methods based on the above chelating

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agents are either not selective, or a masking agent has to be used. However, highly selective, simple and economical methods for routine determination of iron(III) in different sample matrices are still required.

In our previous study (Asan et al., 2003), a simple flow-injection analysis method for the selective and sensitive determination of copper(II) in sea and river water samples, using O-acetylsalicylhydroxamic acid (AcSHA), was developed. In the present study, a simple and economical flow-injection spectrophotometric procedure based on O-acetylsalicylhydroxamic acid (AcSHA) for the selective determination of iron(III) and total iron is described. In this procedure, AcSHA, in the reagent carrier solution, selectively reacts with iron(II) and iron(III) forming a complex with the absorption maxima at 475 nm. The reagent itself is sparingly soluble in water and did not absorb in the visible region of the spectrum, therefore, it might be well suited for flow-injection analysis of iron(III) and total iron. An addition of copper sulphate (1 $\times$ $10^{-4}$ mol L$^{-1}$) into the reagent carrier solution resulted in baseline absorbance, and possible interfering ions were eliminated without a significant decrease in the sensitivity of the method.

**Experimental**

All chemicals used were of analytical reagent grade, and solutions were prepared from double deionised water. Standard iron(II) and iron(III) stock solutions were prepared by dissolving 278.02 mg of iron(II) and 489.96 mg of iron(III) sulphate (Merck; Darmstadt, Germany) in 100 mL of 0.01 mol L$^{-1}$ hydrochloric acid to give 0.01 mol L$^{-1}$ stock solution of iron(II) and iron(III). Iron(II) and iron(III) working standard solutions were prepared daily by suitable dilution of the stock solutions with double deionised water. Standard reference material consisting of 0.085 % Fe (Zn/AI/Cu 43XZ3F) was provided from MBH Analytical Ltd. (UK). Hydrogen peroxide solution of 30 vol. % was obtained from Merck.

AcSHA was synthesised according to the procedure described previously (Asan et al., 2003). A stock solution of AcSHA (0.01 mol L$^{-1}$) was prepared by dissolving 0.095 g of AcSHA in 100 mL of aqueous methanol (2 vol. %).

For the spectrophotometric study, AcSHA complex solutions of various metals were prepared by mixing 1 mL of 1 $\times$ 10$^{-4}$ mol L$^{-1}$ standard solution of each metal in double deionised water with the suitable volume of 1 $\times$ 10$^{-4}$ mol L$^{-1}$ AcSHA stock solution. Reagent carrier solution was composed of AcSHA in a 2 % methanol solution and 1 $\times$ 10$^{-4}$ mol L$^{-1}$ CuSO$_4$ in 0.001 mol L$^{-1}$ HCl 98 % (pH 2.85).

UV-VIS spectra of metal-AcSHA complexes were taken with a Unicam spectrophotometer (GBC Cintra 20, Australia). A Jenway 3040 Model digital pH-meter was used for the pH measurements.

In the FIA system, a peristaltic pump (ISMATEC; IPC, Switzerland) 0.50 mm i.d. PTFE tubing was used to propel the samples and reagent solutions. Samples were injected into the carrier stream by a 7125 model stainless steel high pressure Rheodyne injection valve provided with a 20 µL loop. Absorbance of the coloured complex formed was measured with a UV-VIS spectrophotometer equipped with a flow-through micro cell (Spectra SYSTEM UV 3000 HR, Thermo Separation Products, USA), and connected to a computer incorporated with a PC1000 software programme.

A UNICAM 929 model (Shimadzu AA-68006) flame atomic absorption spectrophotometer with a deuterium-lamp background correction was used for the determination of iron in reference to the FIA method. The measuring conditions were as follows: UNICAM hollow cathode lamp, 10 cm 1-slit burner, air-acetylene flame (fuel gas flow-rate 1.50 L min$^{-1}$), 0.2 nm spectral bandwidth, and 7 mm burner height. The wavelength and the lamp current of iron were 248 nm and 5 mA, respectively.

The FIA system used, similar to that proposed in our previous works (Asan et al., 2003; Andac et al., 2003), is quite simple. The sample solution was introduced into the reagent carrier solution by the Rheodyne injection valve. A water-soluble complex ($\lambda_{\text{max}}$ = 475 nm) was then formed on the passage of the reagent carrier solution in the mixing coil. As a mixing coil, PTFE tubing (50 cm long) was attached before the flow-through detection cell. The absorbance of the coloured complex was selectively monitored in the cell at 475 nm. The transient signal was recorded as a peak, the height of which was proportional to the iron(III) concentration in the sample, and it was used in all measurements. Five replicate injections per sample were made.

Sea and river water samples collected in Nalgene plastics were acidified by adding 1 mL of nitric acid (0.1 mol L$^{-1}$) per 100 mL of sample solution after filtration over a 0.45 µm Millipore Filter (Millford, MA). After the filtration, water samples were injected directly into the FIA system for the determination of iron(III).

Total iron was determined by oxidising iron(II) to iron(III). Hydrogen peroxide was chosen as the oxidising agent for the determination of total iron. A 0.25 mol L$^{-1}$ H$_2$O$_2$ concentration ensured total oxidation of iron(II) into iron(III) (Pons, et al., 2005). Before the determination of total iron, H$_2$O$_2$ (10 mass %) was added to the water sample solution for complete oxidation of iron(II) to iron(III). Then, 20 µL of this solution were injected into the system, as in the procedure described above.

A 0.10 g sample of the certified metal alloy (Zn/AI/Cu 43XZ3F) was dissolved in 12 mL of concentrated HCl and HNO$_3$ ($\phi_i$ = 3 : 1) in a 100 mL beaker. The mixture was heated on a hot plate nearly