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Selective extraction, separation and speciation of iron in different samples using 4-acetyl-5-methyl-1-phenyl-1*H*-pyrazole-3-carboxylic acid

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ABSTRACT

A method for speciation, preconcentration and separation of Fe(II) and Fe(III) in different matrices was developed using solvent extraction and flame atomic absorption spectrometry. 4-Acetyl-5-methyl-1-phenyl-1*H*-pyrazole-3-carboxylic acid (AMPC) was used as a new complexing reagent for Fe(III). The Fe(III)–AMPC complex was extracted into methyl isobutyl ketone (MIBK) phase in the pH range 1.0–2.5, and Fe(II) ion remained in aqueous phase at all pH. The chemical composition of the Fe(III)–AMPC complex was determined by the Job's method. The optimum conditions for quantitative recovery of Fe(III) were determined as pH 1.5, shaking time of 2 min, 1.64×10^{-4} mol L^{-1} AMPC reagent and 10 mL of MIBK. Furthermore, the influences of diverse metal ions were investigated. The level of Fe(II) was calculated by difference of total iron and Fe(III) concentrations. The detection limit based on the 3σ criterion was found to be 0.24 $\mu g\, L^{-1}$ for Fe(III). The recoveries were higher than 95% and relative standard deviation was less than 2.1% ($N = 8$). The validation of the procedure was performed by the analysis of two certified standard reference materials. The presented method was applied to the determination of Fe(II) and Fe(III) in tap water, lake water, river water, sea water, fruit juice, cola, and molasses samples with satisfactory results.

1. Introduction

Iron is the fourth most abundant element in the earth's crust, it is present in a variety of rock and soil minerals both as iron(II) and iron(III). Concerning its biological activity, iron is a highly versatile element, serving as active center of proteins responsible for oxygen and electrons transference in metalloenzymes such as oxidases and dehydratases [1–3].

The effectiveness of a chemical technique of separation and concentration is principally dependent on its selectivity [4]. Chemical speciation has gained an increasing interest in environmental and toxicological analyses. The most important reason, therefore, lies in the fact that the toxicity of an element, its biological availability and transport mechanisms highly depend on the chemical form in which it appears [5]. The speciation of iron in aquatic systems is very important for environmental and biological studies, because its chemical forms such as simple ions, complexes, colloids and particulates influence not only the bioavailability of iron, but also the physico-chemical and toxicological properties of other trace elements and organic substances [6]. The element plays an important role in plant metabolism where it is essential for photosynthetic and respiratory electron transport, nitrate reduction, chlorophyll synthesis and detoxification of reactive oxygen species [7]. Iron deficiency is the single most common nutritional disorder worldwide [8].

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According to our literature survey, speciation of iron(II) and iron(III) has been studied with different techniques such as ETV-ICP-AES and polarography [9,10], flow injection analysis [11], voltammetry [12], flame AAS [13], and capillary electrophoresis [14].

Solvent extraction processes have attracted considerable attention from the view point of the analytical separation and extraction of metals in a pure state [15]. Due to its inherent simplicity, solvent extraction is a remarkable alternative, widely used for the separation of metal ions from aqueous solutions and avoiding the undesirable features associated with the precipitation processes. In fact, solvent extraction plays an important role in hydrometallurgical industries, and thus a great effort has been continuously devoted to the development of new extractants [16].

Solvent extraction using chelating reagents has been widely applied in the fields of analytical and separation technology. A large number of commercial chelating extractants are available and used in solution and in organic diluents such as kerosene [17]. On the other hand, it is still an important subject to develop an extractant with high selectivity for the metal and fast extraction rate enough to be used for industrial applications [18]. The development of selective extractants has expanded the use of solvent extraction for metal recovery and purification, replacing, in some situations, pyrometallorgical techniques [19]. Nowadays, the solvent extraction technique has been increasingly employed to overcome the iron control problem in hydrometallurgical industries [20].

In the present work, we have proposed a method which can be used for the determination of Fe(III) and also for preconcentration and speciation of Fe(II, III) species. The AMPC reagent as a new extractant was proposed for the efficient and selective extraction of Fe(III). The structure of AMPC was presented in Fig. 1, and it has been evaluated regarding its adequacy to accomplish such an aim. The results presented herein summarize the most important features of the Fe(III) extraction and stripping efficiencies for the solvent extraction systems, as well as the selectivity of the extractants for Fe(III) when it appears in the presence of other metals in the aqueous phases. According to our knowledge, flame atomic absorption spectrometry (FAAS) together with the AMPC-MIBK extraction has not been used for the determination of Fe(III). The developed method was tested in the determination of iron in tap water, lake water, river water, sea water, fruit juice, cola, and molasses samples. The method can also be employed for the speciation and separation of iron species in various natural water.

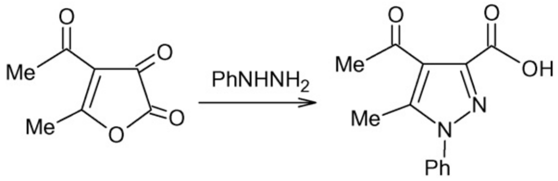

Fig. 1 – Chemical structure of the AMPC reagent.

2. Experimental

2.1. *Reagents and standard solutions*

Details concerning the synthesis and characterization of the AMPC reagent have already been described by Arıcı et al. [21]. The AMPC reagent was synthesized as described in literature (Fig. 1) [21]. The synthesized compound was characterized by melting point, FT-IR and elemental analyses. KNO_3, NH_4Cl, $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ and $Fe(NO_3)_3$ were obtained from Merck (Darmstadt, Germany). All other chemicals from different suppliers had analytical reagent grade. Deionized double distilled water was used for the preparation of the solutions. $1000\,\mu g\,mL^{-1}$ Fe(II) was prepared by dissolving 0.7021 g of $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ in 0.1 M sulfuric acid in a 100 mL volumetric flask [18]. Fe(III) was prepared by dissolving 0.4333 g of $Fe(NO_3)_3$ in 2% HNO_3 in a 100 mL volumetric flask. From these solutions, diluted working solutions were prepared on a daily basis. The AMPC solution (0.08%, w/v) was prepared daily by dissolving the requisite amounts of the AMPC in ethanol immediately before use. H_2O_2 solution (10 mL, 2%) was prepared in water. KNO_3 was added to give a constant ionic strength (μ) of 0.1 M. The glassware used was cleaned by soaking overnight in dilute HNO_3 (1:1, v/v), and then rinsed with distilled water several times.

2.2. *Synthesis of the AMPC reagent*

Phenylhydrazine (1.08 g, 10 mmol) in dry ether (10 mL) was added dropwise to a mixture of 4-acetyl-5-methyl-2,3-dioxo-2,3-dihydrofuran (1.54 g, 10 mmol) and dry ether (30 mL), and the reaction mixture was stirred at room temperature for 1 h. The precipitate was filtered off and crystallized from toluene. Solvents were dried by refluxing with the appropriate drying agent and distilled before use. The yield of the crude product was 68%. A small sample was purified and the synthesized compound was characterized by melting point, FT-IR and elemental analyses. The characterization results achieved were in agreement with the published information [21].

2.3. *Apparatus*

A PerkinElmer model 3110 flame atomic absorption spectrometer (FAAS) equipped with an air-acetylene flame was used for determining the concentration of Fe(III) in aqueous phase after back extraction. The operating parameters for the working element were set as recommended by the manufacturer. The Fe hollow cathode lamp was operated at 30 mA and the 248.3 nm line was used with a spectral bandwidth of 0.2 nm. A pH meter with a glass and calomel electrode pair (Nel pH 900) and a magnetic stirrer (Chiltern) were used. A Jasco Plus model 460 FT-IR spectrophotometer, a Carlo Erba 1108 elemental analyzer and a Buchi 510 melting point apparatus were also used in the experiments. A Hitachi model 150-20 UV–vis spectrophotometer with 1.0 cm quartz cell was used for the measurement of absorption spectra.