# Colorimetric detection, quantification and extraction of Fe(III) in water by acrylic polymers with pendant Kojic acid motifs

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Graphical abstract
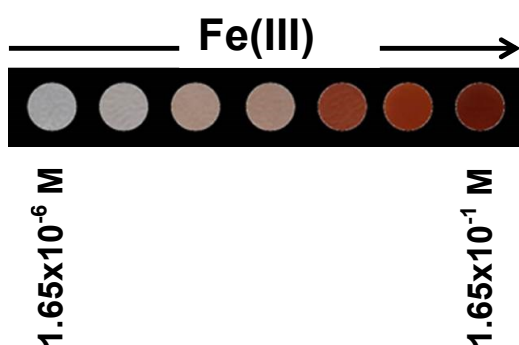
Research highlights

- A colorimetric sensory polymer toward Fe(III) was synthesized
- It was prepared with a monomer derived from Kojic acid, a natural product
- The film-shaped polymer was cut to obtain manageable solid sensory kits
- Fe(III) was efficiently extracted, detected, discriminated and quantified from water
- UV/vis and computer vision-based techniques were used for the Fe(III) analysis

ABSTRACT

We have prepared a solid sensory material for the extraction, detection and quantification of iron(III) in aqueous media. The material is a film-shaped colorless

polymer membrane which exhibits gel behavior. The Fe(III) extraction and sensing characteristics are imparted by a new monomer derived from a natural product, Kojic acid, which has recognized chelating properties toward Fe(III). The sorption of Fe(III) in water on the membrane has been thoroughly characterized, in particular the sorption kinetics, the sorption isotherms and the profiles in function of the pH have also been studied. Fe(III) sorption turned out to follow a pseudo-first order kinetics, taking around 30 min to reach equilibrium. The maximum sorption capacity is about 0.04 mmol/g and the sorption isotherms are well modelled according to Langmuir's equation. The complexes found in the solid phase are in good agreement with the corresponding previously identified in aqueous phase. Moreover, the sorption is highly specific, really a recognition process, and it occurs because of the formation of a colored complex (iron(III)-Kojic acid derivative moieties). Thus, the colorless sensory membrane turns reddish upon immersing in aqueous solutions containing Fe(III). The color output allows for both the qualitative visual determination of the Fe(III) concentration and also the titration of Fe(III) with: a) UV/vis technique (limit of detection of 3.6×10^{-5} M, dynamic range of five decades -lower concentration = 1.65×10^{-6} M-); b) computer vision-based analytical chemistry through the color definition of the sensory membrane (RGB parameters) obtained from a picture taken with a handy device, e.g., an smartphone (limit of detection of 2.0×10^{-5} M).

Keywords

Sensory polymers, Kojic acid, visual detection, iron detection, iron extraction

1. INTRODUCTION

The wide distribution in the environment of iron, as cation in different oxidation states, has an origin both natural and anthropogenic. The latter is caused by its multiple

applications in agriculture, in industry, in construction, in medicine, in the home, and in advanced technological fields. This has led to increasing concerns over their potential effects on the environment and, in parallel, in living beings [1].

Accordingly the detection and quantification of iron salts is a fundamental task in chemistry for its crucial role in living organisms and for being one of those metals extremely dangerous when its concentration exceeds a critical level. Its quantification is still a fundamental task in the clinical chemistry, but it is also of interest in the environmental and the agri-food fields. Nowadays, routine analyses are performed with methods that require trained staff and expensive equipment and techniques, such as atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectrometry (ICP-MS). On the other hand, chemical sensors allow for conversion of concentration of iron salts into signals that can be read by widely available instruments or even by an untrained observer if the signal is a color change (chromogenic sensor). A sensor is a self-contained analytical device able to convert a physical quantity, related to a chemical species concentration, into a signal which can be read by an observer or an instrument [2-8]. Sensors are used in everyday objects and have innumerable applications of which most people are never aware [9].

In recent years we have been working on the development of solid-phase sensors for iron(III) analysis in order to find fast, easy and cheap methods for the quantitative determination of this metal ion [10-13]. In this work we present a novel polymeric membrane for visual iron(III) sensing that features a derivative of Kojic acid as receptor moiety. Kojic acid, a γ-pyrone derivative (5-hydroxy-2-(hydroxymethyl)-4-pyrone), is a natural heterocyclic chelating ligand [14], and anions of Kojic acid and its derivatives behave as bidentate ligands and strongly coordinate to iron(III) via the carbonyl and phenolic hydroxyl groups [15].

The film shaped membrane is a manageable material from which solid sensory kits can be cut (e.g., small sensory discs). The first task to employ a solid phase as a sensor is the characterization of the sorption of the selected target species, studying kinetic and thermodynamic properties. Accordingly, a full characterization of the material was undertaken performing kinetics, isotherms and sorption profiles of iron(III) as a function of pH. Regarding colorimetric iron(III) sensing behavior of the membrane, it is colorless and transparent, but after immersion in iron(III) solutions it turns reddish within minutes. Its performance was evaluated by ultraviolet spectroscopy (UV/vis). Thus, a titration curve was built with the UV/vis data of the spectra taken to the sensory discs put in contact with water solutions at different iron(III) concentrations. Moreover, the titration was also performed by using a picture taken to the sensory discs, namely the color digital definition (RGB parameters) of the above mentioned sensory discs (computer vision-based analytical chemistry). Thus, the solid sensory discs are manageable materials that can be handle without care, stored under ambient conditions for long period of time, and used to measure the concentration of Fe(III) even by non-trained personnel using pictures taken with widely availed devices, such as mobile phones and tablets.

2. EXPERIMENTAL PART

The materials, synthetic procedures and measurements methods and methodologies are described in the Supporting Infomation (ESI) in Section S1.

2.1. Preparation of sensory materials

The sensory monomer derived from the Kojic acid (**3**) was prepared according with the experimental procedure described in the ESI (Section S1) and shown schematically in Scheme 1.

The film-shaped sensory membranes was prepared by the bulk radical polymerization of the hydrophilic monomers 1-vinyl-2-pyrrolidone (**VP**), 2-hydroxyethyl acrylate (**2HEA**), and the monomer derived from the Kojic acid (**3**). Ethylene glycol dimethacrylate (**EGDMA**) was used as cross-linking agent (Scheme 2). The co-monomer molar ratio **VP/2HEA/(3)/EGDMA** was 75/24/1/10. AIBN (1 wt%) was employed as a thermal radical initiator. The bulk radical polymerization reaction was carried out in a silanized glass mould that was 200 μm thick in an oxygen-free atmosphere at 60ºC overnight. After demolding, the film was conditioned at 60ºC for another night. The solid sensory substrates were manufactured from the film shaped membrane by using a puncher to cut out sensory discs (8 mm diameter).

Scheme 1.

Scheme 2

3. RESULTS AND DISCUSSION

Our objective is the preparation of an easily handable solid material for the extraction, detection and quantification of Fe(III) in pure water. The material is a film-shaped polymer network that bears in its structure a derivative of Kojic acid, which acts as a receptor and chemosensory core for Fe(III). The polymer has a cross-linked structure, it is hydrophilic, and behaves as a membrane with gel behavior, allowing Fe(III) ions in water to enter inside the material as solvated species where it interacts with the receptors giving rise to the extraction and sensing phenomena. We have chosen Kojic acid as receptor because it is a natural product and a well-known chelating ligand that strongly coordinate to iron(III) giving rise to red colored complexes [14-16]. Moreover, it has been used for many years for the spectrophotometric determination of iron in different contexts, e.g., in ores [17,18]. Accordingly, we designed and prepared an

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acrylic monomer (**3**) containing the Kojic acid sensory motif for preparing the membrane as colorimetric sensor and solid phase extractant (Scheme 1). The mechanism of the detection and extraction of Fe(III) is the formation of red $Fe(III)_n$:(Kojate motifs)$_m$ chelates with main stoichiometries (n:m) of 1:1, 1:2 and 1:3 (Scheme S1, ESI). The stability constants for the interaction between iron(III) and Kojic acid were reported by Muraki and are log K_1 = 10.20, log K_2 = 8.78, log K_3 = 7.53 [16]. The stoichiometry of $Fe(III)_n$:(Kojate motifs)$_m$ species in solid state, i.e., inside the membrane, and the relative exchange coefficients described below for our system are in agreement with the analogous in solution [16].

3.1. Materials preparation and characterization

The methacrylate sensory monomer (**3**) could not be conventionally prepared by a single step from Kojic acid and methacryloyl chloride and was synthesized following a two-step procedure. Firstly, the treatment of Kojic acid with thionyl chloride led to the reaction of the primary alcohol with the formation of the Kojic acid primary chloro-derivative [19] that led to (**3**) by reaction with potassium methacrylate at 100ºC (no thermal initiated polymerization was observed) [20]. The reaction steps are schematically shown in Scheme 1. The ^{1}H and ^{13}C NMR and FTIR spectra of the intermediates and monomers can be found in the experimental section and in the ESI, Section S1. The potential applicability of the sensory membrane is stressed by the fact that less than 1.6% by weight of the sensory synthetic monomer (**3**) is used in the preparation of the sensory material, *vide infra*, using >98.4% by weight of commercial and inexpensive co-monomers.

The membrane, or film, has good physical appearance and were creasable and handleable. The thermal resistance was evaluated by thermogravimetric analyses (TGA). The degradation temperatures that resulted in a 5% an d 10% weight loss under

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inert and oxidizing atmosphere (T_5) were ~280ºC and ~280ºC, respectively, in agreement with TGA data of copolymers of **VP** and **2HEA** [10,21]. The thermal degradation patterns is affected by the sorption of Fe(III) by the membrane. The immersion of the membrane in water containing relatively low concentration of Fe(III) increase T_5 to 355ºC due to the additional crosslinking caused by the formation Fe(III)$_1$:(Kojic acid moieties)$_2$ and Fe(III)$_1$:(Kojic acid moieties)$_3$ (Figure S5, ESI). Conversely, the immersion in water with higher concentration of Fe(III) lowers T_5 to 300ºC due to a partial displacement or the complex to Fe(III)$_1$:(Kojic acid moieties)$_1$ species with the concomitant diminishment in the crosslinking density (please see below the sorption and sensing studies).

Gel behavior is relevant for the membrane to sense in pure water because the target species enter into the material as solvated species by diffusion. However, the water uptake has to be modulated in order to keep good mechanical properties in the swelled state. For this purpose, a moderate water swelling percentage ranging from 40% to 100% is desirable. The membrane composition was designed to meet this criterion, and its water swelling percentage was 65%.

3.2. Sorption studies

3.2.1. Sorption kinetics and isotherms

In Figure 1, as an example, the kinetic profiles of iron(III) sorption on the membrane is reported. Kinetic experiments are useful principally to select the time needed to reach equilibrium between the two phases. Experiments are performed under acid conditions (pH 2.5) in order to avoid iron(III) hydrolysis reactions.

As it can be see, the iron(III) sorption on the membrane needs around 30 min to achieve the equilibrium. The experimental data are fitted using a HPDM model (homogeneous particle diffusion model) where the diffusion of ions, from the solution to the sorbent, is the slowest step. The relation between the amount of sorbed metal ion in the solid phase (q, mmol g^{-1}) and time (t, min) is formally equal to the pseudo first order kinetic equation [22] and the rate constants (k) obtained is 0.20(2) min^{-1} (R^2=0.979; SE(y) = 0.015).

Figure 1.

In Figure 2 the sorption isotherm of iron(III) on the membrane in solution of 0.1 M KNO_3 at 25°C and pH 2.5 is reported.

Figure 2.

The Langmuir and the Freundlich models are usually used to describe the relationships between q (sorbed quantity in the solid phase, mmol g^{-1}) and C_{eq} (solute concentration when the equilibrium is reached). Their different performances have been reviewed many times [23] and they will not be further commented here.

The Langmuir model was the best to describe the sorption of Fe(III) on the membrane. From the non-linear fitting of the data of Figure 2, a maximum sorption capacity q_{max}= 0.041(2) mmol g^{-1} and K_L= 6.5(9) × 10^3 M^{-1} are computed (R^2 = 0.984; SE(y) = 0.002). The theoretical total number of active sites calculated from the weight percentages of (**3**) in the membrane is 0.07 mmol g^{-1} in sufficient agreement with the q_{max} here obtained.

3.2.2. Sorption profiles

The thermodynamic characterization of ion-exchange and chelating materials is fundamental to describe the separation process and to predict the behaviour of the

analyte sorption on solid phases in different systems. As already pointed out, in particular for ion-exchange and complexing resins [23-25], a metal ion M can be sorbed onto a chelating solid phase through complexation reactions and the general equilibrium is expressed by:

$$\mathrm{M} + n\overline{\mathrm{H}_r\mathrm{L}} \leftrightarrows \overline{\mathrm{MH}_p\mathrm{L}_n} + q\mathrm{H}$$

(1)

where M is the metal ion, $\mathrm{H}_r\mathrm{L}$ the r-protonated form of the active site of the solid phase, H the proton, and the overbar represents species in the solid phase. Charges are omitted for simplicity. This reaction is studied on the basis of sorption profiles in the function of pH. The method is described in several papers and reviews [23-28]. It enables us to describe the sorption curve with an equation obtained by a combination of exchange coefficients $\beta_{1np\mathrm{ex}}$, associated with each possible reaction between the metal ion and the active site, and selected to minimize the difference between the calculated and the experimental sorption profiles.

The exchange coefficient, $\beta_{1np\mathrm{ex}}$, is given by:

$$\beta_{1np\mathrm{ex}} = \frac{[\overline{\mathrm{MH}_p\mathrm{L}_n}] \cdot [\mathrm{H}]^q}{[\mathrm{M}] \cdot [\overline{\mathrm{H}_r\mathrm{L}}]^n}$$

(2)

The exchange coefficients depend on the concentration of the counter ion in the solution and in the solid phase, while the intrinsic complexation constants ($\beta_{1np\mathrm{i}}$) are independent of the composition of the solution, so they characterized the sorption equilibria. The relationship between the exchange coefficient and the intrinsic complexation constant is demonstrated to be [23,24]:

$$\beta_{1np\mathrm{i}} = \beta_{1np\mathrm{ex}} \cdot \frac{\gamma_{\mathrm{H}}^q \cdot \gamma_{\mathrm{C}}^{(m-q)}}{\gamma_{\mathrm{M}}} \cdot \frac{[\mathrm{C}]^{(m-q)}}{[\overline{\mathrm{C}}]^{(m-q)}}$$

(3)

where m is the charge of the metal and γ_X indicates the activity coefficients of the species X. C is the counter ion of the active site of the solid material.

Different experiments are performed under different conditions and the set of intrinsic constants calculated in the first experiment should be equal (within the experimental error) to that determined in any other considered condition. Intrinsic protonation constants are independent of the experimental conditions, so they characterize the sorption reactions. For reasons of simplicity, the active sites in the solid phase are always in analytical excess with respect to the metal ion because these conditions are close to the practical application.

Once the reactions have been identified, it is possible to describe the ligand properties of the solid phase in the considered ionic media and at the punctual pH values, through the partition coefficient, K^*. It represents the ratio of total metal ion in the solid phase to the free metal ion in the solution and is given by the following relation:

$$K^* = \frac{c \cdot V}{[\mathrm{M}] \cdot w} = \sum \frac{\beta_{1npex}\left[\overline{\mathrm{H}_r\mathrm{L}}\right]^n}{[\mathrm{H}]^q}$$

(4)

where c is the concentration of the metal sorbed, V (mL) is the volume of the solution phase and w (g) is the mass of dry solid material. The summation is extended to all the complexes formed by the considered metal ion with the active group of the solid phase.

The strategy for selecting the sorption reactions is to first consider the simplest stoichiometries and reactions equal to those of the "monomeric units" in solution. In this study we selected as input data the complexation constants of the complexes Fe(III)/Kojic acid in aqueous solution.

Some examples of sorption profiles are reported in Figure 3, where the symbols represent the experimental points, while the continuous lines are the calculated sorption curves.

Sorption was studied both in absence and in presence of two different ligands, 2,6-pyridine dicarboxylic acid (PDCA) and sodium oxalate. They compete with the active sites of the membrane, shifting the sorption at a higher pH, making it possible to identify, if any, other complexes of the metal ion with the solid phase.

Figure 3.

A fairly good fitting is obtained assuming, for all the three profiles, the formation of the following complexes in solid phase, with the same set of exchange coefficients: FeL $\log\beta_{101ex}$ = 10(5); FeL$_2$ $\log\beta_{102ex}$ = 19.8(4); FeL$_3$ $\log\beta_{103ex}$ ≈ 25.3; FeHL$_3$ $\log\beta_{113ex}$ = 32.7(9); Fe(OH)L$_3$ $\log\beta_{1-13ex}$ =17.5(3), being the first three exchange coefficients in solid phase in pretty good agreement with the computed conditional constants in solution [16].

From these results, it seems that other two differently protonated species, i.e. FeHL$_3$ and FeL$_3$OH, would be formed in solid phase. These complexes have never been reported before for Kojic acid in aqueous solution, but they are probably promoted by the high concentration of active groups inside the membrane. We have already proved the formation of these apparently unusual complexes in different cases with commercial chelating resins and different metal ions [24,29-32].

3.3. Sensing Fe(III) in aqueous media

3.3.1 Detection an quantification of Fe(III) in water

The immersion of sensory discs cut form the sensory membrane in water containing Fe(III) resulted in a color change of the discs from colorless to red, the color development depending on the Fe(III) concentration.

Thus, a Fe(III) titration curve could be built using a set of 7 sensory discs after immersion overnight in Mili-Q water containing different concentration of Fe(III), from 1.65×10^{-6} to 1.65×10^{-1} M, under acidic conditions (pH = 2, HCl/KCl buffer). A control sensory disc immersed in this medium lacking Fe(III) was also prepared. After that, the discs were pulled out of the aqueous solution and allowed to dry under ambient conditions. The color development within the discs upon increasing concentration of Fe(III) was clearly visible and permitted the semi-quantitative naked eye titration of Fe(III), and their UV/vis spectra allowed for the construction of the titration curve (Figure 4a and 4b). The limits of detection and quantification were 3.6×10^{-5} and 1.1×10^{-4} M, respectively.

There is increasing interest for chemical analysis based on color changes recorded with ubiquitous imaging devices resulting in friendly analytical procedures for in situ and real-time monitoring [33]. Accordingly, a digital picture taken to the discs allowed for the elaboration of a titration curve using the digital color definition (RGB parameters) of the sensory discs (Figure 4c; Section S4, ESI) [10,34]. The limits of detection and quantification were 2.0×10^{-5} and 6.0×10^{-5} M, respectively. To test the applicability of the sensory material to real samples, a test sample containing a concentration of Fe(III) of 3.31×10^{-4} M was prepared using tap water that was buffered at pH = 2 (the concentration of Fe(III) corresponded to the sum of the added and innate tap water ferric ion concentration). Calibration curves obtained with UV/vis spectra and digital pictures (RGB parameters) of reference discs immersed in tap water (buffered at pH = 2; concentration ranging from 1.0×10^{-5} to 1.0×10^{-3} M) allowed for the calculation

of the concentration a of the test sample in fully agreement with the real value (calculated concentration by UV/vis and RGB parameters of digital picures: 3.26×10^{-4} and 3.29×10^{-4} M, respectively).

The limit of detection is relatively high, higher than the US National Secondary Drinking Water Regulations for iron (0.3 mg/L, 5.4×10^{-6} M), and higher, for instance, to that reported by Gupta et al. (1.9×10^{-8} M [2]; 9.5×10^{-7} M [3]; 5.0×10^{-6} M [8]) and by ourselves (2.5×10^{-6} M [10], 1.3×10^{-7} [13]). However, the response of the sensory material could be tuned by modifying the molar ratio of the monomers in the synthesis of the sensory membrane. For instance, it could be improved by increasing the molar ratio of iron receptors (kojic acid derivative monomer (**3**)).

Figure 4.

3.3.2. Response time

Response time is a key parameter for sensor performance for real life applications. Thus, it has been evaluated the response time of the membrane immersed in solution by UV/vis spectroscopy as the time needed to achieve 99% of the absorbance (490 nm) variation (Figure 5). This time was 20 min for a water solution containing a concentration of Fe(III) of, 5×10^{-3} M. This time accounts for the diffusion of the species into the membrane and concomitant reaction with the Kojic acid motifs. This time is in fully agreement with the time needed to reach the equilibrium between the two phases previously analyzed describing the sorption kinetics.

Figure 5.

3.3.3. Interference study

The selectivity study was initially carried out previously to the preparation of the sensory material with a 1.6×10^{-3} M solution of monomer (**3**) in DMA/H$_2$O (50/50). To this solution, a solution of a broad set of cations (Al(III), NH$_4^+$, Ba(II), Cd(II), Ce(III), Cs(I), Co(II), Dy(III), Fe(III), La(III), Pb(II), Li(I), Mg(II), Mn(II), Hg(II), Ni(II), K(I), Rb(I), Sm(III), Na(I), Sr(II), Zn(II), Zr(IV)), and anions (cyanide, acetate, hydroxide, fluoride, perchlorate, dodecyl sulfate, nitrite, ethoxide, hydrogen phthalate, pyrophosphate, persulfate, methanesulfonate, pyrophosphate dibasic, trifluoromethanesulfonate, *p*-toluenesulfonate, bromide, thiocyanate, oxalate, carbonate, benzoate, dihydrogenphosphate, sulfate, chloroacetate, trifluoroacetate, periodate) were added (1.6×10^{-2} M for each species). A red color development was observed for Fe(III), the system remaining silent for the other cations and anions (Figure 6 shows the UV/vis response to the cations). This selectivity was confirmed for the solid sensory membrane both visually and by computer vision-based analysis. Moreover, the sensory discs gave the same response for Fe(III) and for a cocktail of cations (Figure 6; Figure S6 and Table S5, ESI).

Figure 6.

4. CONCLUSIONS

We have used Kojic acid, a natural and proven chelating agent for iron(III), to prepare a colorimetric sensory polymer as a solid film (membrane). The Kojic acid derivative, chemically anchored to the polymer backbone, behaved as excellent receptor for Fe(III) in water media. The characterization of the sorption of Fe(III) on the membrane showed that the sorption followed a pseudo-first order kinetics, taking around 30 min to reach

equilibrium. The sorption isotherms are well modelled according to Langmuir's equation, and the maximum sorption capacity was about 0.04 mmol/g. The complexes found in the solid phase are in pretty good agreement with the correspondent previously identified in aqueous phase. Colorless discs cut from the sensor membrane (8 mm diameter), as solid titration kits, turned red upon being in contact with water solutions containing Fe(III). The color development permitted both the visual concentration estimated by the naked eye and the titration with the UV/vis technique, achieving for Fe(III) a limit of detection of 3.6×10^{-5} M with a dynamic range determination was of five decades (lower concentration = 1.65×10^{-6} M). In parallel, pictures taken to the kits permitted the titration using the color definition of the sensory discs as analytical input (limit of detection of 2.0×10^{-5} M). Thus, the color development of the sensory system and the practicable solid kits enable the visually use of these materials by all people, regardless of their background; concomitantly, portable devices, e.g., tablets and smartphones, allow for the out-of-lab quantification of target species in an in-situ, fast and costless fashion.

Acknowledgments

Supporting information

Experimental (intermediates and membrane characterization) and principal component analysis (PCA) data.

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