Talanta 130 (2014) 90–95

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

ω-Thio nitrilotriacetic chemically modified gold electrode for iron determination in natural waters with different salinity

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ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form
11 June 2014
Accepted 18 June 2014
Available online 24 June 2014

Keywords:
Chemically modified electrodes
Iron
Natural waters
Electrochemical sensors
Self-assembled monolayer

ABSTRACT

The preparation, characterization and analytical application of a chemically modified gold electrode (CME), based on ω-thio nitrilotriacetic acid derivative (*N*-[5-[[[[20-(acetylthio)-3,6,9-trioxaeicos-1-yl]oxo]carbonyl]amino]-1carboxypentyl]iminodiacetic acid) self-assembled monolayer (SAM), have been described. The electrode has been characterized by electrochemical techniques and tested for its response towards metallic ions, demonstrating to be effective for the determination of ionized iron at sub—μg L^{-1} level by differential pulse cathodic stripping voltammetry (DPCSV). The analytical response towards iron in natural water (tap water, marine water) and the interference of ions usually present and chelating agents (humic acids and EDTA as model ligand of high complexing capacity) have been evaluated.

1. Introduction

Iron is one of the most abundant element in the Earth's crust; it plays an essential role in photosynthesis, and is a limiting growth nutrient for phytoplankton in some parts of the open ocean [1]. Its most common oxidation states are Fe(II) and Fe(III); Fe(II) is a relatively soluble species in water, that is rapidly oxidized in oxygen rich environments. Conversely, Fe(III) forms strong complexes and is thermodynamically stable in water albeit of low solubility [2], but photoreduction can convert it to Fe(II) [3]. Overall, Fe concentration in natural waters is strongly dependent on the solubility of the present complexes, so that can vary greatly from 10^{-6} M for river water down to 10^{-9} M for coastal sea water and 10^{-11} M for ocean water [4]. Although the World Health Organisation (WHO) does not issue a health based guideline value for iron [5], permissible values in drinking water ranges from 5.36 μM (0.3 mg L^{-1}) to 53.6 μM (3 mg L^{-1}), as levels higher than this causes water to become discoloured and taste metallic.

In view of these premises, several methods for the detection of trace amounts of iron in various samples have been developed. Analytical techniques include spectroscopic techniques such as atomic emission [6] and graphite furnace atomic absorption spectrometry [7], spectrophotometric [8,9], luminescent [10,11] and electrochemical methods, such as stripping voltammetry proceeded by adsorptive collection of electroactive complexes of iron [12] or potentiometry [13]. Among the different techniques, electrochemical methods usually enjoy of instrumental simplicity and lower price. In a recent review concerning the different electrochemical methods employed for the determination of iron, voltammetric techniques using mercury as an electrodic material were stated as the most sensitive; on the other hand, newer approaches use platinum, and carbon in its various allotropic forms, the latter being a cheap and benign replacement material for mercury [14]. In particular, stripping voltammetry allows direct determination of trace metals in real samples and it is widely used, due to its ability to preconcentrate iron ions as its complexes (detection limits from 10^{-9} M to 10^{-12} M); it has a wide linear dynamic range (typically two orders of magnitude), and in some cases can be used to measure several elements simultaneously. Furthermore, the instrumentation can easily be taken into the field, as it is lightweight, compact, and readily automated [15]. Sensitive detection of Fe(III) has been carried out to levels below the WHO guideline limit at unmodified edge plane pyrolytic graphite electrode and screen printed electrode using square wave voltammetry [16]. However, the use of solid electrodes is often precluded due to memory effects, passivation of the surface and high background currents. Thus, approaches involving modified electrodes are in this way encouraged. In fact, chemical modification of the electrode surface can lead to an increased electrocatalytic activity, and better analytical selectivity and sensitivity are often achieved. Examples of important modification strategies are self-assembled monolayers (SAMs), in particular SAMs on gold surfaces, that allow manipulation in molecular scale to obtain highly ordered and stable recognition systems [17,18]. SAM onto

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http://dx.doi.org/10.1016/j.talanta.2014.06.034
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gold surfaces can be prepared from thiols, disulfides, and sulphides; it resists desorption over a wide range of pressure, temperature, pH, and electrical potential. So, due to their physical and chemical resistance, as well as from the selectivity that can be obtained modulating the chemical nature of the monolayer, they have been used for trace determination of different types of analyte [19–21]. However, to the best of our knowledge, there is only one report about determination of iron(III) at a SAMs gold electrode, prepared with 2-mercaptosuccinic acid [22]. The described SAM was used for Fe(III) determination in tap and mineral waters and in a pharmaceutical sample approved for the management of iron deficiency [23]. The current is linearly dependent on *p*Fe at low iron concentration, up to about 0.3–0.4 mg L^{-1}, with LOD and LOQ of 1.6 μg L^{-1} and 5.5 μg L^{-1}, respectively.

Starting from the consideration that NTA is a strong ligand for metal ions, and that ω-derivatized NTA terminated thiols are commercially available (Sigma-Aldrich) or easy synthesizable [24–26] we were encouraged to use *N*-[5-[[[[20-(acetylthio)-3,6,9-trioxaeicos-1-yl]oxo]carbonyl]amino]-1 carboxypentyl]iminodiacetic acid (Acethyl Thio NTA: ATNTA) to form a SAM on gold electrodes, exploiting its ability to bind iron, due to the high complexation constant of the parent molecule NTA for this ion (Fe(III): log K_f=15.9; Fe(II): log K_f=8.3 [27]).

In this paper, we report the preparation and full characterization by electrochemical methods of the Au-SAM (chemically modified electrode, CME) and differential pulse cathodic stripping voltammetry (DPCSV) for quantitative determination of iron. Application of the developed method to the analysis of real samples of natural and marine waters was examined, and low detection limit (LOQ 0.03 μg L^{-1}) have been observed also in presence of potentially iron chelating ligands commonly found in natural waters, i.e. humic substances (HA) and strong complexing agents investigated chosing EDTA and NTA as model ligands.

2. Experimental section

2.1. Materials and reagents

Reagents of the purest grade available were purchased from Sigma-Aldrich and used as received. Milli-Q water was used throughout to prepare solutions. Iron(III) standard (Aldrich, standard for ICP-OES, 1000 mg L^{-1}) was used daily to prepare standard solutions of 100 mg L^{-1} and 1 mg L^{-1}.

$Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ solutions were prepared from the $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ salts (Aldrich). All glassware was carefully cleaned with concentrated nitric acid and then rinsed with Milli-Q water in order to avoid contamination.

Electrochemical measurements were carried out with BASI PWR-3 power module and EF-1085 C-3 cell stand, equipped with a gold (1.6 mm^2 diameter), eventually modified, working electrode; an Ag/AgCl/NaCl (3 M NaCl, saturated with AgCl) reference electrode and a platinum wire as auxiliary electrode, both obtained from BASI.

Static contact angle goniometry measurements were performed with a KSV CAM200 instrument, by employment of the sessile drop technique, with water as the solvent.

N-[5-[[[[20-(Acetylthio)-3,6,9-trioxaeicos-1-yl]oxo]carbonyl]amino]-1carboxypentyl]iminodiacetic acid (ATNTA) was synthetized by following a multistep procedure previously described in literature [26]. KCl buffer solution (0.1 M in Milli-Q water) was conserved over Chelex (1 g/100 mL) and diluted with Milli-Q water prior to use.

Snow was taken on Simplon Pass (CH) during March 2012. Tap water was from Pavia aqueduct (2012) and natural sea water from Ligurian Sea (Spotorno, Savona, sampled in 2012).

Synthetic seawater was prepared according to know methods [28].

ICP-MS-DRCe (inductively coupled plasma equipped with mass spectrometric detector and direct reaction cell) was used for iron determination; the instrument was a Perkin Elmer Elan DRC instrument, and the standard procedures suggested by the manufacturer were followed.

2.2. Gold electrode pre-treatment

The electrode gold disk cross section exposed (diameter 1.6 mm) was abraded with successively finer grades alumina (from 1 μm to 0.05 μm), rinsed with water, and briefly cleaned in an ultrasonic bath to remove any trace alumina from the surface. Abrasion favours oxidation of gold surface (as can be noticed by cyclic voltammetry), so it was necessary to perform an electrochemical cleaning before the CME preparation, by cycling the potential between 0.0 V and 1.40 V in 0.5 M H_2SO_4 solution, scan rate of 200 mV s^{-1}, until Au oxidation and reduction peak currents reach a constant value.

2.3. Electrode modification

The bare gold electrode was dipped overnight in a solution containing: 2.5 mM ATNTA, 2.5 mM 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 2.5 mM tributylphosphine in methanol, previously saturated with EDTA. The modified electrode obtained was then abundantly rinsed with ethanol and Milli-Q water before use.

2.4. Electrodes characterization

Before modification, bare gold electrode area was estimated electrochemically by Cyclic Voltammetry (CV) according to the modified form of the Randles–Sevcik equation [29], using 0.1 M ferrocene in acetonitrile with an Ag/AgCl acetonitrile non-aqueous reference electrode (BAS) in 0.1 M tetrabutylammonium perchlorate.

The modified electrode was characterized with usual electrochemical techniques and the presence of the SAM was checked by measuring the double layer capacitance before and after SAM formation, being related to the effective thickness, the dielectric constant, the order of the SAM [30,31] and the presence of functional groups able to influence the dielectric constant of the monolayer [32]. The CV method used [33] ensures values unaffected by faradaic contributions.

The variation of capacitance for different immersion times in the ATNTA solution can be used to follow the adsorption kinetics of the thiol onto the gold substrate: it is known [33] that the measurement of interfacial capacitance provides a convenient way for evaluating the degree of surface coverage, θ, of organic adsorbates. θ is the fraction of the electrode area covered with the monolayer film. It can be obtained using known methods [34,35].

Surface coverage (Γ, mol cm^{-2}) can be estimated by reductive desorption in alkaline ($pH > 11$) solution of the adsorbed thiol from electrode surface [36].

To check the effective formation of the SAM, we also employed electroactive probes, such as ferrocyanide and hexaamminoruthenium [29]. The behaviour of the CME was examined by CV, at 100 mV s^{-1} scan rate in 0.1 M KNO_3, pH 7.0, 1 mM $[Fe(CN)_6]^{3-/4-}$ (E_i=−200 mV, E_f=+500 mV) or 1 mM $[Ru(NH_3)_6]^{3+/2+}$ (E_i=+200 mV, E_f=−500 mV) [37].

In addition to electrochemical techniques, we checked the presence of the monolayer by means of static water contact angle goniometry, acquired employing the sessile drop technique [38,39].

2.5. Response of the SAM electrode towards iron

To evaluate the response of modified electrode towards metallic ions and iron in particular, cyclic voltammetry (CV) and differential pulsed cathodic stripping voltammetry DPCSV were employed.

Various buffer solution and pHs were tested. The shape of iron stripping signal was evaluated both at lower (between 6 and 2) and higher (up to 8) pH values with ionic strength in the ranges 0.1–1 M.

The CME has been investigated for the determination of Fe ion in natural water samples. Metal ions were preconcentrated under constant stirring (300 rpm) from the sample, to which 0.1 M KCl was added, by applying a suitable potential at the modified electrode, chosen in order to avoid monolayer desorption, and determined in cathodic stripping voltammetry (for further details on the DPCSV parameters, see below).

The SAM response towards iron was before evaluated in synthetic samples at different ionic strengths, with and without EDTA and HA, to evaluate the influence of ligands often present in environmental waters. Quantitative analysis was performed by the standard addition method.

3. Results and discussion

3.1. SAM preparation and characterization

Bare gold electrode area was estimated to be 0.02319(±5) cm^2, in good accordance with geometrically calculated gold electrode area (0.0201 cm^2) indicating a well-polished surface with low roughness.

The preparation of the SAM starting from ATNTA is simple, but some skilfulness are needed (see Supplementary information, SI, Fig. S1).

First of all, the preparation of the SAM via in situ hydrolysis of the acetylated derivative ATNTA (2.5 mM) avoided loss of product [40].

Moreover, the in-situ deprotection with DBU, consisting of a basic cleavage of the acetyl moiety [41], eluded the formation of disomogeneous and highly unstable monolayers [40], that are instead observed using ammonia as a base [40,42,43]. The in situ deprotection is performed in the presence of tributhylphosphine as sacrificial reductant to avoid the oxidation of the thiols to disulphides [41].

The modified electrode was prepared in a methanolic solution saturated with tetraacidic EDTA to prevent the presence of metallic impurities in the SAM. Moreover, shaking the SAM electrode for a few minutes in 0.1 M EDTA pH=7 was a good remedy when the blank is nevertheless noisy.

Surface coverage *vs.* time for 2.5 mM concentration of NTA is shown in Fig. 1. The experiment was performed using a solution of ATNTA prepared as described before, and let for 2–3 h at room temperature before use, to guarantee complete deprotection of the acetyl moiety by DBU. The absorption process is complete within 2 h, in good accordance with results reported by other authors [44]. SAM preparation is however usually prolonged overnight, for rearrangement and stabilization.

Different characterizations (as depicted below) were performed on the SAM, prepared in the optimized manner as described in Section 2.3. After 12 h rearrangement and stabilization adsorption.

Bare gold electrode double layer capacitance was 88.8(±5) µF cm^{-2}, in accordance with literature data [29], while SAM electrode capacitance was 46.4(±2) µF cm^{-2} (mean values and standard deviations were calculated from three independent measurements on the same electrode). As expected, the bare gold electrode capacitance was higher than that of the SAM, which is dependent on the monolayer thickness and porosity [43]. The difference between the two capacitance values (80%), suggested that the SAM is an open structure and not well-packed monolayer [45].

Γ was calculated to be 9.74×10^{-10} mol cm^{-2}; the high surface coverage obtained is due to the greatly ordered structure obtained onto the gold surface.

Fig. 2 shows the response of the CME to the two electroactive probes, $[Fe(CN)_6]^{4-/3-}$ and $[Ru(NH_3)_6]^{3+/2+}$. As can be observed (continuous curve), the reversibility of the $[Fe(CN)_6]^{4-/3-}$ redox probe is completely lost after electrode modification, due to the electronic repulsion between the doubly deprotonated NTA terminals ($pKa_1=1.9$; $pKa_2=2.5$; $pKa_3=9.7$ [27]) and the negatively charged redox probes.

Instead, response of the positively charged probe $[Ru(NH_3)_6]^{3+/2+}$ showed a complete reversibility of the signal at the SAM electrode (dashed curve in Fig. 2), as evaluated by anodic and cathodic peaks ratio (which is close to 1) and from the peak-to-peak potential separation ($E_{pa}-E_{pc}$: ΔE_p) (ca. 60 mV, close to 57 mV that is the value expected for a reversible redox couple exchanging one electron). This

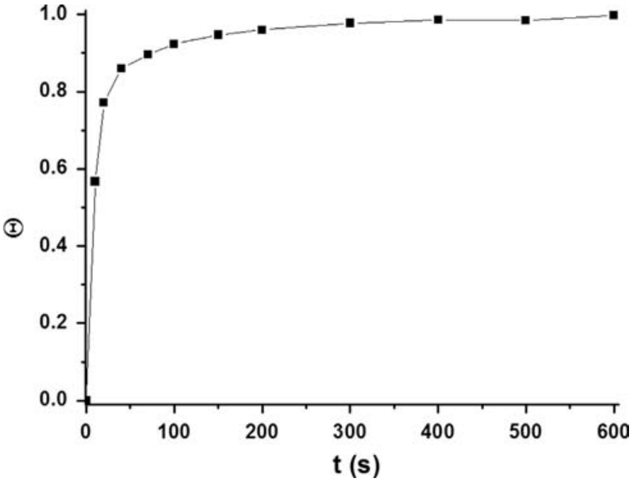

Fig. 1. ATNTA adsorption kinetic onto gold electrode. The experiment was performed using a solution of ATNTA let for 2–3 h at room temperature before use, to guarantee complete deprotection of the acetyl moiety by DBU. Conditions: 2.5 mM ATNTA, 2.5 mM DBU and 2.5 mM tributylphosphine in methanol.

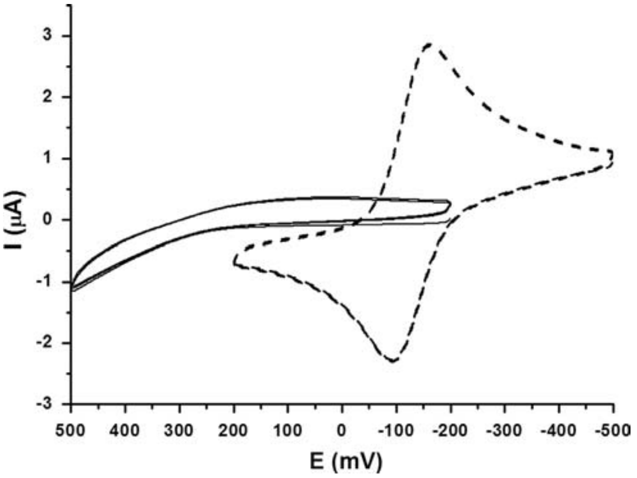

Fig. 2. CV of $Fe(CN)_6^{3-}$ (continuous line) and of $Ru(NH_4)_6^{3+}$ (dotted line) at ATNTA SAM, 5 cycles each. Conditions: CV at 100 mV s^{-1} scan rate in 0.1 M KNO_3, pH 7.0, 1 mM $[Fe(CN)_6]^{3-/4-}$ ($E_i=-200$ mV, $E_f=+500$ mV) or 1 mM $[Ru(NH_3)_6]^{3+/2+}$ ($E_i=+200$ mV, $E_f=-500$ mV).

behaviour is consistent with the absence of electrostatic repulsion between the probe and the negatively charged monolayer, and was already observed in similar cases, although the exact electron transfer mechanism is not fully understand (permeation of the redox probe towards pinhole in the SAM or electron transfer by tunneling effect to the SAM/probe complex are supposed to be the principal mechanisms) [46].

Static water contact angle measurements, acquired by means of the sessile drop technique, resulted of 58(±3)° for the unmodified gold surface and of 10(±1)° for the CME surface, showing the presence of a hydrophilic layer, in agreement with the chemico-physical properties of the ATNTA adsorbed.

3.2. Response of the SAM electrode towards iron. Cyclic voltammetry

To characterize the behaviour of the SAM towards iron(III), first investigations involved cyclic voltammetry (CV) in a wide potential range. Fe(III) presents a reversible peak at −230 mV in KCl 0.1 M (pH=7). The monolayer rapidly saturated in highly concentrated Fe(III) solution (e.g. submitted to five CV cycles in 10 mg L^{-1} Fe(III) in 0.1 M KCl pH=7, $E_i = +350$ mV, $E_f = -500$ mV, $\nu = 100$ mV s^{-1}), and CV, after medium exchange with iron free KCl 0.1 M ($E_i = +350$ mV, $E_f = -500$ mV, $\nu = 100$ mV s^{-1}) showed both anodic and cathodic peaks (see Fig. 3). The peaks diminished from scan to scan and are completely removed after immersion of the electrode for a few minutes in 0.05 M Na_2H_2EDTA.

In this way, a preconcentration of Fe from a 10 mg L^{-1} 0.1 M KCl solution for 30 s at open circuit, followed by medium exchange and CV in iron-free medium (0.1 M KCl, $E_i = +300$ mV $E_f = -500$ mV) confirmed that iron behaves as a surface-confined redox couple, as peak current is linearly dependent on scan speed in the range 5–100 mV s^{-1}, with regression line I(μA)=0.0029 mV s^{-1} +0.1181 $R^2 = 0.898$. The anodic and cathodic peak potentials are observed at −230 mV and −270 mV, respectively. The peak-to-peak potential separation (ΔE_p) is small and almost independent of the potential scan rate, with peak width of ca. 100 mV, as expected for the (reversible, surface confined) $\text{Fe(III)} + e^- \rightarrow \text{Fe(II)}$ conversion; the difference of the E_p (ca. 40 mV) of the surface confined couple is far from ideality and does not conform to theoretical prediction (0 mV) reasonably due to the resistance of the SAM [47]. In this way, it has been possible to simultaneously evaluate the amount of iron able to saturate the monolayer and the stoichiometry of bounded ATNTA: iron [45]. This ratio could be calculated by comparing the degree of the SAM surface coverage Γ, obtained by reductive desorption in KOH, and that of the complex saturated with Fe^{3+}, Γ_1, evaluated as described in [48], which resulted to be $1.10 \cdot 10^{-9}$ mol cm^{-2}, not significantly different from the value of Γ of 1.02×10^{-9} mol cm^{-2} calculated for the SAM. This indicated that a 1:1 complex was formed. It has to be noted that iron concentration greater than 10 mg L^{-1} or longer deposition times lead to the same result, confirming that the monolayer was fully saturated with iron. Moreover medium exchange was essential, as the contribution to the peak height of free Fe(III) in solution in which it is present at mg L^{-1} levels cannot be neglected.

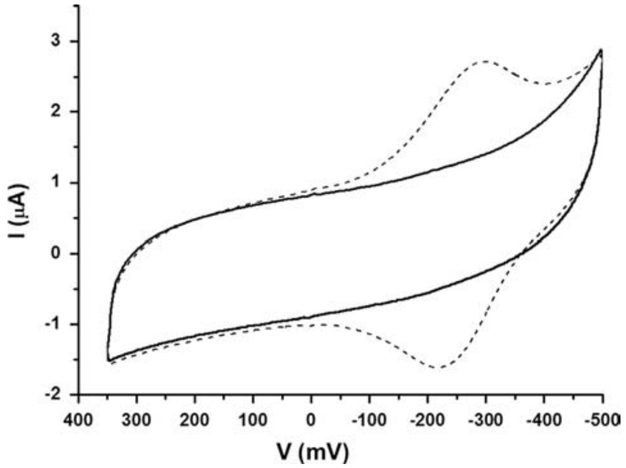

Fig. 3. CV at ATNTA SAM: blank (continuous line) and after accumulation with Fe^{3+} (dotted line) after media exchange (iron free KCl 0.1 M, pH=7, $E_i = +350$ mV, $E_f = -500$ mV, $\nu = 100$ mV s^{-1}); a reversible peak at −230 mV is observed. Accumulation conditions: five CV cycles in 10 mg L^{-1} Fe(III) in 0.1 M KCl pH=7, $E_i = +350$ mV, $E_f = -500$ mV, $\nu = 100$ mV s^{-1}

3.3. Response of the SAM electrode towards iron—Stripping voltammetry

The SAM was shown to be able to preconcentrate Fe(II) and Fe (III) with equal sensitivity and response from argon-saturated samples to which 0.1 mol L^{-1} KCl was added, as the positive accumulation potential used to attract iron to the surface is also capable to oxidize Fe(II) to Fe(III). The preconcentrated metal ion was stripped in DPCSV ($E_i = +350$ mV, $E_f = -500$ mV, $\nu = 100$ mV s^{-1}, pulse amplitude 50 mV, pulse repetition 100 ms, pulse width 40 ms, sampling time 10 ms: these parameters were kept constant).

Unlike what observed in CV for solution at high (10 mg L^{-1}) Fe (III) concentration when the monolayer is completely saturated, during the stripping analysis only a negligible part of the complexing groups on the SAM surface are involved, so that during the stripping scan all the Fe accumulated is released into the solution without the need of electrode cleaning from scan to scan.

The amount of the preconcentrated metal ion depends on several parameters, such as the nature of the supporting electrolyte, its pH, the preconcentration time and potential. The effect of each parameter was evaluated by maintaining fixed all the other, and results are those below reported. The standard parameters used for 30 μg L^{-1} Fe(III) were: 0.1 M KCl pH=7, accumulation time 60 s, accumulation potential +300 mV. Concerning the nature of the supporting electrolyte, its concentration and pH, (KCl, KNO_3, trisodium citrate, acetic acid/sodium acetate pH=4 buffer, ammonium chloride/ammonia buffer pH=8.5, trisodium nitrilotriacetate), the best results were obtained in 0.1 M potassium chloride at pH in the range 7±1. To keep almost constant the pH with the standard additions, iron standard solution was prepared at pH about 5.

At pH <7, the conditional complexation constant of iron would give satisfactory selectivity and sensitivity (log K_f for Fe(III)=8 at pH=3 [27]) but the lifetime of the monolayer would be reduced and less defined stripping peaks are obtained.

The influence of accumulation potential was also investigated; although accumulation can be performed at open circuit, this did not offer advantages in terms of sensitivity of the method.

For this reason, different accumulation potentials were tested; as can be seen in SI Fig. S2a, peak potential linearly increased with deposition potential in the range 0–+400 mV with a least squares regression I(μA)=8.1(±4)·10^{-4} mV+1.7(±1) $R^2 = 0.9941$. A plateau is observed for $E_{\text{dep}} > 400$ mV However, though greater sensitivity could be obtained, an accumulation potential $E_{\text{dep}} = +300$ mV was chosen to avoid a premature damage of the SAM surface. As expected, longer preconcentration times (t_{prec}) increased the amount of metal ion accumulated at the SAM surface with a corresponding enhance in the peak current and more favourable detection limits, until saturation was reached, as can be seen in SI Fig. S2b.

Concerning the optimum pH of the supporting electrolyte (KCl 0.1 M), it was noted that higher signals are obtained in the range ($5 < \text{pH} < 7$), while peak potential decreases linearly from +50 mV (at pH=3) to −210 mV (at pH=7); the regression line observed is E_p(mV)=−85(±3) pH+320(±10). At pH >7 the peak potential does not change (see SI Fig. S2c). This behaviour suggests that an exchange of 2 H^+ is involved in the complexation at the monolayer, and that at pH >7 the monolayer is fully deprotonated.

With a preconcentration time of 60 s, linearity was observed from 1 μg L^{-1} up to 90 μg L^{-1} with a regression line I(μA)=0.0133 (±2) μg L^{-1}+0.0003(±1) R^2=0.9962; the voltammetric curves in the range 5–80 μg L^{-1} are shown in Fig. 4. In this case, LOD of 0.3 μg L^{-1} (5.5 nM) and LOQ of 1 μg L^{-1} (18 nM) were found. Preconcentration times of 300 s were usually suitable for metal ions concentrations in the range 0.05–1.5 μg L^{-1}, with a regression line of I(nA)=0.019(±2) ng L^{-1}+0.53 R^2=0.9964 (notes that in this case the current is expressed as nano Amperes and not in micro Amperes). The voltammograms obtained in this concentration range are reported as inset in Fig. 4. LOD of 0.01 μg L^{-1} (0.2 nM) and LOQ of 0.03 μg L^{-1} (0.5 nM) were found.

In the described condition, the SAM electrode is stable for at least 40 deposition/scan cycles. The calibration curves obtained in different days using SAM prepared each times (within laboratory reproducibility) showed constantly similar results in terms of LOD, LOQ and precision. The variation on the slope of the calibration curve is in the order of ±30%, but a decrease in the slope is also accomplished by a parallel decrease in the blank current, so that the sensitivity remains unchanged (at 95% confidence limit, n=30). When standard additions are made with Fe(II) instead of Fe(III) solution, the same results are obtained at the applied potential, since the Fe(II) preconcentrated at the electrode is oxidized to Fe(III).

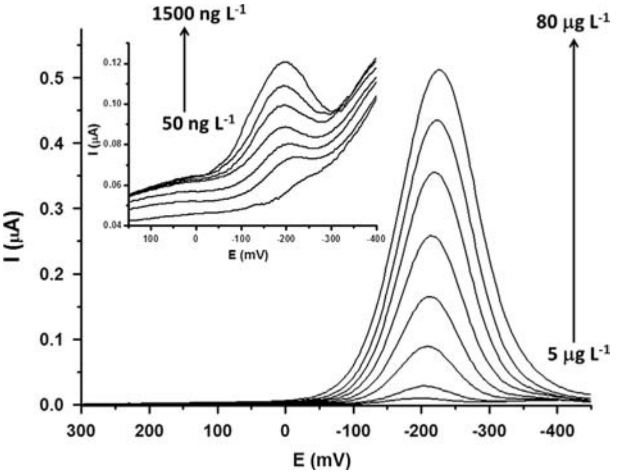

Fig. 4. DPCSV curves of Fe^{3+} at ATNTA SAM (KCl 0.1 M, pH 7) in the range 5–80 μg L^{-1} (t_{dep}=60 s, accumulation potential +300 mV) and 50–1500 ng L^{-1} (inset; t_{dep}=300 s). Electrochemical conditions as reported in the text.

3.3.1. *Interferences-influence of complexants and organic matter*

The behaviour of the CME in 0.1 M KCl neutral solutions containing different anions or cations usually presents in natural water other than iron was verified. Cu(II), Zn(II), Co(II), Ni(II), Pb(II) did not interfere up to a 20:1 metal ion/iron weigh ratio. Common anions (nitrates, carbonates, chloride, phosphates) did not interferes also at 1000:1 ratio with iron. Calcium and magnesium cause a decrease in Fe(III) intensity but still allowing its determination, though with lower sensitivity: in fact, at 1000:1 Ca (or Mg): Fe ratio, the signal is reduced by 10% with respect to the one observed in the absence of the interferences. Nevertheless, the determination of Fe(III) in waters containing up to tens (>300 mg L^{-1}) of mg L^{-1} of Ca is still possible increasing the deposition time. The presence of ligands, i.e. hydrogen carbonate, HA or EDTA/NTA, was tested. pH was fixed by adding to the test solution HCl 0.01 M or KOH 0.01 until neutrality was reached.

Very interestingly, humic substances and hydrogen carbonate ions did not cause any interference even at concentration 200 time larger than iron; EDTA or NTA added to the solution did not interfere up to molar ratio of 20 with respect to iron. Higher concentrations, not expected in natural water samples, reduce Fe signal (see point 3.1, where a concentrated EDTA solution is used to clean the electrode surface from accumulated metal ions). In this way, we can assume that by this method is determined the total iron concentration present in natural water, as illustrated in the next section.

3.4. *Analysis of natural water samples*

Tap and synthetic marine water samples spiked with Fe(III) were analyzed and the results are shown in Table 1. Natural waters at different salinity, containing Fe were also analyzed, and the results compared to those measured by inductively coupled plasma mass spectrometry (ICP-MS), coupled with a dynamic reaction cell (DRC), depending on iron concentration. The similar values obtained showed again that by the proposed method is measured the total iron concentration, including that fraction present as complexes with organic matter.

It must be stressed that the method is particularly useful for the analysis of total iron in high salinity water: in this case, no supporting electrolyte is required, so that any possible contamination is avoided, contrary to the determination by ICP, which requires sample dilution and consequent loss of sensitivity, to reduce problems connected with the high salinity of the sample (interferences, occlusion of the nebulizer). Recoveries ranged from 90% to 120%.

Table 1
Iron determination in different water samples. Electrochemical conditions described in the text.

	Fe(III) added	Sample concentration	Recovery [c]
Snow	0	<LOD[a,b]	
Conductivity 13 μS cm^{-1}	0.2 μg L^{-1} Fe(III)	0.18(±2) μg L^{-1}[a]; <LOD [b]	90(±11)%
	1 μg L^{-1} Fe(III)	1.1(±2) μg L^{-1}[a]; 1.3(±2)[b]	120(±18)%
Tap water	0	<LOD [a,b]	105(±1)%
Conductivity 256 μS cm^{-1}	5 μg L^{-1} Fe(III)	5.3(±2) μg L^{-1}[a]; 5.4(±2) μg L^{-1}[b]	
Sea water, synthetic	0	<LOD[a,b]	98(±1)%
Conductivity 50 mS cm^{-1}	5 μg L^{-1} Fe(III)	4.9(±3) μg L^{-1} [a]; 5.2(±4) μg L^{-1}[b]	
Sea water, natural	0	5.1(±3) μg L^{-1} [a]; 5.2(±4) μg L^{-1}[b]	107(±1)
Conductivity 49.9 mS cm^{-1}	5 μg L^{-1} Fe(III)	10.8(±4) μg L^{-1} [a]; 11.2(±4) μg L^{-1}[b]	

[a] By SAM electrode.
[b] By ICP-DRC-MS (LOD 0.3 μg L^{-1}).
[c] From the mean value of ICP-DRC-MS and CME.

4. Conclusions

In the present proposal, we describe the preparation and analytical application of a gold CME based on ANTNA, a ω-thio nitrilotriacetic acid derivative.

The device allows total iron determination in natural waters at ng L^{-1} level, without any sample pre-treatment, which is instead essential for spectroscopic (e.g. ICP-MS for which preconcentration is required, at these levels) [49] or other electrochemical (digestion with oxidants or acids to remove organic matter) techniques.

In detail, the most sensitive electrochemical methods so far described refer to the use of mercury electrodes [14], highly discouraged due to its toxicity [50]. Furthermore, some of these require UV pre-treatment of the sample to remove organic matter.

Methods employing electrodes of material different from mercury have been also described.

Among the 22 methods reported in Ref. 14 basing on modified electrodes, for only two the LOD is lower or comparable with our method, but a poor reproducibility in the preparation of the electrodes is of concern. Additionally, rapid deterioration of the signal [51,52] is to be expected due to the nature of the modifiers.

On contrast, the method proposed here is mercury free, and the total iron in natural waters can be directly determined at the SAM electrode, without neither pre-treatment of the sample nor addition of any reagent. Furthermore, the employed SAM gold electrode is sensitive enough to be applied to natural samples without preconcentration, and it can directly operate in highly saline (marine) waters. Moreover, it allows a quantification of the total iron concentration, that is an important and complementary information with respect to the speciation data obtained by other methods [14]. Contrary to other chemical modified electrodes described in literature [14] gold electrodes based on SAM [53] are reproducible, easy to prepare, with no loss of sensitivity during the analysis time; for these reasons, they appear as an attractive option with respect to already existing electroanalytical methods.

It has to be stressed that LOD and LOQ, which are better than those measured by ICP-DRC-MS in tap and mineral water (LOD of 300 ng L^{-1}), at this CME are obtained also for high salinity waters, with recovery ranging from 90% to 120%.

Acknowledgments

The authors would like to thank Prof. Piersandro Pallavicini and Dr. Giacomo Dacarro (Dipartimento di Chimica, University of Pavia) for goniometry contact angle measurements. This work was principally supported by PRIN 2009 - 2009YRH27R_001 Research Programs of International Relevance, from Ministero della Pubblica Istruzione Rome (MIUR, Italy).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.06.034.

References

[1] J.H. Martin, R.M. Gordon, S.E. Fitzwater, Nature (London) 345 (1990) 156–158.
[2] X. Liu, F.J. Millero, Mar. Chem. 77 (2002) 43–54.
[3] W.L. Miller, D. Kester, J. Mar. Res. 52 (1994) 325–343.
[4] C.M.G. Van den Berg, M. Nimmo, O. Abollino, E. Mentasti, Electroanalysis 3 (1991) 477–484.
[5] World Health Organisation, Guidelines for Drinking-Water Quality, second ed., World Health Organisation, Geneva, 1996.
[6] X.C. Duan, R.L. McLaughlin, I.D. Brindle, A. Conn, J. Anal. At. Spectrom. 17 (2002) 227–231.
[7] M. Niemela, H. Kola, K. Eilola, P. Peramaki, J. Pharm. Biomed. Anal. 35 (2004) 433–439.
[8] C.I. Measures, J. Yuan, J. Resing, Mar. Chem. 50 (1995) 3–12.
[9] S. Blain, P. Treguer, Anal. Chim. Acta 308 (1995) 425–432.
[10] H. Bagheri, A. Gholami, A. Najafi, Anal. Chim. Acta. 424 (2000) 233–242.
[11] C. Yi, W. Tian, B. Song, Y. Zheng, Z. Qi, Q. Qi, Y. Sun, J. Lumin. 141 (2013) 15–22.
[12] P. Ugo, L.M. Moretto, D. Rudello, E. Birriel, J. Chevalet, Electroanalysis 13 (2001) 661–668.
[13] W.H. Mahmoud, Anal. Chim. Acta 436 (2001) 199–206.
[14] M. Lu, N.V. Rees, A.S. Kabakaev, R.G. Compton, Electroanalysis 24 (2012) 1693–1702.
[15] K.A. Howell, E.P. Achterberg, C.B. Braungardt, A.D. Tappin, P.J. Worsfold, D. R. Turner, Trends Anal. Chem. 22 (2003) 828–835.
[16] M.i.n. Lu, Richard G. Compton, Electroanalysis 25 (5) (2013) 1123–1129.
[17] a) A. Ulman, Chem. Rev. 96 (1996) 1533–1554;
b) I. Turyan, D. Mandler, Anal. Chem. 69 (1997) 894–897.
[18] H.O. Finklea, in: A.J. Bard, I. Rubinstein (Eds.), Electroanalytical Chemistry: A Series of Advances, vol. 19, Marcel Dekker, New York, NY, 1996, p. 109.
[19] D. Mandler, I. Turyan, Electroanalysis 8 (1996) 207–213.
[20] E. Chow, J.J. Gooding, Electroanalysis 18 (2006) 1437–1448.
[21] A. Profumo, D. Merli, M. Pesavento, Anal. Chim. Acta 557 (2006) 45–51.
[22] R.K. Shervedani, A. Hatefi-Mehrjardi, A. Asadi-Farsani, Anal. Chim. Acta 601 (2007) 164–171.
[23] S. Beshara, H. Lundqvist, J. Sundin, M. Lubberink, V. Tolmachev, S. Valind, G. Antoni, B. Langstrom, B. Danielson, Br. J. Haematol. 104 (1999) 288–295.
[24] J.K. Lee, Y.-G. Kim, Y.S. Chi, W.S. Yun, I.S. Choi, J. Phys. Chem. B 108 (2004) 7665–7673.
[25] R. Valiokas, G. Klenkar, A. Tinazli, A. Reichel, R. Tampè, J. Piehler, B. Liedberg, Langmuir 24 (9) (2008) 4959–4967.
[26] G.B. Sigal, C. Bamdad, A. Barberis, J. Strominger, G.M. Whitesides, Anal. Chem. 68 (1996) 490–497.
[27] ⟨http://www.veredlungschemikalien.basf.de/ev-wcms-in/internet/en_GB/function/conversions:/publish/content/EV/EV5/products/ca/doc/trilon_a.pdf⟩.
[28] ⟨http://publishing.cdlib.org/ucpressebooks/view?docId=kt167nb66r&chunk.id=d3_5_ch06&toc.id=ch06&brand=eschol⟩.
[29] F. Zavarise, D. Merli, A. Profumo, Anal. Chim. Acta 668 (2010) 177–181.
[30] A. D'Annibale, R. Regoli, P. Sangiorgio, T. Ferri, Electroanalysis 11 (7) (1999) 505–510.
[31] C.E.D. Chidsey, D.N. Loiacono, Langmuir 6 (1990) 682–691.
[32] J.A.M. Sondag-Huethorst, L.G.J. Fokkink, Langmuir 11 (1996) 2237–2241.
[33] I. Tredici, D. Merli, F. Zavarise, A. Profumo., J. Electroanal. Chem. 645 (2010) 22–27.
[34] B.B. Damaskin, O.A. Petrii, V.V. Batrakov, Adsorption of Organic Compounds on Electrodes, Plenum, New York, NY, 1971.
[35] H.H. Bauer, Electrodics, Wiley, New York, NY (1972) 81.
[36] M.M. Walczak, D.D. Popenoe, R.S. Deinhammer, B.D. Lamp, C. Chung, M. D. Porter, Langmuir 7 (1991) 2687–2693.
[37] A. Profumo, F. Zavarise, D. Merli, I. Tredici, G. Alberti, S. Protti, M. Fagnoni, Anal. Chim. Acta 598 (2007) 58–64.
[38] C.D. Bain, E.B. Troughtoyt, Y. Tao, J. Evall, G.M. Whitesides, R.G. Nuzzo, J. Am. Chem. Soc. 111 (1989) 321–335.
[39] C.D. Bain, J. Evall, G.M. Whitesides, J. Am. Chem. Soc. 111 (1989) 7155–7164.
[40] J.M. Tour, L. Jones, D.L. Pearson, J.J.S. Lamba, T.P. Burgin, G.M. Whitesides, D. L. Allara, A.N. Parikh, S. Atre, J. Am. Chem. Soc. 117 (1995) 9529–9534.
[41] A. Singh, D.H. Dahanayaka, A. Biswas, L.A. Bumm, R.L. Halterman, Langmuir 26 (16) (2010) 13221–13226.
[42] M.I. Bèthencourt, L. Srisombat, P. Chinwangso, T.R. Lee, Langmuir 25 (2009) 1265–1271.
[43] C.S. Barkschat, S. Stoycheva, M. Himmelhaus, T.J.J. Müller, Chem. Mater. 22 (1) (2010) 52–63.
[44] F.S. Damos, R.C.S. Luz, A.A. Sabino, M.N. Eberlin, R.A. Pilli, L.T. Kubota, J. Electroanal. Chem. 601 (2007) 181–193.
[45] D. Merli, F. Zavarise, I. Tredici, M. Pesavento, A. Profumo, Electroanalysis 24 (4) (2012) 825–832.
[46] L. Sun, B. Johnson, T. Wade, R.M. Crooks, J. Phys. Chem. 94 (1990) 8869–8887.
[47] M.E. Gomez, A.E. Kalfer, J Chem Educ. 69 (6) (1992) 502–505.
[48] C.M.A. Brett, A.M.O. Brett, Electrochemistry Principles, Methods and Applications, Oxford Science Publications, New York, NY (1993) 186.
[49] ⟨http://www.perkinelmer.com/CMSResources/Images/44-152005APP_NexION%20300D-seaFASTSeawater.pdf⟩.
[50] ⟨http://ec.europa.eu/environment/chemicals/mercury/⟩.
[51] Z. Gao, P. Li, Z. Zhao, Talanta 38 (1991) 1177–1184.
[52] R.-I. Stefan, S. Ghebru Bairu, J.F. van Staden, Instrum. Sci. Technol. 31 (4) (2003) 411–416.
[53] Ø. Mikkelsen, C.M.G. van den Berg, K.H. Schrødera, Electroanalysis 18 (1) (2006) 35–43.