Determination of Iron: Electrochemical Methods

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Abstract
Iron is an abundant element in the environment which plays an important role in environmental and biological systems. In particular, its essential function in photosynthesis has been seen as a limiting factor for phytoplanktons in ocean waters. Thus, sensitive speciation and determination of iron is of major interest, and many techniques have been established for analytical purposes. Electrochemical methods have been commonly explored due to their inexpensive, simple and rapid nature, with adsorptive stripping voltammetry (AdSV) being widely used due to its ability to complex and preconcentrate iron ions for ultrasensitive detection. This paper aims to present a review of recent determinations of trace iron using electrochemical methods.

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1 Introduction

Iron is one of the most common elements in the Earth’s crust and exists naturally in the environment in mineral species, rock, groundwater and seawater [1]. It plays an important role in environmental, industrial, human and biological systems [2], and as such, it is of key interest for analytical study. Iron determination in seawater is of major interest due to its importance in oceanic biogeochemistry [3–6]. In waters, iron uptake is influenced by its oxidation state and complexation by ligands and as a consequence, has been found to be a limiting growth nutrient for phytoplankton [3,7]. This imposes important implications for air-sea exchange of carbon dioxide which could be a cause of concern for marine life. Its biological activity is often monitored as it is one of the key trace elements for living organisms and is seen to play an essential part in photosynthesis, acting as an enzyme cofactor in plants [8]. Redox reactions are reliant on iron-containing enzymes whereby electron transport is facilitated by oxidation state change of the metal. Iron is an essential metal for life and plays several key roles within humans [9]. It is found in bulk in haemoglobin in the red blood cells where it complexes to molecular oxygen and transports this around the body [10]. As a carrier of oxygen to the cells, deficiency of iron in the body can interfere with vital functions and lead to leathargy, fatigue and anaemia [11].

Iron exists in many oxidation states ranging from −II to +VIII [12], however it is most commonly seen as ferrous (+II) and ferric (+III) ions in the environment. Thermodynamic properties of the iron species vary greatly. Fe(II) is a soluble species in water, however it is rapidly oxidised in oxygen rich environments. On the other hand, Fe(III) forms stronger complexes and is thermodynamically stable in water albeit of low solubility [13], but photo-reduction of the species converts it to Fe(II) [14]. In seawater, natural Fe(III) chelators exist and some believe up to 99% of iron in waters is found complexed to organic ligands and thus its concentration is low except when extremely stable complexes are formed [15]; concentration of iron ranging from 0.1 nM to 10 nM [16,17] has been suggested. It has also been reported that the concentration of dissolved iron in freshwater is greater than that of seawater [18] due to the proximity to terrestrial and continental shelf sources. Soluble iron species in natural waters can vary from 10⁻⁶ M for river water, to 10⁻⁹ M for coastal sea water and to 10⁻¹¹ M for ocean water [19]. The World Health Organisation (WHO) does not issue a health based guideline value for iron [20], however permissible values in drinking water ranges from 0.3–3 mg L⁻¹, as levels greater than this causes water to become discoloured and taste metallic.

The abundance of iron and its variable oxidation states in the environment calls for their accurate determination and quantification. Many analytical methods have been developed to detect and quantify iron; these include voltammetry [21], flow injection analysis [17], chromatography, chemiluminescence [22], spectrophotometry [23] and spectrofluorescence [24]. Spectrophotometric methods [17,25,26] have been widely used, however, these are relatively expensive for use in ultra trace determination of metal ions and can suffer from interferences. The size and weight of the instruments also restricts their use to land based experiments.
Electrochemical methods such as stripping voltammetry have been favored due to their inexpensive, simple and rapid nature [27,28]. Anodic and cathodic stripping voltammetry, in particular, have shown many benefits such as good selectivity and highly sensitive determination [29]. As well as this, square wave voltammetry and differential pulse voltammetry are commonly utilized for ultra sensitive detection. Direct reduction of Fe(III) to elemental metal occurs at around -1.5 V vs. SCE [30], however it cannot be analytically employed in acidic solutions as the signal for hydrogen reduction coincides with that of the voltammetric signal for iron. In addition, iron also has extreme redox potentials and due to the low solubility of iron in mercury for polarographic methods [31-33], voltammetric stripping of iron via the metal in its elemental form is limited. As a result of this, trace iron is a metal that cannot be quantified by conventional ASV.

Determining dissolved iron concentration in waters may be difficult without preconcentration, and as such, complexation can be carried out prior to sample determination. A practical method for such determination of low levels of iron is cathodic stripping voltammetry (CSV). In ocean waters, when iron becomes complexed with organic ligands, concentration of iron is deduced by taking advantage of ligand competition between natural ligand present in the medium and the added ligand used for voltammetric detection [34-36]. Concentration of the labile iron can be calculated from a linear plot made from: 

$$\frac{[Fe^{3+}]}{[FeL]} = \frac{[Fe^{3+}]}{C_L} + 1/\left(K_{FeL}/C_L\right)$$

where $[FeL]$ is the concentration of iron complexed by the natural ligand, $L$, $C_L$ is the total concentration of $L$, and $K_{FeL}/C_L$ is the conditional stability constant of the complex [34].

Specific adsorption of a complex of the metal ion with the chelator occurs first at the electrode surface, followed by reductive stripping to Fe(II). The reduction current is then measured to give the concentration of the adsorbed metal ion. Without chelation, it may be difficult to accurately determine Fe$^{2+}$ and Fe$^{3+}$ concentrations due to the reversibility of the Fe$^{2+}/$Fe$^{3+}$ couple at a bare electrode. One main advantage of CSV includes the ability to determine the chemical speciation of iron; it is important to determine the speciation of iron as well as its concentration in waters. Pehkonen [12] noted that whilst iron may be the limiting nutrient for phytoplankton growth, Fe(II) is probably the preferred nutrient. A common procedure for iron speciation involved first complexing Fe(II) with a chelating agent then determining its concentration. Following from this, Fe(III) is reduced to Fe(II) from which the total iron concentration is found, and then by subtraction of Fe(II) from the total iron, concentrations of each species can be calculated [37,38]. Being a long and complicated approach to speciation of iron, more modern techniques for simultaneous determination of Fe(II) and Fe(III) have been devised [39,40].

At subnanomolar levels of iron, sensitivity of metal ions by adsorptive stripping voltammetry can be seen to be improved by their complexation or chelation with specific ligands. This technique employs a preconcentration step before voltammetric measurements, which allows highly sensitive measurements of metal ions to be made. Chelating reagents for iron determination include catechol [41], 1-nitroso-2-naphthol (NN) [19], solochrome violet RS [42], cupferron [43], 2-(2-thiazolylazo)-p-cresol (TAC) [44] and 1,2-cyclohexanedione dioxime [45]. The use of chelates, however, changes the reduction potential of the complex with respect to the iron. Catalytic enhancement with adsorptive stripping voltammetry is another technique for decreasing limits of detection [45-48].

Traditionally, the most sensitive working electrode for trace metal detection had been the hanging mercury drop electrode [49]; however, nowadays analytical methods involving mercury electrodes are avoided. Due to the drawbacks of mercury toxicity [50,51], development for mercury-free electrodes has been of obvious interest and one of the main materials for electrode design is carbon. Carbon electrodes such as carbon paste (CPE), glassy carbon (GCE), edge plane pyrolytic graphite (EPPG) [52-54] are analytically useful materials and avoid the toxic complications arising from mercury. Under optimised conditions, it can provide selective determination with minimum interferences. Diamond paste electrodes have also shown to be a very promising material for iron detection. This new technique was investigated by Stefan et al. [21], giving the most sensitive voltammetric determination of iron to date with a limit of detection of 13 pM. Many methods involving chemical modification of the electrode surface have also been explored; this will be covered later in the text.

In this paper, we review recent (post-millennium) publications for sensitive iron determination to provide a timely and much needed update of the field, which has developed significantly since the landmark reviews of Pehkonen [12] and Achterberg [18] in 1995 and 2001, respectively. Our focus will be directed towards electrochemical methods for detection. A range of methodologies is summarised and a collection of tables with limits of detection and analytical method for each electrode material is included. Tables 1, 2 and 3 are provided in the text, reviewing iron analyses using the different electrodes.

2 Electrochemical Methods

Many different electrochemical methodologies for Fe(II) and Fe(III) detection have been reported and recent voltammetric determinations are reviewed here. The most common method used has been adsorptive cathodic stripping voltammetry (AdCSV). In this method, ligands are used to complex with iron and this adsorbs onto the surface of the working electrode. By holding the electrode at
A specific potential, the complex is preconcentrated prior to reductive stripping of the complex back into solution, allowing a very low detection limit to be achieved; \[ \text{Fe}^{2+} + n \text{e}^{-} \rightarrow \text{Fe}^{n+} \]. Further lowering of detection limits by extending the deposition time for adsorption and using catalytic oxidants has also been reported. Major advantages of AdCSV include low cost, compact and portable instrumentation and good sensitivity which is useful for on board detection.

A variety of electrode materials have been used, and in the following, three main materials; mercury, platinum and carbon, have been detailed. The sections detail all the different voltammetric methods used with the different electrode materials.

### 2.1 Mercury

Mercury based electrodes such as hanging mercury drop electrodes (HMDE) and mercury film electrodes (MFE) have been commonly used for analytical stripping analysis owing to their high resistivity, large hydrogen overpotential and reproducibility [28,49,55]. Sensitive detection of iron has been achieved with many authors reporting detection limits in the nanomolar [19,41], and even picomolar range [36,46]. Whilst the majority of iron determination in the 20th century was performed using mercury electrodes, mercury toxicity concerns [51,56] have led to the use of mercury dwindling in recent years, and research has turned towards alternative electrodes with reports of iron determination using mercury based electrodes becoming rare.

One of the earliest voltammetric studies of iron on a mercury electrode was carried out by Brainina and Roizenblat [57] in 1963 using cathodic stripping voltammetry (CSV) at a mercury drop electrode (MDE), giving a 10 µM detection limit. Many followed, including Berge and Drescher [58] who looked into exchange reactions for the determination of iron. Here, iron displacing lead from lead-EDTA complex was determined by anodic stripping voltammetry down to a concentration of 0.4 nM at a HMDE. The most sensitive detection of iron, pre-2000, was reported by Gledhill and Van den Berg [34]. These authors used catalytic cathodic stripping voltammetry (CCSV) to take advantage of ligand competition between the NN (1-nitroso-2-naphthol) ligand and natural ligands present in seawater, in the presence of H₂O₂. The dissolved Fe(II) is oxidised to Fe(III) in the presence of the oxidising agent, and Fe(III) forms a complex with the ligand which subsequently adsorbs onto the HMDE electrode during the deposition step. During the voltammetric scan, the Fe(III) complex is reduced to Fe(II), but is then reoxidised by H₂O₂. The reoxidised Fe(III) contributes again to the reduction current, greatly enhancing the sensitivity of the stripping method. Whilst a very sensitive detection limit of 0.8 pM was achieved, the authors also used this technique to investigate the organic speciation of iron in seawater. Fe(II) was first masked with 2–2’-dipyridyl so that Fe(III) could be determined; the Fe(II) concentration could then be calculated by subtraction.

It can be seen that use of mercury electrodes sometimes eliminates the need for surface modification for analytical study, however, in most cases, a complexing agent is required for successful stripping voltammetry by adsorptive cathodic stripping voltammetry (AdCSV). Some commonly used complexing agents for AdCSV include catechol [41], 1-nitroso-2-naphthol (NN) [59], and solochrome violet [42]. The structures of these ligands are shown in Figure 1.

Van den Berg and Huang [41] complexed iron with catechol and used cyclic voltammetry to characterise the potential of the catechol-Fe(III) complex. Catechol is quite easily oxidized and can thus act as a reducing agent in some cases; as well as this, the Fe(III) oxidation state is stabilized as a result of complexation by catechol ions. This direct determination of dissolved iron was applied to seawater and a detection limit of 0.6 nM was achieved. However, despite being a sensitive analytical method, the technique was not able to determine Fe(III) and Fe(II) simultaneously and speciation of iron could not be distinguished.

A similar complex-based adsorptive approach was performed by Wang and Mahmoud [42], with solochrome violet RS (SVRS) as the complexing agent for Fe(III). Iron was chelated with SVRS and adsorbed onto a HMDE before reductive stripping of the species was used to determine sensitive detection of iron. The method relies on effective interfacial accumulation of the Fe(III)/SVRS chelate onto the mercury electrode. Although the technique offers similar detectability as the catechol-based adsorptive approach, Wang and Mahmoud report
shorter preconcentration times, extended linear range, and less interferences from iron(II), copper and lead to give a LoD of 0.7 nM. Another frequently used complexing agent is 1-nitroso-2-naphthol (NN), most commonly taken advantaged of by Van den Berg et al. [19,34,60] to complex Fe(III). In 1991, Van den Berg and Mentasti [19] reported a sensitive method to determine trace levels of iron in seawater using adsorptive deposition of the iron complex on the mercury drop electrode (MDE). Although a sensitive detection of 0.2 nM Fe could be seen, this required a 10 minute deposition time of the iron complex on the electrode. NN as a complexing ligand yielded highly sensitive results towards Fe(III); the authors attributed this to the strong complexing ability with Fe(III) because they contain π-orbital electrons which apparently improves adsorption of the complexes on the mercury drop [61]. The analytical method described looks exclusively at the concentration of Fe(III) as oxidation of Fe(II) to Fe(III) is performed at the electrode surface before subsequent complexation and reduction.

Many more authors have reported a range of different voltammetric determination of iron at mercury electrodes, a collection of these have been included Table 1.

Post-millennium, the most sensitive account of iron determination was reported by Obata and Van den Berg [46] who were able to detect picomolar levels of iron in seawater using catalytic cathodic stripping voltammetry. Adsorptive accumulation of the iron complex, Fe(III)-2,3-dihydroxynaphthalene (DHN), onto a static mercury drop electrode in the presence of bromate ions was followed by cathodic stripping of the species. The reductive current was catalytically enhanced by the oxidizing agent, BrO₃⁻, and after 60 s adsorption time, gave a detection limit of 13 pM. The authors also claim to achieve even lower limits of detection by extending the adsorption time. Obata and Van den Berg used several ligands, and evaluated their use for the detection of iron. It was seen that the Fe(III)-2,3-dihydroxynaphthalene (DHN) complex gave the highest sensitivity, suggesting greater stability of the complex. The new catalytic method gave very sensitive results, which was subsequently applied to iron determination in the North Atlantic Ocean. Following on, in 2006, Van den Berg [62] reported the chemical speciation of iron in seawater by cathodic stripping voltammetry using 2,3-dihydroxynaphthalene (DHN) as an adsorptive and competing ligand.

In 2000, Croot and Johnsson [44] reported sensitive determination of iron and its speciation by cathodic stripping voltammetry in seawater using competing ligand 2-(2-thiazolylazo)-p-cresol (TAC). A detection limit of 0.1 nM using sensitive competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV) with an iron-TAC complex could be seen. Nagui et al. used cathodic stripping voltammetry with NN to determine the total dissolved iron concentration and its speciation in freshwater. Determination of Fe(III) complexation by natural organic ligands was determined by competitive ligand equilibration method. A detection limit of 1.8 nM was achieved.

Ghoneim et al. [63] carried out the simultaneous determination of iron with 10 other elements (Cd, Pb, Cu, Sb, Bi, Se, Zn, Mn, Ni and Co) in water by adapting the conditions of the sample to optimise the detection of each element. Differential pulse anodic stripping voltammetry (DPASV) with a hanging mercury drop electrode (HMDE) was used for direct simultaneous determination of the metal elements. An ordered set of procedures was used involving varied pHs to detect each of the elements in turn; iron was detected last after 2-(5-bromo-2-pyridyldazo)-5-diethylaminophenol (5-Br-PADAP) was added to solution and determined by DPAdSV. 5-Br-PADAP was needed as a complexing agent for iron and a preconcentration time applied before a detection limit of 0.39 nM was determined. Witter et al. [64] measured the total iron concentration by cathodic stripping square wave voltammetry (CSSWV) to give a detection limit, after an 8 minute deposition period, of 0.15 nM. The authors employed a competitive ligand exchange stripping (CLECSV) technique for the speciation of iron by establishing competition between the added ligand (NN) and the natural organic ligands present for the complexation of added Fe(III).

Mikkelsen and Schroder [65] monitored Fe(II) using a dental amalgam sensor electrode using differential pulse anodic stripping voltammetry to detect iron in the nanomolar region. The authors present solid amalgam electrodes as a non toxic material with unique sensitivity for bivalent iron. Detection limits for 180 s preconcentration gave a value of 9.0 nM for Fe(II). Mikkelsen et al. [66] presented a new method for the determination of iron in estuarine and coastal seawater based on differential pulse anodic stripping voltammetry (DPASV) at a rotating Ag-alkyl disk electrode. The Ag-alkyl mercury electrode allowed very sensitive detection to be carried out, with a limit of detection of 0.3 nM for iron, and as well as this, iron speciation could be carried out by using chelating agents such as EDTA to mask the electrochemically labile species.

In 2005, Stozhko et al. [67] determined iron in natural and drinking waters by stripping voltammetry using a thick film graphite containing electrode modified with calomel. Addition of pyrocatechol allowed an iron complex to be formed for preconcentration at the electrode, and a sensitive detection of 0.36 nM Fe(III) was achieved. In the course of analysis, a very thin droplet-like mercury coating is formed, but despite this, the electrode can be considered safe because after analysis, the thin mercury layer can be easily and completely converted back to calomel. The authors report a “non toxic” procedure for determining trace amount of Fe(III) in natural an drinking waters.

Another report using catechol, together with dimethylglyoxime (DMG), for iron complexation was carried out by Echeandia [68] in 2011. Adsorptive cathodic stripping voltammetry with the mixed ligands was performed at
Table 1. Iron analyses using mercury electrodes. **Technique:** ASV, Anodic Stripping Voltammetry; CSV, Cathodic Stripping Voltammetry; AdCSV, Adsorptive Cathodic Stripping Voltammetry; CV, Cyclic Voltammetry; PSA, Potentiometric Stripping Analysis; DPP, Differential Pulse Polarography; CLE, Competitive Ligand Exchange; DPV, Differential Pulse Voltammetry; SWV, Square Wave Voltammetry. **Electrode:** MDE, Mercury Drop Electrode; HMDE, Hanging Mercury Drop Electrode; DME, Drop Mercury Electrode; HME, Hanging Mercury Electrode; TFGME, Thick Film Graphite Modified Electrode. **Modifier/complexing agent:** ANSA, 1-amino-2-naphthol-4-sulfonic acid; SVRS, Solochrome Violet RS; TEA, Triethanolamine; 5-ASA, 5-aminosalicylic acid; NN, 1-nitroso-2-naphthol; B-T, Bis-(2-hydroxymethyl)iminotris(hydroxymethy)methane; BG, Brilliant Green (triphenylmethane dye); PBA, N-phenylnbenzohydroxamic acid; 5-Br-PADAP, 2-(5-bromo-2-pyridylazo)-5-diethlyaminophenol; DCDT, 5,5-dimethylcyclohexan-1,2,3-trione 1,2-dioxime 3-thiosemicarbazone; TAC, 2-(2-thiazolylazo)-p-cresol; Tri-BAP, tributylammonium perchlorate; DMG, dimethylglyoxime; DHN, 2,3-dihydroxynaphthalene; SA, salicylaldoxime. **Other:** N/A, not applicable, NR, not reported

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<th>Modifier/Complexing agent (if any)</th>
<th>Speciation</th>
<th>LoD (M)</th>
<th>Year</th>
<th>Reference</th>
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<td>Tri-BAP</td>
<td>Fe(III)</td>
<td>1.5 × 10⁻⁵</td>
<td>2001</td>
<td>[111]</td>
</tr>
<tr>
<td>CLE-CV</td>
<td>MDE</td>
<td>NN</td>
<td>Fe(III)</td>
<td>1.3 × 10⁻⁹</td>
<td>2000</td>
<td>[64]</td>
</tr>
<tr>
<td>CSV</td>
<td>MDE</td>
<td>DHN</td>
<td>Fe(III)</td>
<td>1.3 × 10⁻⁵</td>
<td>2001</td>
<td>[46]</td>
</tr>
<tr>
<td>DPASV</td>
<td>DME</td>
<td>Ammonium oxalate</td>
<td>Fe(II)</td>
<td>9.0 × 10⁻⁹</td>
<td>2003</td>
<td>[65]</td>
</tr>
<tr>
<td>DPCSV</td>
<td>HMDE</td>
<td>NN</td>
<td>Fe(III)</td>
<td>1.8 × 10⁻⁹</td>
<td>2004</td>
<td>[112]</td>
</tr>
<tr>
<td>ASV</td>
<td>TFGME</td>
<td>Calomel, Pyrocatechol</td>
<td>Fe(II) + Fe(III)</td>
<td>3.6 × 10⁻⁶</td>
<td>2005</td>
<td>[67]</td>
</tr>
<tr>
<td>CSV</td>
<td>MDE</td>
<td>DHN</td>
<td>Fe(II) + Fe(III)</td>
<td>1.1 × 10⁻⁹</td>
<td>2006</td>
<td>[62]</td>
</tr>
<tr>
<td>AdCSV</td>
<td>HMDE</td>
<td>SVRS</td>
<td>Fe(II)</td>
<td>3.2 × 10⁻⁸</td>
<td>2008</td>
<td>[113]</td>
</tr>
<tr>
<td>AdCSV</td>
<td>HMDE</td>
<td>DGN, Catechol</td>
<td>Fe(II) + Fe(III)</td>
<td>1.3 × 10⁻⁹</td>
<td>2011</td>
<td>[68]</td>
</tr>
<tr>
<td>CLE/CV</td>
<td>HMDE</td>
<td>Humic substances SA, DHN</td>
<td>Fe(II) + Fe(III)</td>
<td>NR</td>
<td>2011</td>
<td>[114]</td>
</tr>
</tbody>
</table>
a HMDE and a detection limit of 1.29 nM iron could be
determined. This procedure is suitable for the direct si-
multaneous detection of five metals, Co, Cu, Fe, Ni and
V, in sediment pore waters.

2.2 Platinum
Platinum was not widely used analytically in the 20th
century, however, modern analytical research using it as an
electrode material has recently become more prevalent.
In 1972, Young and Laitinen [69] reported the first ac-
count of voltammetric determination of iron at a platinum
electrode. Cathodic stripping of iron had previously been
investigated by Brainina [57,70] but at a HMDE, a low
limit of detection was achieved with a value of 70 µM for
ferrous ions. Not long after, Cox and Majda [71] looked
into the detection of Fe(III) and Fe(II) using a adeno-
sine-5’-monophosphate modified platinum electrode. It
was found using cathodic stripping voltammetry, that a
nonlabile complex with Fe(III) can be readily plated
onto platinum, and subsequent reduction to the iron (II)
complex gives the stripping peak.

Two decades later, the determination of iron on platni-
um electrodes was revisited by several authors. Strycker
et al. [72] looked into the electrochemical behaviour of
iron in molten enamel using a rotating platinum disc elec-
trode. Initial experiments at a platinum disc electrode
characterised by cyclic and square wave voltammetry
showed that due to a slow chemical equilibration between
Fe(II) and Fe(III) in homogeneous solution, it was not
possible to calculate the analytical concentration of
Fe(III). However, further investigation with rotating disc
chronoamperometry was carried out, and the Fe(II) and
Fe(III) equilibrium concentrations could successfully be
determined. The next account of iron stripping from
a platinum electrode by Barbosa et al. [73] involved the
voltammetric dissolution of an iron-zinc alloy film. Here,
a Fe-Zn alloy film was deposited on platinum. It was seen
that only one anodic stripping peak was produced, sug-
gest that Fe and Zn in the film dissolved simultaneous-
lly; iron as Fe(III) and zinc as Zn(II), which gives great in-
sight to its kinetic studies.

Subsequent determination of iron were all performed
at a rotating platinum electrode – the increase in mass
transport leads one to believe that more sensitive limits
of detection may be achieved. This is the not case howev-
er, as Jin and Botte [39] and Scheers et al. [74] in 2009
[40,79], with the active surface being modified in some in-
stances. A list of iron determinations using carbon elec-
trodes [77,78] and glassy carbon electrodes
determined and using a platinum rotating disc electrode,
a detection limit of 0.13 µM for Fe(II) and 0.26 µM for
Fe(III) was given.

A Pt-silver alloy electrode was used by Diao and Sumi
[75] to measure Fe(3+), however with linear sweep voltam-
metry, a limit of detection can only be reported to a value
of 1.2 mW with iron sulfides in suspension.

It can be seen that a number of platinum electrodes
have been used for the detection of iron with fairly low
limits of detection. Though fairly expensive, platinum is
environmentally friendly and can be used in the most
cases, unmodified. Table 2 gives a summary of iron analy-
yses using platinum electrodes.

2.3 Carbon
Carbon is an ideal replacement material for mercury as it
possesses properties that lend itself adequately for analyti-
cal study [52–54,76]. Carbon is also widely used due to
its cheap and disposable nature. Some popular carbon
electrodes used for the determination of iron are carbon
paste electrodes [77,78] and glassy carbon electrodes
[40,79], with the active surface being modified in some in-
stances. A list of iron determinations using carbon elec-
trodes, together with their limits of detection is given in
Table 3.

Carbon electrodes were used by many authors pre-
2000. Despite being one of the earliest accounts of iron
determination at a carbon electrode, Florence [80] was
able to achieve one of the lowest limits of detection of
the time at a rotating glassy carbon electrode. Since iron
could not be determined directly by anodic stripping vol-
tammetry, a rotating glassy carbon electrode with a thin
mercury film deposited in situ was used to investigate
Determinaion of Iron

Table 2. Iron analyses using carbon electrodes. CSV, Cathodic Stripping Voltammetry; SWV, Square Wave Voltammetry; DP, Differential Pulse; ASV, Anodic Stripping Voltammetry; EM2C2, Electrochemical Measurement of Multivalent Cations Concentration; RDE, Rotating Disk Electrode; NR, not reported; N/A, not applicable

<table>
<thead>
<tr>
<th>Technique</th>
<th>Electrode</th>
<th>Modifier/Complexing agent (if any)</th>
<th>Speciation</th>
<th>LoD (M)</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSV</td>
<td>Pt ring-disk</td>
<td>1,10-Phrenanthroline</td>
<td>Fe(II)</td>
<td>7.0×10⁻⁷</td>
<td>1972</td>
<td>[69]</td>
</tr>
<tr>
<td>CSV</td>
<td>Pt wire</td>
<td>Adenosine-5-monophosphate</td>
<td>Fe(II) + Fe(III)</td>
<td>1.0×10⁻⁸</td>
<td>1980</td>
<td>[71]</td>
</tr>
<tr>
<td>SWV</td>
<td>Pt disk</td>
<td>N/A</td>
<td>Fe(III)</td>
<td>NR</td>
<td>2004</td>
<td>[72]</td>
</tr>
<tr>
<td>DPASV</td>
<td>Rotating Ag-alloy disk</td>
<td>N/A</td>
<td>Fe(II)</td>
<td>3.0×10⁻⁴</td>
<td>2005</td>
<td>[66]</td>
</tr>
<tr>
<td>ASV</td>
<td>Pt disk</td>
<td>Fx10-Zn alloy film</td>
<td>Fe(III)</td>
<td>NR</td>
<td>2005</td>
<td>[73]</td>
</tr>
<tr>
<td>EM2C2</td>
<td>Pt-RDE</td>
<td>N/A</td>
<td>Fe(II) + Fe(III)</td>
<td>2.0×10⁻⁵</td>
<td>2009</td>
<td>[39]</td>
</tr>
<tr>
<td>DPASV</td>
<td>Pt-RDE</td>
<td>Food chelators (lactate, phytabte)</td>
<td>Fe(II) + Fe(III)</td>
<td>1.3×10⁻⁵</td>
<td>2010</td>
<td>[74]</td>
</tr>
<tr>
<td>CSV</td>
<td>Pt-Ag twin electrode</td>
<td>Silver sulfide</td>
<td>Fe(II)</td>
<td>1.2×10⁻⁵</td>
<td>2010</td>
<td>[75]</td>
</tr>
</tbody>
</table>

One of the most sensitive limits of detection was reported by Yang et al. [82] in 1995 at a glassy carbon electrode by modifying the surface with Nafion for the cathodic stripping determination of Fe(III). The authors realised a Nafion coated electrode facilitated the preconcentration of the iron complex. Nafion has been proved to be an ideal polymer for chemically modified electrodes as it is very chemically inert, non-electroactive, hydrophilic, thermally stable and insoluble in water. Here, Yang et al. described the cathodic stripping voltammetry of iron based on the preconcentration of Fe(III)-α,α-bipyridine (BP) complex on the Nafion modified electrode. Optimum concentration of the complexing agent was determined, and with a 2 minute preconcentration time, Fe(III) was detected to a limit of 0.89 nM. Application of this technique was successfully used to determine iron concentrations in fountain water and longan fruit. Differential pulse voltammetry (DPV) was applied by many authors as a means for sensitive detection of iron, with limits of detection ranging from 0.3 µM [83], by complexing iron(II) with 5-aminoisophthalic acid (AIPA), to

Fe³⁺. Here, a chemical exchange reaction between ferric ion and bismuth-EDTA was used to successfully determine iron to a limit of 9 nM. Other accounts of iron determination were in between the region of 0.1 µM and 0.1 nM. Stulikova and Vydra [81] have been the only other authors to report voltammetry of iron at a rotating carbon electrode. In this case, Fe(III) was detected at a glassy carbon rotating disk electrode. After de-aeration with nitrogen, a limit of detection of 0.1 µM could be achieved in acidic media by cathodically scanning to a lower potential.

One of the most sensitive limits of detection was reported by Yang et al. [82] in 1995 at a glassy carbon electrode by modifying the surface with Nafion for the cathodic stripping determination of Fe(III). The authors realised a Nafion coated electrode facilitated the preconcentration of the iron complex. Nafion has been proved to be an ideal polymer for chemically modified electrodes as it is very chemically inert, non-electroactive, hydrophilic, thermally stable and insoluble in water. Here, Yang et al. described the cathodic stripping voltammetry of iron based on the preconcentration of Fe(III)-α,α-bipyridine (BP) complex on the Nafion modified electrode. Optimum concentration of the complexing agent was determined, and with a 2 minute preconcentration time, Fe(III) was detected to a limit of 0.89 nM. Application of this technique was successfully used to determine iron concentrations in fountain water and longan fruit. Differential pulse voltammetry (DPV) was applied by many authors as a means for sensitive detection of iron, with limits of detection ranging from 0.3 µM [83], by complexing iron(II) with 5-aminoisophthalic acid (AIPA), to
10 nM [77] by modifying carbon paste electrodes with 1, 10-phenanthroline and Nafion.

In the 21st century, limits of detection of ion using carbon electrodes were seen to be several orders of magnitude lower than that reported previously. The most sensitive detection of iron was reported by Stefan et al. [21] using a new electrode design based on diamond paste. Differential pulse anodic stripping voltammetry was used to detect Fe(III) to a limit of 0.1 pM using natural diamond powder cast with paraffin oil. The superiority of the monocrystalline diamond as an electrode material was seen over carbon allotrope based electrodes such as glassy carbon electrodes. Here, lower background currents and noise signals were seen, there was a wide electrochemical potential window, it was electrochemically stable and there was very low capacitance. The electrode looks to be a promising new material for sensitive detection, especially since no modification of the surface is needed, and no complexing agents were required for the detection of Fe(III).

Many authors have used glassy carbon electrodes, however the surface is generally modified for detection of Fe(III). In 2001, Ugo et al. [84] used Nafion coated glassy carbon electrodes (NCE) for preconcentrating and detecting Fe\(^{2+}\) and Fe\(^{3+}\) cations from aqueous solutions. The authors realised, like Yang et al. [82], that Nafion proved to be a good electrode modifier for preconcentration of iron complexes. First, using cyclic voltammetry, the ion-exchange voltammetric (IEV) determination of preconcentrated iron, which takes advantage of the preconcentration capability and selectivity of thin films, could be determined in the μM range. However, lower detection limits could be achieved by combination of the Nafion coated electrodes with multiple square wave voltammetry (MSWV), giving a detection limit of 2.5 nM. Although voltammetric measurements at the NCE give only the overall iron concentration, open circuit potential measurements performed before starting the voltammetric scan can determine speciation of iron.

More voltammetric iron determination at glassy carbon electrodes were reported by Lu et al. [79], Ugo et al. [85] and Segura et al. [86]. All three accounts involved the modification of the electrode surface; this included chitosan, ionomers such as Nafion and 1-(2-piridylazo)-2-naphthol (PAN) respectively. The authors noticed the enhanced ability to increase the preconcentration of iron complexes onto a modified carbon electrode surface, to give lower limits of detection. Lu et al. [79] were able to detect total iron concentration to a limit of 0.18 μM using cathodic stripping voltammetry and took advantage of the instability of Fe(C\(_2\)O\(_4\))\(_3\)\(^3-\) to light and the reductive effects of C\(_2\)O\(_2\)\(^2-\). It was found that using C\(_2\)O\(_2\)\(^2-\) as a complexing agent and reductant, there was no reductive stripping signal for iron on a bare unmodified glassy carbon electrode. However, sensitivity of the electrode was vastly enhanced with a chitosan modified glassy carbon electrode (CMGCE), indicating obvious adsorptive behaviour. Previous authors have demonstrated the ability for iron ions to be preconcentrated by Nafion, however, since both Fe(II) and Fe(III) species are equally preconcentrated, redox speciation to distinguish between the two oxidation states is very difficult. Ugo et al. [85] used ionomer coated glassy carbon electrodes to combine potentiometric and voltammetric measurements with anion exchanger Tosflex and cation exchanger Nafion. This method allowed for the determination and speciation of iron ions at trace concentration levels. Segura et al. [86], like previous authors, also combined the use of a complexing agent and subsequently preconcentrates the iron complex onto a modified carbon surface. Here, a complex of iron with PAN is adsorbed onto a bismuth coated glassy carbon electrode (BiFE). The authors use square wave adsorptive stripping voltammetry (SWAdSV) and an adsorption time of 60 s to obtain a limit of detection of 1.79 nM for Fe(III); it was also noted that more sensitive results could be achieved using longer adsorption times.

The most recent paper regarding iron detection on a glassy carbon electrode was by Anguiano et al. in 2012 [87]. Modification of GCEs with Multiwall Carbon Nanotubes (MWCNTs) in the presence of Pt nanoparticles was presented as an effective electrocatalytic material for metallic pollutants detection. The GCE modified with CNTs have not been claimed to show better performance than conventional carbon electrodes. The use of Pt nanoparticles helps to facilitate the electron transfer and “electrocatalytic properties”. The constructed electrodes were incorporated as amperometric detectors of ionic iron electro-reduction using the Flow Injection Amperometric (FIA) technique in aqueous solution, exhibiting a detection limit of 3 nM. Application of this has been used on samples of polluted soil in Guanajuato, Mexico. The other carbon electrode regularly used for iron detection is the carbon paste electrode (CPE). Carbon paste electrodes are well known materials for analytical purposes. Its simple fabrication and its ability to be easily modified is often utilized for important selectivity towards target species. In the detection and speciation of iron, many authors chose to modify the CPE or use complexing agents such that preconcentration of iron occurs better to get a more sensitive limit of detection. A recent publication by Gholivand et al. [88] employed a differential pulse anodic stripping voltammetric procedure for the determination of Fe(II) at a carbon paste electrode modified with dithiodianiline (DTDA) and gold nanoparticles. Though a complexing agent was not used, the accumulation of Fe(II) at the surface of the modified electrode was based on the complex formation between the metal ion and the modifier, DTDA. After preconcentration, an anodic stripping peak was given where a detection limit of 0.05 nM could be calculated.

Ghoneim [30] found that by complexing Fe(III) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenyl (5-Br-PADAP), iron could be accurately detected using square wave adsorptive cathodic stripping voltammetry at a CPE. Without need for surface modification of the electrode, this technique was used to simultaneously detect...
Mn(II), Cu(II) and Fe(III) in tap, bottled and ground water to a detection limit of 1.67 nM.

Kladavec et al. [89] reported the anodic dissolution of iron at a paraffin impregnated graphite electrode by linear and cyclic voltammetry. Voltammetric analysis was carried out on the oxidation of iron powder and although the quantification of iron was not determined, it was seen that the pH values of the electrolyte solution as well as particle size fraction significantly influence the course of the dissolution of iron powder. Electrochemical determination of the Fe(II)/(III) ratio in ceramic materials using carbon paste and composite electrodes was carried out by Domenech-Carbo et al. [90]. Carbon paste electrodes were fabricated by mixing graphite powder with a polymer modifier and voltammetry on clay samples were carried out. This technique, based on micro sample attachment to graphite/polyester composite electrodes, describes the electrochemistry of iron in terms of reductive dissolution processes of Fe(III) and oxidative dissolution processes of Fe(II).

3 Conclusions

From this collection of recent reports on iron determination, it can be seen that analytical studies in this field is active. Many sensitive voltammetric methods have been used, with limits of detection as low as 13 pM in some cases [46]. This is greatly within the WHO [20] guideline for iron concentration, where an acceptable level in fresh water is quoted at 0.3–3 mg L$^{-1}$. Although iron in drinking water is not a health concern, concentrations above 0.3 mg L$^{-1}$ can cause food and water to become discoloured and taste metallic. The development of sensitive determination allows for important insight into the biogeochemistry of iron in waters, and further speciation of iron ions can be made. A collection of tables summarising the voltammetric technique and electrode material is included within the text, giving the detection limit in each account. With nontoxic electroanalytical methods being at the forefront of analytical research, there looks to still be a wide scope for carbon as an electrode material for iron determination, with only glassy carbon electrodes and carbon paste electrodes dominating the field presently. Building on the use of previously discussed methods such as adsorptive stripping analysis, coupled with oxidative catalysts and complexing agents, further advancement in the field of iron determination and speciation can be hoped to be made.

References


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