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Journal of Pharmaceutical and Biomedical Analysis
16 (1998) 1373–1379

JOURNAL OF
PHARMACEUTICAL
AND BIOMEDICAL
ANALYSIS

Trace iron determination in aminoisophthalic acid using differential-pulse cathodic stripping voltammetry at carbon paste electrodes

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Received 10 April 1997; received in revised form 15 July 1997

Abstract

Application of differential-pulse cathodic stripping voltammetry using a carbon paste electrode (consisting of carbon powder and liquid paraffin) have been investigated for trace determination of iron in 5-aminoisophthalic acid (AIPA). Samples were dissolved in 1 M HCl, pH was adjusted to 4–5 after addition of EDTA. Voltammetric measurements were performed after filtration. No sample decomposition (mineralization) was necessary. The method showed a good linearity between current and concentration from 3×10^{-7} to 5×10^{-5} mol dm^{-3} of iron, with a detection limit of 3×10^{-7} mol dm^{-3} (resp. 1 ppm in solid AIPA). The results agreed well to those obtained by atomic absorption spectrometry (AAS) using electrothermic atomisation. For AAS measurement, however, microwave digestion of samples was necessary. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Iron determination; Trace analysis; Voltammetry; Carbon paste electrode

1. Introduction

5-Aminoisophthalic acid (AIPA) represents an important intermediate in the syntheses of X-ray diagnostics [1]. In the first step, AIPA is iodinated to the 2,4,6-iodo-substituted derivative (this is important as the presence of iodine atoms develops the contrasts desired during X-ray treatments). However, just this reaction is strongly influenced by the presence of traces of iron ions. For this purpose, a proper voltammetric procedure was developed.

The reduction potential of iron ions to the metal (≈ -1.5 V vs. SCE) is unexploitable for polarographic or voltammetric measurements. In acidic solutions, the signal is overlapped with that arising from hydrogen reduction, and hydrolysis of iron ions will occur in more weakly acidic media. Above this, determination using stripping voltammetry via Fe^0 is limited by a low solubility of iron in mercury, whereas the deposited form of iron depends on the current density and other parameters [2]. Formation of intermetallic compounds with zinc and manganese can be an additional source of complications [3]. Exploiting the

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PII S0731-7085(97)00193-3

reduction of iron(III) to iron(II), the signal is overlapped by oxidation of the electrode material of mercury electrodes; therefore, citrate, oxalate or tartarate media have been used as complexants for polarographic determinations because in such media the reduction potential is much more negative [4]. Indirect methods based on the determination of lead(II) [5] or bismuth(III) [6] displaced from the complex with EDTA have been suggested as well for the determination of iron(III) traces.

To achieve lower detection limits, adsorptive voltammetry offers some advantages using catechol [3,7], Solochrome Violet RS [8], nitrosonaphtol [9], and others [10,11] as reagents. Solochrome Violet RS also has been used for a constant-current stripping determination of iron(III) [12]. In contrast to the other reagents, Solochrome Violet RS forms a complex only with iron(III), which can be used in speciation studies [8,12]. However, such measurements are influenced by the ease of oxidation of iron(II) by atmospheric oxygen.

Probably the lowest detection limit (10 ng dm^{-3}) has been achieved using an adsorptive catalytic stripping voltammetric procedure based on the reduction of adsorbed complexes of iron(III) with hydroxamic acids in the presence of H_2O_2, which reoxidates the reduced adsorbed species [13]. Various other catalytic determinations are based on the reduction of the iron(III) complex with *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid, which is reoxidized by $KBrO_3$ [14]. A carbon paste electrode (spectral carbon, paraffin oil) has been used for determination of traces iron(III) in a medium of HCl, where formation of $[FeCl_4]^-$ ions was expected [15].

Chemically modified electrodes have been applied as well to the trace determination of iron. Glassy carbon [16] or carbon paste (graphite powder, nujol) modified with Nafion [17] have been used for the preconcentration of the iron-bipyridyl complex. Trace levels of hexacyanoferrate in wine have been determined with an Amberlite LA2 liquid ion exchanger modified carbon paste electrode (spectral carbon, liquid paraffin) [18].

In voltammetric trace analysis of pharmaceuticals, strong interferences from the organic matrix with the determination of metals can be expected [19]. These disturbances together with poor solubility of the samples usually require mineralization of the sample (e.g. microwave digestion). Nevertheless, as demonstrated in the paper presented here, it is sometimes possible to elaborate conditions for the voltammetric determination of the traces of iron where no sample pretreatments are necessary.

2. Experimental

2.1. Reagents

All reagents—iron(II) sulphate heptahydrate, sodium hydroxide, hydrochloric acid, potassium chloride, 1,10-phenanthroline monohydrate, bathophenanthroline, ethylendiaminetetraacetic acid (EDTA), ethanol, methanol (all from Lachema, Brno, CZ)—were of analytical-reagent grade and were used without further purification. For graphite furnace atomic absorption spectrometric (GFAAS) validation, hydrochloric and nitric acids of the Suprapure quality (Merck) were used. Samples of 5-aminoisophthalic acid (AIPA) were purchased from Synthesia (Pardubice, CZ).

The supporting electrolyte was a 1 M solution of KCl prepared by dissolving KCl either in redistilled water, or in the water sample (for water analysis). Redistilled de-ionised water was used throughout, in which no iron could be detected (with regard to the base-line of voltammetric measurements, this was better than water purified by a Milli Q^+ system from Millipore). The supporting electrolyte was deaerated with argon (Synthesia). For the preparation of the carbon paste electrode, carbon powder Sigradur G (HTW GmbH, Meitingen, D) and liquid paraffin (clear colourless mixture of saturated hydrocarbons with boiling point up to 360°C) were used.

2.2. Apparatus

For voltammetric measurements, a polarograph PA3 (Laboratorní přístroje, Prague, CZ) was used in combination with a recorder XY 4103 (Laboratorní přístroje). The cell consisted of a conical

glass vessel, equipped with a mechanic glass stirrer. All measurements were carried out in the three-electrode configuration using a platinum plate and a Ag/AgCl electrode (RAE 111, Crytur, Turnov, CZ) as auxilliary and reference electrodes, resp. A piston type carbon paste electrode (CPE) as described earlier [20] was used as working electrode.

For reference determinations, a graphite furnace atomic absorption spectrometer (GFAAS) with Zeeman background correction (Hitachi Z-9000) was used. Mineralizations were performed with a microwave digestion system MDR-1200 Mega (Milestone GmbH, D).

All laboratory glass was treated with diluted HNO_3 and rinsed with redistilled water. Dosing of small volumes was performed by a micropipette Varipipette 3000 (Plastomed, Poland) with a volume range up to 200 μl.

3. Procedures

3.1. Preparation of carbon paste electrodes

Carbon pastes were prepared by mixing 1 g of carbon powder with 0.5 ml of liquid paraffin; the material was allowed to rest for 24 h in order to provide reproducible measurements. It should be mentioned that, although the composition of the pastes when repeating their preparation was always the same, each electrode showed a little different behaviour. The electrode material was applicable for about 1 month approximately. In weakly acidic solution (pH 4–4.5), the working potential range was from +1.3 to −0.4 V. Purity of the carbon powder was checked using emission spectral analysis.

3.2. Sample preparation

In weakly acidic solutions (applicable for CPEs described above), AIPA is only slightly soluble. Therefore, pretreatments utilizing its good solubility in strong acids were investigated. As a result, 0.3–1.0 g of the AIPA sample were transferred into a 100-ml volumetric flask, 25 ml of 1 M HCl was added and the sample was dissolved. Then 0.6 ml of 0.01 M EDTA was added; the solution was stirred and the pH adjusted with 1 M NaOH to a pH of 4–4.5, where more than 90% of AIPA precipitated again. Then the samples were mildly heated and cooled to the room temperature, and placed into a refrigerator for 24 h. The precipitate was filtered off before the voltammetric measurement, and the clear solutions were equilibrated to 20°C. A volume of 10 ml of the sample solution was placed into the electrolytic cell.

The procedure used for the water sample preparation was as follows: 0.75 g of KCl was placed to the volumetric flask and filled to 100 ml with water sample. A volume of 10 ml of the sample solution was placed to the voltammetric cell, and both 50 μl of 1 M HCl and 200 μl 0.01 M EDTA were added.

3.3. Voltammetry

A volume of 10 ml of the sample solution was deaerated with argon for 15 min. All measurements were done under argon atmosphere. Parameters for the differential pulse cyclovoltammetry were: scan rate 50 mV s^{-1}; pulse amplitude 50 mV; pulse duration 100 ms; pulse interval 100 ms; initial potential (E_{in}) +250 mV; final potential (E_{fin}) −350 mV; supporting electrolyte 1 M KCl; pH was adjusted by 1 M HCl. Optimized voltammetric parameters were: accumulation and initial potential (E_{in}), +250 mV; accumulation time (t_{acc}), 80 s; final potential −350 mV; scan rate 20 mV s^{-1}; FSDPV mode; pulse amplitude 50 mV; pulse duration 100 ms; pulse interval 100 ms. Before each measurement, the electrode surface was renewed, smoothed off with filter paper and rinsed with water. The peak heights were evaluated manually from the recorded output by fitting a tangent to the peak base. For evaluation of concentrations, the standard addition procedure was used.

3.4. AAS measurements

For the electrothermic atomic spectroscopic determination of iron, the samples had to be mineralized prior to analysis preferably by microwave digestion. 0.3–0.4 g of the sample were

weighted into the digestion vessels of Teflon and mixed with 5 ml of a mixture of HNO_3/HCl (4:1 v/v). The parameters of the temperature program were: 2 min/250 W; 0.5 min/0 W; 8 min/250 W; 6 min/450 W; 4 min/600 W; 5 min/350 W; ventilation 5 min; cooling 15 min. After the mineralization, the solutions were transferred into volumetric flasks and made up with water to 25 ml. For the determination with GFAAS, mineralized solutions (20 μl) of AIPA were dosed into the graphite cuvette by an autosampler. Parameters of the measurement: wavelength 248.3 nm; slit 0.2 nm; carrier gas (argon) flow 200 ml min^{-1}; sample volume 20 μl; modifier Mg. Atomization procedure: drying 80–120°C/30 s, ashing 600°C/30 s, atomizing 2700°C/4 s, cleaning 2800°C/3 s. The concentration of iron was evaluated by the standard addition method.

4. Results and discussion

Since AIPA is only slightly soluble in water, but more in acids and bases (e.g. 1 M HCl, 1 M NaOH), these media were investigated as supporting electrolytes. But they were not suitable since they led to a partial disintegration of the unmodified electrode material. Similar effects were observed when using organic solvents (methanol or ethanol) mixed in various ratios with water (1:1–1:10). But the electrode is usable in fairly acidic or alkaline solution. In neutral or weakly alkaline media, iron signal (for AIPA and EDTA) was worse developed than in acidic, nonreproducible, consisting of two overlapping peaks. Optimal peak shape and reproducibility of the response was found at pH between 4–5. In more acidic solutions, the interfering effect of hydrogen increased. Finally, a solution of 1 M KCl containing EDTA (10^{-4} M) was found as an optimal supporting electrolyte.

Using an unmodified CPE containing paraffin oil as a pasting liquid, signals of iron in 1 M KCl supporting electrolyte were observed, showing a peak potential at approx. + 350 mV. These peaks were symmetrical and well reproducible; a linear calibration was obtained. However, in the presence of AIPA, the reduction potential of iron(III) was shifted to ≈ -200 mV. The current response caused by hydrogen evolution was close to a broad iron peak, which therefore complicated evaluation of the peak height. The shift of the peak potential to significantly more negative values indicates complex formation of iron with AIPA. To improve the quality of results, various complexing ligands were studied, which were added to the supporting electrolyte and which were able to complex both types of iron, Fe^{2+} and Fe^{3+}, giving peaks between -200 (start of the hydrogen wave) and + 500 mV (start of the AIPA response). Such ligand is EDTA, which forms stable complexes with both iron(III) and iron(II). As shown in Fig. 1, the potential of iron(III) in cyclovoltammograms was shifted from -200 mV to ≈ -140 mV by the presence of EDTA. No effect of AIPA on the iron peak was found. The response was well reproducible, and a linear calibration curve was obtained. The detection limit of 1 ppm was determined in solid samples of AIPA, which corresponds to the concentration of 3×10^{-7} mol dm^{-3} in solution. The dependence of signal on the iron concentration in solution was linear in the range of 3×10^{-7}–5×10^{-5} mol dm^{-3} (Fig. 2).

Both peak position and its shape were affected by the initial potential and the scan direction. Best results were obtained with an E_{in} of + 250 mV and scanning in negative direction. The response depended only slightly on the accumulation time, but the reproducibility was improved by using $t_{acc} = 40$–80 s. Deformation of the peak shape occurred at the accumulation times higher than 200 s. As can be seen from these results, a sorption of the complex on the electrode surface was insignificant similarly to that on hanging mercury drop electrode (HMDE) [3]. High, sharp but nonreproducible peaks at ≈ -50 mV ($E_{in} = -400$ mV) were obtained when scanning in anodic direction; the response depended on the accumulation time (Fig. 3).

In order to verify the results obtained with real samples of AIPA, reference determinations were made using GFAAS. For this the samples had to be mineralized by microwave digestion prior to analysis. The results of both methods (shown in Table 1) correlated very well (Fig. 4).

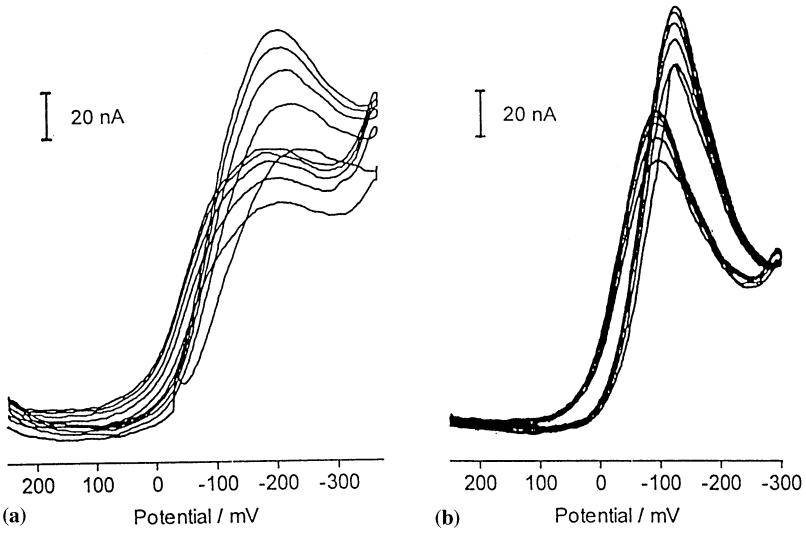

Fig. 1. Differential pulse cyclovoltammogram of iron (4×10^{-5} mol dm^{-3}) in AIPA solutions (A) without and (B) with the presence of EDTA (10^{-4} M). Supporting electrolyte: 1 M KCl, pH 4 adjusted by 1 M HCl; scan rate 50 mV s^{-1}; pulse 50 mV; initial potential +250 mV; final potential −350 mV.

It should be noted that a possible loss of iron during AIPA re-precipitation was one of the main points of interest and was checked by both comparison of the results of AAS and voltammetric analysis, and the standard addition procedure. In the second method, an AIPA (analytical-reagent grade) was dissolved in 1 M HCl and the solution was distributed among two volumetric flasks, when standard solution of iron(II) was added to one of them. Then the same procedure as described above (EDTA addition, neutralization and determination) was applied with the assay of the iron addition of approx. 92–95%.

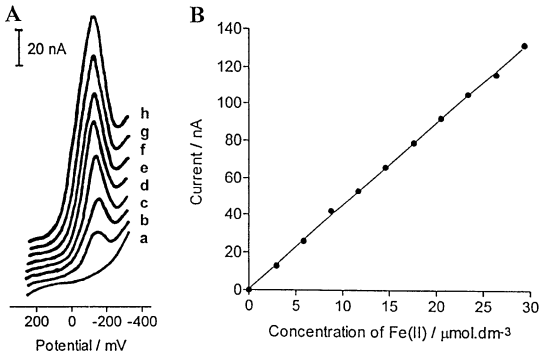

Fig. 2. Differential pulse voltammograms of iron in AIPA solutions containing EDTA (A) and a calibration plot (B); supporting electrolyte 1 M KCl, pH 4, 10^{-4} M EDTA; scan rate 20 mV s^{-1}, accumulation potential E_{acc} +250 mV, accumulation time t_{acc} 80 s. Concentration of iron (a) 0, (b) 2.93×10^{-6}; (c) 5.86×10^{-6}; (d) 8.79×10^{-6}; (e) 1.17×10^{-5}; (f) 1.46×10^{-5}; (g) 1.76×10^{-5}; (h) $2.05. 10^{-5}$ mol dm^{-3}.

The procedure was also successfully applied to the determination of iron in drinking water. Samples of 'Good Water' (trade mark of the spring mineral water from HBSW České Budějovice, CZ) and tap water were analyzed. In the tap water and 'Good Water', concentrations of iron of 0.166 ± 0.005 and 0.140 ± 0.013 mg dm^{-3} (mean ± S.D.) were found. The 'Good Water' producer declared maximum concentration of iron of 0.2 mg dm^{-3}; the upper limit for the concentration of iron in the tap water in CZ is 0.3 mg dm^{-3} [21].

With the voltammetric method presented in this paper it is possible to determine iron in AIPA without sample digestion. This fact yields to shorten the time of the analyses as compared with other methods (e.g. GFAAS), and to simplify handling of the samples. The procedure can also

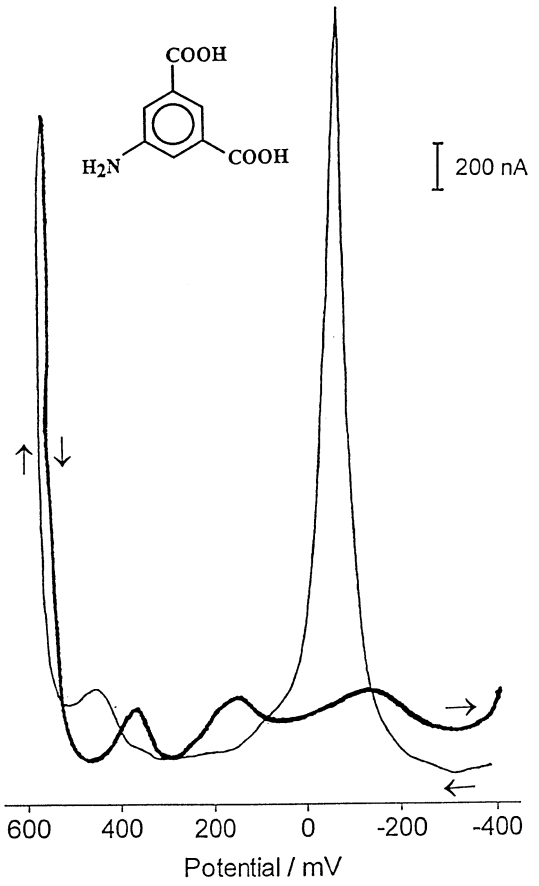

Fig. 3. Differential pulse cyclovoltammogram of iron (4×10^{-5} mol dm^{-3}) in AIPA solution; E_{in} −400 mV; t_{acc} 80 s; supporting electrolyte saturated solution of AIPA in 1 M KCl; pH 4 adjusted by 1 M HCl. Concentration of EDTA was 1×10^{-4} mol dm^{-3}. Thin line anodic; thick line cathodic scan.

be applied to the determination of iron in water samples.

Acknowledgements

Financial supports from Grant Agency of the Czech Republic (under Project No. 203/96/1024) and the AKTION Austrian-Czech Academic Exchange Programme (Project No. 5p1) are highly appreciated.

Table 1
Comparison of results obtained by the voltammetric procedure with GFAAS measurements

Sample	Iron content [ppm] found by			
	Voltammetry[a]		GFAAS[b]	
	Mean	S.D.	Mean	S.D.
AIPA1	16.2	0.9	16.2	0.4
AIPA2	16.3	1.5	16.2	0.4
AIPA3	8.1	0.95	8.1	0.5
AIPA4	5.9	1.0	4.6	0.4
AIPA5	17.5	0.8	17.7	0.6

[a]Standard deviation (S.D.) calculated for 10 replications.
[b]Standard deviation calculated for 15 replications.

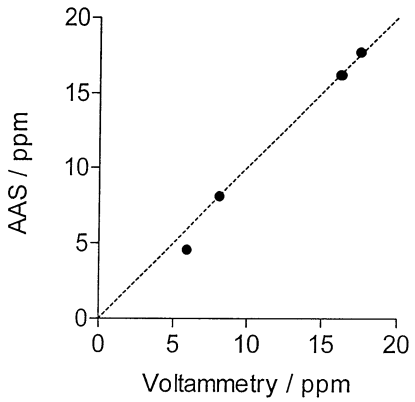

Fig. 4. Comparison of assays in AIPA samples by the voltammetric and GFAAS procedures (dashed line is the axis of the quadrant).

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