

Application Bulletin 439/1

Voltammetric determination of iron in water samples with a Bi drop electrode

Summary

Iron is an essential element in the human diet and is found in many natural and treated waters. Therefore, the World Health Organization (WHO) does not issue a health-based guideline value for iron. However, levels greater than $\beta(\text{Fe}) = 2 \text{ mg/L}$ causes water to become discolored and taste metallic. Higher concentrations of iron in surface waters can indicate the presence of industrial effluents or outflow from other operations and sources of pollution. Because of this, precise, rapid, and accurate iron determination at low concentrations in environmental and industrial samples is of great importance. This can be achieved with the method described in this Application Bulletin.

The determination is carried out with the 884 Professional VA and can be successfully applied to tap water, mineral water, and sea water samples. Direct voltammetric determination of the iron triethanolamine (TEA) complex on the non-toxic Bi drop electrode does not include an enrichment step. This system utilizes catalytic signal enhancement allowing both the detection at very low levels (LOD of 0.005 mg/L) and measurements in a wide range of concentrations up to 0.5 mg/L. The same measuring solution is used for sensor activation and determination of iron.

Samples

Tap water, mineral water, and sea water

Instruments and accessories

884 Professional VA manual for MME	2.884.0110
Electrode equipment with Bi drop electrode for 884 Professional VA	6.5339.080
Containing:	
Stirrer for 884	6.1204.500
Measuring vessel 10 mL	6.1415.210
Threaded stopper	6.1446.040
Cap	6.2753.210
viva 2.1	6.6065.21X

Electrodes

WE	Bi drop electrode	6.0346.000
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RE	Ag/AgCl reference electrode	6.0728.120
	Ag/AgCl/c(KCl) = 3 mol/L	
	Electrolyte vessel	6.1245.010
	Filled with c(KCl) = 3 mol/L	
AE	Glassy carbon rod	6.1247.000
	Electrode holder	6.1241.120

Overview

The Application Bulletin describes the following methods:

Activation/cleaning of Bi drop electrode

A new sensor needs to be activated first. The activation must be carried out prior to the first use, and whenever the sensor has not been used for more than 1 hour. If the electrode needs to be cleaned either before, in between, or after determinations, the procedure described in the subchapter «Activation/cleaning of the Bi drop electrode» should be used.

Determination of iron

In an alkaline electrolyte (pH 10), the Fe(III) ions are directly reduced at the surface of the Bi drop electrode to Fe(II). The analytical signal is enhanced by the presence of KBrO_3 which reoxidizes the reduced Fe(II) to Fe(III). The triethanolamine in the electrolyte prevents the formation and precipitation of Fe(III) hydroxides in the alkaline measuring solution.

Standard operating procedure

- Activation of the Bi drop electrode
- Determination of cadmium and lead in a blank or a check standard solution to validate electrode performance
- Determination of samples
- Rinsing of the Bi drop electrode with ultrapure water
- Dry storage in the storage vessel 6.2008.040

For more information about the standard operating procedure please refer to the comments in the chapters «Activation/cleaning of the Bi drop electrode» and «Comments» at the end of this document.

Reagents

- Fe standard stock solution, $\beta(\text{Fe}) = 1 \text{ g/L}$, commercially available
- Nitric acid, $w(\text{HNO}_3) = 65\%$, for trace analysis*, CAS 7697-37-2
- Sodium hydroxide solution, $w(\text{NaOH}) = 30\%$, for trace analysis*, CAS 1310-73-2
- Triethanolamine, $w(\text{triethanolamine}) \geq 99.0\%$, for analysis, CAS 102-71-6
- Potassium bromate, $w(\text{KBrO}_3) \geq 99.8\%$, for analysis, CAS 7758-01-2
- Hydrogen peroxide solution, $w(\text{H}_2\text{O}_2) = 30\%$, for trace analysis*, CAS 7722-84-1
- Ultrapure water, resistivity $>18 \text{ M}\Omega \cdot \text{cm}$ (25 °C), type I grade (ASTM D1193)

*e.g. Honeywell Fluka TraceSELECT® or Merck Suprapur®

Solutions

Supporting electrolyte	$c(\text{NaOH}) = 1 \text{ mol/L}$ $c(\text{triethanolamine}) = 0.1 \text{ mol/L}$ $c(\text{KBrO}_3) = 0.04 \text{ mol/L}$ 10 mL sodium hydroxide solution, 1.32 mL triethanolamine, and 0.67 g potassium bromate are dissolved and filled up to 100 mL with ultrapure water in a volumetric flask.
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Standard solutions

Standard addition solution 1	$\beta(\text{Fe}) = 10 \text{ mg/L}$ 1 mL Fe standard stock solution and 0.1 mL nitric acid are added and made up to 100 mL with ultrapure water in a 100 mL volumetric flask.
Standard addition solution 2	$\beta(\text{Fe}) = 1 \text{ mg/L}$ 10 mL Fe standard addition solution 1 and 0.1 mL nitric acid are added and made up to 100 mL with ultrapure water in a 100 mL volumetric flask.

Sample preparation

- Ground water, drinking water, sea water, and mineral water can usually be analyzed directly.

- Water that contains interfering organic substances is digested using the 909 UV Digester: 10 mL acidified water sample ($\text{pH} = 2$) with $10 \mu\text{L } w(\text{HNO}_3) = 65\%$ and $100 \mu\text{L } w(\text{H}_2\text{O}_2) = 30\%$ are irradiated for 90 min at 90 °C.

Activation/cleaning of the Bi drop electrode

Analysis

10 mL ultrapure water and 1 mL supporting electrolyte are pipetted into the measuring vessel. The activation or cleaning is carried out using the parameters given under «Parameters for activation/cleaning». The measuring solution is purged for 5 minutes before the activation/cleaning.

Measuring solution

10 mL ultrapure water

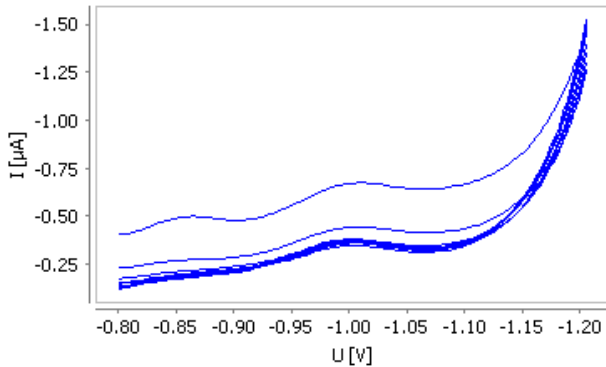
1 mL supporting electrolyte

Parameters for activation/cleaning

Voltammetric	
Measuring mode	DP – Differential pulse
Cyclovoltammetric pretreatment	
Start potential	0.2 V
Vertex potential	-1 V
No. of cycles	10
Potentiostatic pretreatment	
Potential	-2 V
Waiting time	15 s
Sweep	
Start potential	-0.8 V
End potential	-1.2 V
Potential step	0.006 V
Potential step time	0.1 s
Pulse amplitude	0.05 V
Potentiostat	
Highest current range	2 mA
Lowest current range	200 μA

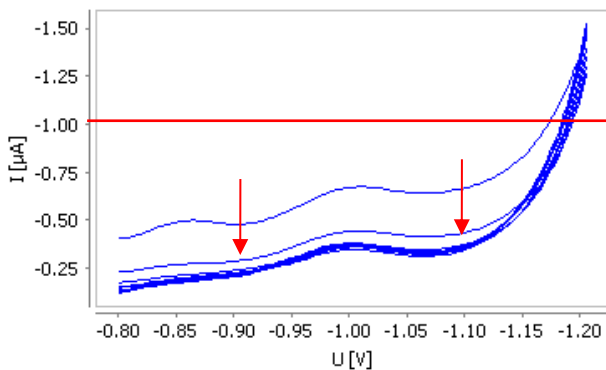
More detailed method parameters can be found in the method printout, which is available as a separate document.

Example



Comments

The current at -0.9 V and -1.1 V should not be more negative than -1 µA. If the current is more negative than -1 µA, further cleaning is required.



Determination of Fe

Analysis

10 mL sample and 1 mL supporting electrolyte are pipetted into the measuring vessel. The determination is carried out using the parameters given under «Parameters for determination of Fe». The measuring solution is purged for 5 min before the determination.

Measuring solution

10 mL sample

1 mL supporting electrolyte

Quantification is carried out by two additions of standard addition solution 2.

Parameters for determination of Fe

Voltammetric

Measuring mode DP – differential pulse

Cyclic voltammetric pretreatment

Start potential 0.2 V

Vertex potential -1 V

No. of cycles 2

Potentiostatic pretreatment

Potential -2 V

Waiting time 5 s

Sweep

Start potential -0.75 V

End potential -1.25 V

Potential step 0.006 V

Potential step time 0.1 s

Pulse amplitude 0.05 V

Potentiostat

Highest current range 2 mA

Lowest current range 200 µA

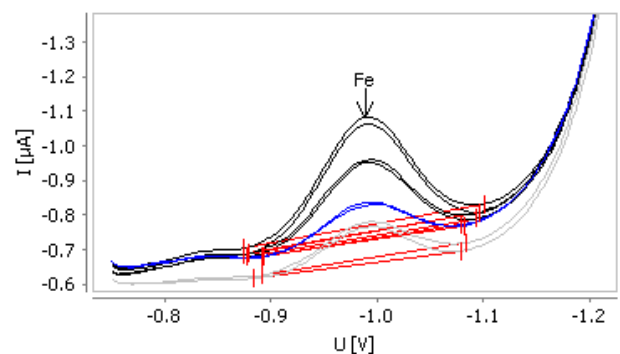
Substance

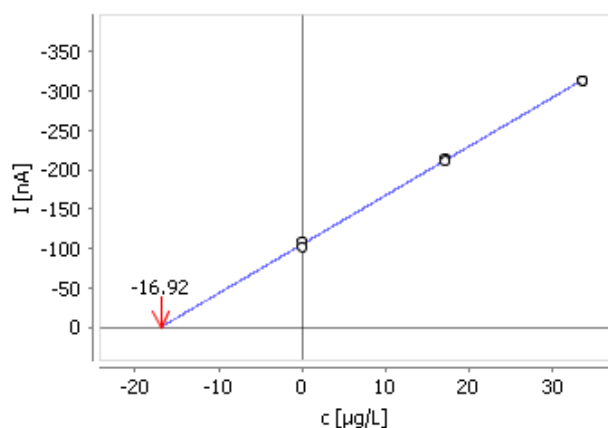
Name Fe

Characteristic potential -1 V

More detailed method parameters can be found in the method printout which is available as a separate document.

Example determination in tap water sample spiked with $\beta(\text{Fe}) = 20 \mu\text{g/L}$





Results

Sample	$\beta(\text{Fe})^*$ $\mu\text{g/L}$	RSD	Recovery
Check standard $\beta(\text{Fe})$ = 5 $\mu\text{g/L}$	4.67	1%	94%
Check standard $\beta(\text{Fe})$ = 20 $\mu\text{g/L}$	19.26	1%	96%
Tap water	< LOD		
Tap water spiked with $\beta(\text{Fe}) = 20 \mu\text{g/L}$	18.5	4%	93%
Mineral water	< LOD		
Mineral water spiked with $\beta(\text{Fe}) = 50 \mu\text{g/L}$	46.2	1%	92%
Sea water	< LOD		
Sea water spiked with $\beta(\text{Fe}) = 20 \mu\text{g/L}$	20.4	8%	102%

* - mean value of 3 determinations

RSD - relative standard deviation

Recovery – Recovery of the spiked amount

Comments

Electrode activation, electrode cleaning

Prior to the first use, the Bi drop electrode has to be activated by using the procedure described under «Activation/cleaning of the Bi drop electrode». This procedure can be used for both the activation and cleaning of the Bi drop electrode, and is repeated until the background current is more positive than $-1 \mu\text{A}$. It is recommended to run the activation/cleaning procedure if the electrode has not been used for more than one hour.

Electrode storage

When the electrode is not used for <12 h (e.g., overnight), it can be stored in diluted cleaning electrolyte (10 mL ultrapure water + 1 mL cleaning electrolyte). Keeping the electrode in ultrapure water or a different solution will cause the bismuth drop to turn black, which will require the aggressive regeneration of the surface (see «Regeneration of the Bi drop electrode»).

When the electrode is not used for a longer period of time, it must be stored dry. Before storage, thoroughly rinse the Bi drop with ultrapure water and leave it to dry. When the electrode is completely dry, store it in the storage vessel 6.2008.040 for mechanical protection.

Blackening of the Bi drop electrode

When the electrode has been stored under unsuitable conditions, the bismuth drop surface tends to turn completely black as soon as the first potential in the method is applied. To the best of our knowledge, this behavior does not depend on the measuring solution or the first applied potential. When the bismuth drop has turned black, the electrode has to be regenerated as described under «Regeneration of the Bi drop electrode».

Regeneration of the Bi drop electrode

If the bismuth drop is covered with a black film (not dark gray), proceed as follows:

Dip the black-colored bismuth drop for a short period of time (3–5 s) in concentrated nitric acid ($w(\text{HNO}_3) = 65\%$), rinse thoroughly with ultrapure water and perform the electrochemical cleaning procedure as described under «Activation/cleaning of Bi drop electrode». The electrochemical cleaning procedure may have to be repeated several times, always in a new cleaning solution, until the baseline current is more positive than $-1 \mu\text{A}$.

No other procedures, such as e.g. prolonged cleaning without treatment with nitric acid, results in a satisfactory baseline. It is necessary to remove a portion of the bismuth surface to restore the performance.

The regeneration procedure is aggressive to the electrode and should be carried out only when the surface of the bismuth drop has turned completely black, but not when it is only dark gray. The treatment with nitric acid can only be repeated 2–3 times in the lifetime of the electrode. Then the Bi drop electrode cannot be recovered anymore.

Automation

When the Bi drop electrode is used in an automated system, it is recommended to run one activation/cleaning method at the end of the determination series, and to keep the measuring vessel filled with the measuring solution (diluted cleaning electrolyte). It is important that the Bi drop electrode is stored in the cleaning electrolyte to prevent the Bi drop from turning black. However, the electrode should not be in solution for more than 12 hours (see «Electrode storage»). If the electrode is kept in the cleaning electrolyte for more than 12 hours, repeated cleaning/activation is required.

Interference of heavy metals

To evaluate the effect of heavy metals on the Fe determination, a check standard solution of $\beta(\text{Fe}) = 50 \mu\text{g/L}$ was placed in the measuring cell and $x \text{ mg/L}$ of metal of interest (Cu, Cd, Pb, and Mn) were successively added. The shape of the background current, height, and shape of the iron peak were evaluated.

Cu	Cu does not interfere with the Fe determination up to a concentration of $\beta(\text{Cu}^{2+}) = 3 \text{ mg/L}$ in the measuring vessel.
Cd	Cd does not interfere directly with the Fe determination up to concentration of $\beta(\text{Cd}^{2+}) = 50 \mu\text{g/L}$.
Pb	At the potential of -0.85 V , a peak can be observed when Pb is added to the solution. Already $\beta(\text{Pb}^{2+}) = 0.5 \text{ mg/L}$ in the measuring vessel increases the background current and decreases the Fe peak by 20%. Further increases in Pb concentration have no significant effect on the Fe peak height.
Mn	Mn affects the Fe peak drastically. For $\beta(\text{Mn}^{2+}) = 100 \mu\text{g/L}$, the Fe peak decreases by ca. 20%. For $\beta(\text{Mn}^{2+}) = 200 \mu\text{g/L}$, the Fe peak decreases by ca. 50%. Further increases of the Mn concentration in the measuring vessel have no effect on the Fe peak.
O ₂	The presence of O ₂ in the measuring solution affects the shape of the background current and decreases the sensitivity of the method. Therefore, purging is strongly recommended.

Limit of detection

The limit of detection was set to the smallest possible concentration which can be determined with the recovery rate of 50% in a check standard solution and is ca. $\beta(\text{Fe}) = 5 \mu\text{g/L}$.

Linear range

The method is linear between $\beta(\text{Fe}) = 5 \mu\text{g/L}$ and $\beta(\text{Fe}) = 1 \text{ mg/L}$.

Working range of the method

With two standard additions of 200 μL standard addition solution 1 ($\beta(\text{Fe}) = 200 \mu\text{g/L}$), the method is suitable for samples with iron concentrations between $\beta(\text{Fe}) = 100 \mu\text{g/L}$ and $\beta(\text{Fe}) = 500 \mu\text{g/L}$. For samples with lower iron concentrations, standard addition solution 2 should be used.

Fe(II) and Fe(III)

With this method it is not possible to differentiate between Fe(II) and Fe(III). Both oxidation states exhibit a signal with the same sensitivity.

Deposition

This iron determination is a direct reduction. Therefore, the sensitivity cannot be enhanced by a deposition.

Blank

As both triethanolamine and potassium bromate can be contaminated with iron, it is essential to determine a blank value for the reagents.

Reproducibility and recovery rate

The overview for reproducibility and recovery rate is shown in the following illustration.

