Metrohm

Application Bulletin 317/2 e

Determination of iron in the µg/L-range by polarography

Summary

This Application Bulletin describes two methods for the determination of iron at the Multi-Mode Electrode.

Method 1, the polarographic determination at the DME, is recommended for concentrations of β(Fe) > 200 µg/L. For this method the linear range is up to β(Fe) = 800 µg/L.

For concentrations < 200 µg/L method 2, the voltammetric determination at the HMDE, is to be preferred. The detection limit for this method is β(Fe) = 2 µg/L, the limit of quantification is β(Fe) = 6 µg/L. The sensitivity of the method cannot be increased by deposition.

Iron(II) and iron(III) have the same sensitivity for both methods

These methods have been elaborated for the determination of iron in water samples. For water samples with high calcium and magnesium concentrations such as, for example, seawater, a slightly modified electrolyte is used in order to prevent precipitation of the corresponding metal hydroxides. The methods can also be used for samples with organic loading (wastewater, beverages, biological fluids, pharmaceutical or crude oil products) after appropriate digestion.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode	
909 UV Digester	2.909.0014

Electrodes

WE	Multi-Mode Electrode pro Mercury drop capillary	6.1246.120 6.1226.030
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Pt rod electrode	6.0343.x00

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Sodium hydroxide, w(NaOH) = 30%, for trace analysis*, CAS 12200-64-5
- Triethanolamine, w($C_6H_{15}NO_3$) ≥ 98%, for analysis, CAS 102-71-6
- Potassium bromate, $KBrO_3$, for analysis, CAS 7758-01-2
- Fe^{3+} standard stock solution, β(Fe^{3+}) = 1 g/L (commercially available)
- Nitric acid, w(HNO_3) = 65%, for trace analysis*, CAS 7697-37-2
- Citric acid monohydrate, $C_6H_8O_7 \cdot H_2O$, for trace analysis*, CAS 5949-29-1
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

Solutions

Supporting electrolyte	c(NaOH) = 0.3 mol/L c($KBrO_3$) = 0.1 mol/L c(TEA) = 0.05 mol/L 0.373 g triethanolamine, 0.835 g $KBrO_3$ and 1.5 mL NaOH are dissolved in approx. 40 mL ultrapure water in a 50 mL volumetric flask. After cooling to room temperature the solution is made up to the mark with ultrapure water.

Standard solutions

Fe standard solution	β(Fe^{3+}) = 10 mg/L 1.0 mL Fe^{3+} standard stock solution (1 g/L) and 0.1 mL HNO_3 (65%) are transferred to a 100 mL volumetric flask and made up to the mark with ultrapure water.

Sample preparation

- Tap water, surface waters, mineral waters and drinking waters can usually be analyzed without pretreatment.

Organic matter often interferes with voltammetric determinations and therefore sample solutions usually have to be digested.

- Low polluted waste waters can be digested with the 909 UV Digester.
  - Add 50 - 100 µL hydrogen peroxide w(H_2O_2) = 30% to 10 mL acidified samples (pH = 2). The quartz tubes are irradiated for 90 min at 90 °C. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel. The blank value of this digestion is relatively small.
- Filters, filter residues and samples with organic matter (foods, pharmaceutics etc.) must be digested.
  - High-pressure asher
  - Microwave digestion

  Both techniques oxidize the samples in a closed digestion vessel by means of a mixture of concentrated mineral acids.
  - According to Application Bulletin113, open wet digestion with H_2SO_4 and H_2O_2.

Method 1: Polarographic determination for Fe concentrations > 200 µg/L

Summary

Triethanolamine forms a complex with iron. The formation of this complex prevents the precipitation of iron in the alkaline electrolyte used. The signal obtained during the measurement shows the reduction of iron(III) to iron(II).

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

The potassium bromate contained in the supporting electrolyte then oxidizes Fe^{2+} back to Fe^{3+}, which means that it is again available for reduction. In this way a much higher iron concentration is simulated than is actually present. This catalytic enhancement leads to considerably larger signals.

This method is suitable for samples with iron concentrations above 200 µg/L. Method 2 is recommended for samples with lower iron concentrations; this is described later.

Analysis

Measuring solution

10 mL sample

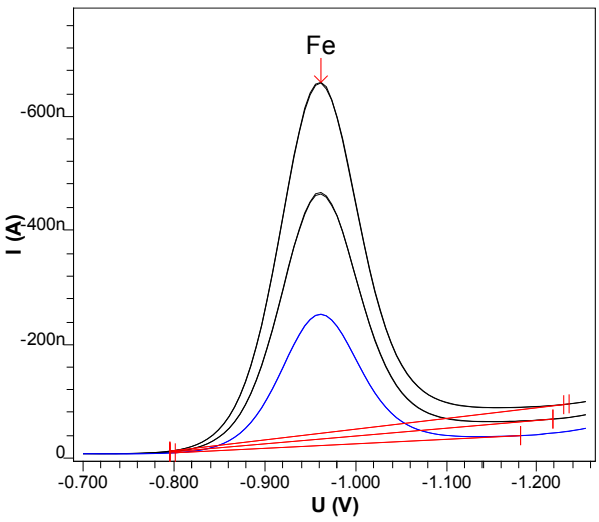
2 mL supporting electrolyte

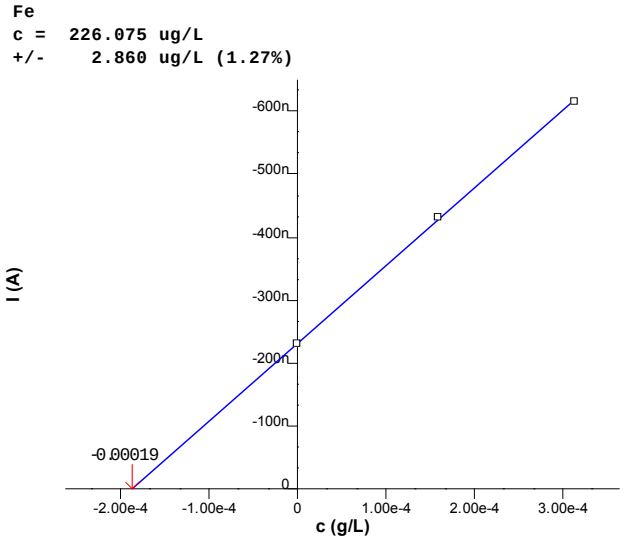
The pH of the measuring solution should be pH = 12 … 12.4.

Parameters

Voltammetric	
Electrode operating mode	DME
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	5 s
Sweep	
Start potential	-0.7 V
End potential	-1.25 V
Potential step	0.006 V
Potential step time	0.5 s
Sweep rate	0.012 V/s
Pulse amplitude	0.05 V
Substance	
Name	Fe
Characteristic potential	-0.96 V

Example





Method 2: Voltammetric determination for Fe concentrations < 200 µg/L

Summary

Triethanolamine forms a complex with iron. The formation of this complex prevents the precipitation of iron in the alkaline electrolyte used. The signal obtained during the measurement shows the reduction of iron(III) to iron(II).

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

The potassium bromate contained in the supporting electrolyte then oxidizes Fe^{2+} back to Fe^{3+}, which means that it is again available for reduction. In this way a much higher iron concentration is simulated than is actually present. This catalytic enhancement leads to considerably larger signals.

As this method is a direct voltammetric determination and not an adsorptive stripping voltammetry method, increasing the sensitivity by deposition of Fe triethanolamine complex and subsequent stripping is not possible.

This method is suitable for samples with iron concentrations up to 200 µg/L. Method 1 in this Application Bulletin is recommended for samples with higher iron concentrations.

Result

Sample	Tap water (spiked)
Sample size	10 mL
β(Fe)	226 µg/L

Comments

- Detection limit: β(Fe) = 5 µg/L
- Limit of quantification: β(Fe) = 15 µg/L.
- Linear range: up to 800 µg/L
- For higher iron concentrations it is possible to prepare the supporting electrolyte without potassium bromate. This avoids the catalytic enhancement with the result that the sensitivity of the determination is reduced by a factor of about 40.
- Under the measuring conditions given above a signal is obtained for both Fe^{2+} and Fe^{3+} at -0.96 V. The sensitivity of the two oxidation states is comparable.

Analysis

Measuring solution

10 mL (diluted) sample

2 mL supporting electrolyte

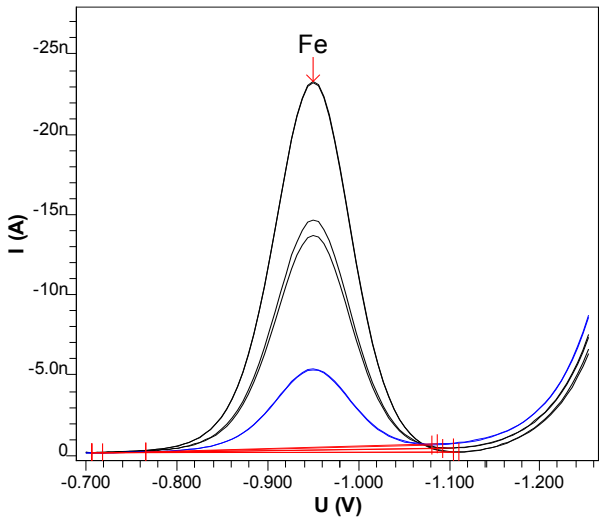
The pH of the measuring solution should be pH = 12 … 12.4.

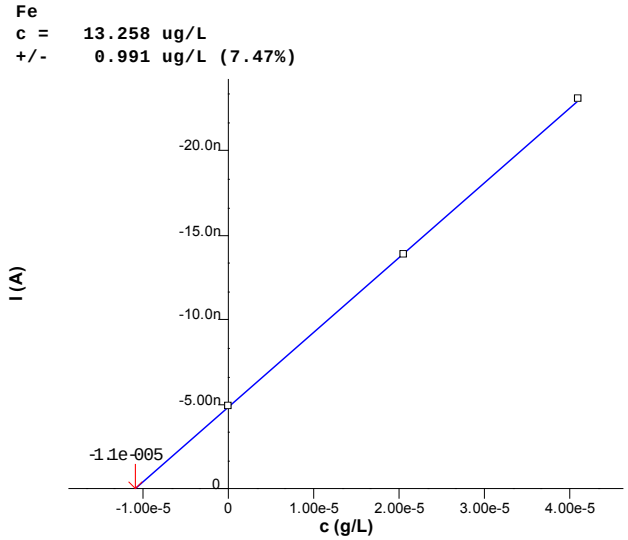
Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	5 s
Sweep	
Start potential	-0.7 V
End potential	-1.25 V
Potential step	0.006 V
Potential step time	0.5 s
Sweep rate	0.012 V/s
Pulse amplitude	0.05 V
Pulse time	s
Substance	

Name	Fe
Characteristic potential	-0.96 V

Example





Result

Sample	Tap water
Sample size	10.0 mL
Reagent blank β(Fe)	3.5 µg/L
Measuring result β(Fe)	13.3 µg/L
Result – blank β(Fe)	9.8 µg/L

Comments

- As both triethanolamine and potassium bromate are contaminated with iron it is essential to determine a blank value for the reagents.
- When measuring the blank value a shoulder appears on the iron signal at approx. -0.8 V. After the addition of a foreign ion (e.g. Pb^{2+}) this shoulder disappears again.
- Detection limit: β(Fe) = 2 µg/L
- Limit of quantification: β(Fe) = 6 µg/L.
- Linear range: up to 200 µg/L
- For higher iron concentrations it is possible to prepare the supporting electrolyte without potassium bromate. This avoids the catalytic enhancement with the result that the sensitivity of the determination is reduced by a factor of about 40.

Determination of seawater

Because of the increased concentrations of calcium and magnesium ions a modified supporting electrolyte must be used for seawater:

Supporting electrolyte for seawater	c(NaOH) = 5 mol/L c(citric acid) = 1.56 mol/L c($KBrO_3$) = 0.1 mol/L c(TEA) = 0.05 mol/L 16.4 g citric acid monohydrate are dissolved in 15 mL ultrapure water in a 50 mL volumetric flask. 25 mL NaOH, 0.373 g triethanolamine and 0.835 g $KBrO_3$ are added. After cooling to room temperature the solution is made up to the mark with ultrapure water. Caution: the solution becomes very hot!

The citrate contained in the solution complexes the calcium and magnesium ions present. The pH of the measuring solution must be between 12.0 and 12.4 in order to obtain usable signals. If the pH is too low no signal can be measured. If the pH is above 12.4 then calcium and magnesium precipitate as hydroxides.

Measuring solution

10 mL seawater sample

2 mL supporting electrolyte for seawater

The pH of the measuring solution should be pH = 12 … 12.4.

This modified electrolyte can be used for both method 1 and method 2.

Interferences from other metal ions

Possible interferences to the peak of $\beta(Fe^{3+})$ = 100 µg/L have been investigated for the following ions under the measuring conditions given for method 2. If nothing to the contrary is mentioned, tests have been carried out at an excess of 200:1.

Element	Remarks
Al^{3+}	No interference
Bi^{3+}	No interference, peak at -0.64 V, tested up to 600:1
Cd^{2+}	No interference, peak at -0.68 V, tested up to 500:1
Co^{2+}	No interference
Cr^{3+}	No interference
Cr^{6+}	Interference by peak at -1.0 V
Cu^{2+}	No interference, tested up to 500:1
In^{3+}	No interference up to a ratio of 10:1. At concentrations $\beta(In^{3+})$ > 1 mg/L interference by a peak at -1.0 V and a further peak at -1.25 V is observed.
Mn^{2+}	From a concentration of $\beta(Mn^{2+})$ = 20 mg/L signals occur at -0.12 V; -0.29 V, interference by peak at -1.2 V.
Ni^{2+}	No interference
Pb^{2+}	No interference, peak at -0.67 V
Sb^{3+}	No interference
Sb^{5+}	No interference. peak at -0.12 V
Se^{4+}	No interference
Se^{6+}	No interference
Sn^{2+}	No interference
Sn^{4+}	No interference
Zn^{2+}	No interference, peak at -1.38 V, tested up to 1000:1
Li^{+}	No interference
K^{+}	No interference
Ca^{2+}	No interference, precipitate from approx. $\beta(Ca^{2+})$ = 20 mg/L → electrolyte for seawater
Mg^{2+}	No interference, precipitate from approx. $\beta(Mg^{2+})$ = 0.1 g/L → electrolyte for seawater
Na^{+}	No interference

Interference from non-metals

Element	*Remarks*
Cl^{-}	No interference
I^{-}	No interference
NO_2^{-}	No interference
NO_3^{-}	No interference
PO_4^{3-}	No interference
SO_4^{2-}	No interference

References

- Henze, Neeb: „Elektrochemische Analytik, Springer Verlag 1986, p. 184 ff

Appendix

Report for the example determination iron in tap water according to method 1

```
======== METROHM 797 VA COMPUTRACE (Version 1.3.1.84) (Serial No. 5195) ========
 Determination  : 0901191649_tap water + 200 ppb Fe.dth
 Sample ID      : tap water + 200 ppb Fe
 Creator method : mk                Date : 2008-11-14          Time:  11:11:06
 Creator determ.: mk                Date : 2009-01-19          Time:  16:49:30
 Modified by    :                   Date : 2009-05-26          Time:  09:25:17
--------------------------------------------------------------------------------
 Method         : Recovery.mth
 Title          : Determination of Fe  (TEA method)
 Remark1        : 10 mL water + 2 mL electrolyte (0.05M TEA, 0.1M KBrO3, 0.3M NaOH)
 Remark2        : + 200 µL addition (10 ppm Fe3+)
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.000 mL
--------------------------------------------------------------------------------
 Substance      : Fe
 Conc.          : 188.322 ug/L
 Conc.dev.      :   2.372 ug/L     ( 1.26%)
 Amount         :   2.260 ug
 Add.amount     :   2.000 ug

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.962  -230.6  -230.2     0.497       0.0
 1 - 2  -0.962  -229.9
 2 - 1  -0.962  -429.8  -431.1     1.827    -200.8
 2 - 2  -0.962  -432.4
 3 - 1  -0.962  -614.6  -615.0     0.573    -183.9
 3 - 2  -0.962  -615.4


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Fe           std.add.      -2.307e-007  -1.225e-003   3.482e-009      0.99987

 Solutions
--------------------------------------------------------------------------------

  No. Content                                          Predose (mL)
  --- ------------------------------------------------ ------------
   1  10 ppm Fe3+                                      -------


 Final results                        +/- Res. dev.   %     Comments
---------------------------------    ------------------    -------------------

 Fe:
 Fe               =  225.986  ug/L    2.846        1.259
```

Method print for the determination of iron according to method 1 (Fe > 200 µg/L)

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB317_1 Det of Fe_DME.mth
Title           : Determination of Fe  (TEA method)
Remark1         : 10 mL sample + 2 mL electrolyte
Remark2         : Electrolyte (0.05M TEA, 0.1M KBrO3, 0.3M NaOH)

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Sample
Sample amount (mL): 10.000
Cell volume (mL): 12.000

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                            : DP - Differential Pulse

Highest current range           : 10  mA
Lowest current range            : 100 nA

Electrode                       : DME
```

```
Stirrer speed (rpm)                : 2000

Initial electr. conditioning       : Yes
Standard deviation                 : 0.50 %

No. of additions                   : 2
No. of replications                : 2

Measure blank                      : No
Addition purge time (s)            : 60

Initial purge time (s)             :      300

Sweep
Equilibration time (s)             :    5.000
Start potential (V)                :   -0.700
End potential (V)                  :   -1.250
Voltage step (V)                   :    0.006
Voltage step time (s)              :    0.500
Sweep rate (V/s)                   :    0.012
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040

Cell off after measurement         :      Yes

Peak evaluation
-------------------------------------------------------------------------------
Regression technique               : Linear Regression
Peak evaluation                    : Height
Minimum peak width (V.steps)       : 5
Minimum peak height (A)            : 1.000e-010
Reverse peaks                      : No
Smooth factor                      : 4
Eliminate spikes                   : Yes

Substances
-------------------------------------------------------------------------------
Fe                        : -1.000 V   +/- 0.100 V

Standard solution         : 1   10.000 mg/L
Addition volume (mL)      : 0.200

default                   : Final result (Fe) =
                            Conc * (12 / 10) * (1e+006 / 1) + 0 - 0

Baseline
-------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
-------------------------------------------------------------------------------
Fe        Sample      yes       ---       ---     linear      wholePeak
          Addition 1  yes       ---       ---     linear      wholePeak
          Addition 2  yes       ---       ---     linear      wholePeak
-------------------------------------------------------------------------------
```

Report for the example determination iron in tap water according to method 2

```
======== METROHM 797 VA COMPUTRACE (Version 1.3.1.84) (Serial No. 3150) ========
 Determination  : 0811241617_tap water + 10 ppb Fe.dth
 Sample ID      : tap water + 10 ppb Fe
 Creator method : mk               Date : 2008-11-14          Time:  11:11:06
 Creator determ.: mk               Date : 2008-11-24          Time:  16:17:06
 Modified by    : ---              Date :                     Time:
-------------------------------------------------------------------------------
 Method         : Recovery.mth
 Title          : Determination of Fe  (TEA method)
 Remark1        : 10 mL sample + 2 mL electrolyte (0.05M TEA, 0.1M KBrO3, 0.3M N
aOH)
 Remark2        : + 25 µL addition (10 ppm Fe3+)
-------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  12.100 mL
-------------------------------------------------------------------------------
 Substance      : Fe
 Conc.          :  10.957 ug/L
 Conc.dev.      :   0.819 ug/L     ( 7.47%)
 Amount         : 132.584 ng
 Add.amount     : 250.000 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.950   -4.86   -4.87     0.020      0.00
 1 - 2  -0.950   -4.89
 2 - 1  -0.950  -13.38  -13.85     0.664     -8.97
```

```
 2 - 2  -0.950  -14.32
 3 - 1  -0.950  -23.12  -23.07     0.066     -9.22
 3 - 2  -0.950  -23.02


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 Fe           std.add.      -4.836e-009  -4.413e-004   5.384e-010      0.99929

 Solutions
-------------------------------------------------------------------------------

  No. Content                                          Predose (mL)
  --- ------------------------------------------------ ------------
   1  10 ppm Fe3+                                      0.010


 Final results                        +/- Res. dev.   %     Comments
-----------------------------------   -----------------    -------------------

 Fe:
 default           =   13.258  ug/L    0.991        7.471
```

Method print for the determination of iron according to method 2 (Fe < 200 µg/L)

```
-------------------------------------------------------------------------------
 Method parameters
-------------------------------------------------------------------------------
Method          : AB317_2 Det of Fe_HMDE.mth
Title           : Determination of Fe  (TEA method)
Remark1         : 10 mL sample + 2 mL electrolyte
Remark2         : Electrolyte (0.05M TEA, 0.1M KBrO3, 0.3M NaOH)

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Sample
Sample amount (mL): 10.000
Cell volume (mL): 12.000

Voltammetric parameters
-------------------------------------------------------------------------------
Mode                            : DP - Differential Pulse

Highest current range           : 10  mA
Lowest current range            : 100 nA

Electrode                       : HMDE
Drop size (1..9)                : 4
Stirrer speed (rpm)             : 2000

Initial electr. conditioning    : Yes
Standard deviation              : 0.50 %

No. of additions                : 2
No. of replications             : 2

Measure blank                   : No
Addition purge time (s)         : 60

Initial purge time (s)          :      300

Conditioning cycles
Start potential (V)             :   -1.200
End potential (V)               :   -0.100
No. of cycles                   :        0

Hydrodynamic (measurement)      :      No
Cleaning potential (V)          :   -0.100
Cleaning time (s)               :    0.000
Deposition potential (V)        :    0.000
Deposition time (s)             :    0.000

Sweep
Equilibration time (s)          :    5.000
Start potential (V)             :   -0.700
End potential (V)               :   -1.250
Voltage step (V)                :    0.006
Voltage step time (s)           :    0.500
Sweep rate (V/s)                :    0.012
```

```
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040

Cell off after measurement         :      Yes

Peak evaluation
-------------------------------------------------------------------------------
Regression technique               : Linear Regression
Peak evaluation                    : Height
Minimum peak width (V.steps)       : 5
Minimum peak height (A)            : 1.000e-010
Reverse peaks                      : No
Smooth factor                      : 4
Eliminate spikes                   : Yes

Substances
-------------------------------------------------------------------------------
Fe                        : -1.000 V   +/- 0.100 V

Standard solution         : 1   10.000 mg/L
Addition volume (mL)      : 0.025

default                   : Final result (Fe) =
                            Conc * (12 / 10) * (1e+006 / 1) + 0 - 0

Baseline
-------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
-------------------------------------------------------------------------------
Fe        Sample      yes       ---       ---     linear      wholePeak
          Addition 1  yes       ---       ---     linear      wholePeak
          Addition 2  yes       ---       ---     linear      wholePeak
-------------------------------------------------------------------------------
```