Metrohm

Application Bulletin 199/4 e

Determination of sulfide and sulfite by polarography

Summary

Sulfide and sulfite can be determined polarographically without any problems. For sulfide, polarography is performed in an alkaline, for sulfite in a slightly acidic primary solution. The method is suitable for the analysis of pharmaceuticals (infusion solutions), wastewater, flue gas water, photographic solutions, etc.

Instruments

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

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

Method 1: Sulfide determination

Reagents

All of the used reagents must be of analysis quality (for analysis).

- Sodium hydroxide, w(NaOH) = 30 %, for analysis, CAS 1310-73-2
- Sodium sulfide, Na_2S, for analysis, CAS 27610-45-3
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

Solutions

Diluted NaOH solution	c(NaOH) = 0.1 mol/L 5 mL sodium hydroxide is made up to 500 mL with ultrapure water.

Standard solutions

Sulfide standard solution	β(sulfide) = 1 g/L The standard solution is prepared from Na_2S with oxygen free sodium hydroxide solution c(NaOH) = 0.1 mol/L.

Analysis

Measuring solution

10 mL diluted sodium hydroxide solution

(purge for 5 min with nitrogen)

10 mL (diluted) sample

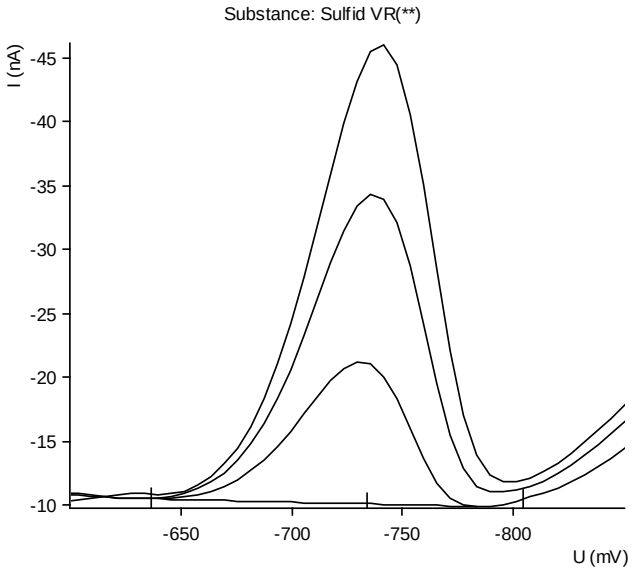
(mix while stirring without nitrogen)

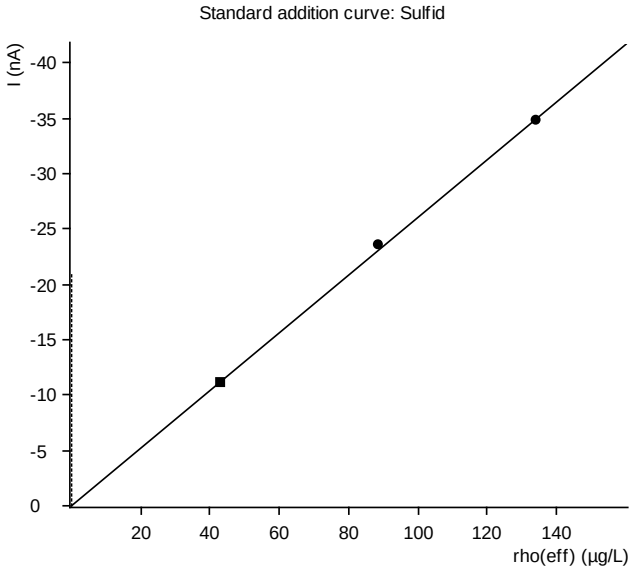
The concentration is determined by standard addition.

Parameters

Voltammetric	
Electrode operating mode	SMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	10 s
Sweep	
Start potential	-0.5 V
End potential	-0.9 V
Potential step	0.006 V
Potential step time	0.6 s
Sweep rate	0.01 V/s
Pulse amplitude	0.05 V
Substance	
Name	Sulfide
Characteristic potential	-0.75 V

Example





Result

Sample size	1.0 mL
β(sulfide)	475.2 µg/L

Comments

- When the 797 VA Computrace is used the purging has to be done manually prior to the start of the method.
- After the addition of a sample solution or standard solutions, purging with nitrogen may no longer be performed, otherwise loss of sulfide could occur.
- A linearity test was performed between 0.02 and 2 mg/L: Between 0.02 and 0.25 mg/L at the SMDE and between 0.25 mg/L and 2 mg/L at the DME (bigger Hg-drop). The sulfide determination is linear up to 1.6 mg/L.
- The determination limit for sulfide lies by 20 µg/L.

Method 2: Sulfite determination

Reagents

All of the used reagents must be of analysis quality (for analysis).

- Sodium hydroxide, for analysis, w(NaOH) = 30 %, CAS 1310-73-2
- Acetic acid, for analysis, w(CH_3COOH) = 100 %, CAS 64-19-7
- Sodium sulfite, Na_2SO_3, for analysis, CAS 7757-83-7
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

Solutions

Acetate buffer (pH 4.6)	c(NaOH) = 0.2 mol/L, c(CH_3COOH) = 0.4 mol/L 10 mL sodium hydroxide and 11.1 mL acetic acid are made up to 500 mL with ultrapure water.

Standard solutions

Sulfite standard solution	β(sulfite) = 1 g/L The standard solution is prepared from Na_2SO_3 with oxygen free ultrapure water.

Analysis

Measurement solution

10 mL acetate buffer

(deaerate 5 minutes with nitrogen)

10 mL (diluted) sample

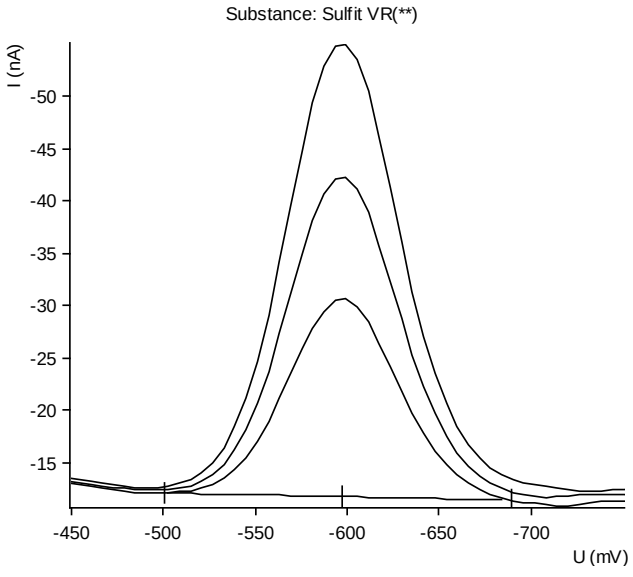
(without degassing with nitrogen, stir for 10 seconds)

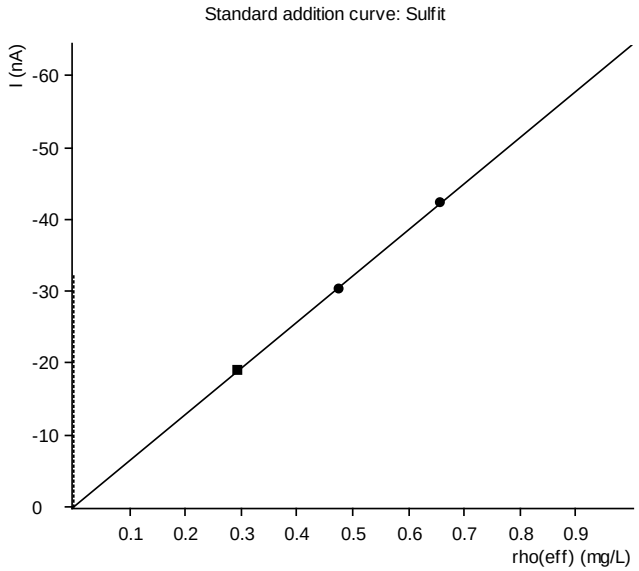
The concentration is determined by standard addition.

Parameters

Voltammetric	
Electrode operating mode	DME
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	10 s
Sweep	
Start potential	-0.4 V
End potential	-0.85 V
Potential step	0.006 V
Potential step time	0.4 s
Sweep rate	0.015V/s
Pulse amplitude	0.05 V
Substance	
Name	Sulfite
Characteristic potential	-0.6 V

Example





Result

Sample size	1.0 mL
β(sulfite)	3.2 mg/L

Comments

- With the 797 VA Computrace the purging has to be done manually before the start of the method.
- After addition of a sample solution or standard solution, purging with nitrogen may no longer be performed, otherwise sulphur dioxide can escape. (mix only with stirring).
- In the presence of sulfide, a peak appears at -0.45 V. This cannot be used for quantitative analyses. (Acidic medium - high volatility of hydrogen sulfide).
- Sulfite can also be determined in 1 mmol/L hydrochloric acid as supporting electrolyte.
- Should sulfide and sulfite be determined together in the same sample, the sulfide must first be determined in alkaline solution, and after addition of 250 µL 50% acetic acid / 10 mL acetate buffer, sulfite can be analysed.
- In the presence of thiosulfate, two overlapping peaks can be observed between -0.14 V and -0.28 V. With thiosulfate contents up to ca. 100 µg/initial mass, only one peak appears at -0.28 V. This can be used for quantitative analyses.
- The determination of sulfite should be performed immediately upon taking the sample, because sulfite solutions are not stable.

References

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Appendix

Report for the example determination of sulfide according to method 1

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : AD_DME_S             User:                      Date: 1993-05-21
 Modified    : 1993-05-21 09:44:37  Run :  0                   Time: 09:33:08
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        Standard                                                        1 mL
--------------------------------------------------------------------------------
 Method  :  A199S_A2
 Title   :  Bestimmung von Sulfid an der DME mittels Std.Add.
 Remark1 :  Bestimmung von Sulfid mittels Standardaddition
 Remark2 :
--------------------------------------------------------------------------------

  Substance : Sulfid                                          Comments
  Mass conc.:    475.2 ug/L            Mass     : 475.2 ng   ------------------
  MC.dev.   :     54.5 ug/L (11.5%)    Add.mass :   500 ng
  Cal.dev.  :    -                     V0.sample:     1 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -734   -11.07  -11.07
              10   -740   -23.38  -23.38            -12.31
              20   -743   -34.44  -34.44            -11.06

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Sulfid       std.add.     -1.126e-08   -2.606e-04                 4.715e-10

 Final results                         +/- Res.dev.   %      Comments
 ---------------------------------     -----------------     ------------------
     Sulfid =   475.24 ug/L               54.5    11.5
```

Method print for the determination of sulfide according to method 1

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0100) ==================
 Method: AB199_1 .mth         OPERATION SEQUENCE
 Title : Determination of Sulfide with SMDE. AB199 Part 1
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  -------------------------
 1    DOS/M                V.added      10.000 mL
 2    REM                  10 mL 0.1 mol/L NaOH
 3    PURGE
 4    STIR          300.0  Rot.speed      2000 /min
 5    0PURGE
 6    SMPL>M               V.fraction          mL     V.total              L
 7    (ADD
 8      NOP         10.0
 9      SEGMENT            Segm.name   pol
10      ADD>M              Soln.name   S-Std          V.add         0.050 mL
11    ADD)2
12    END

 Method: AB199_1              SEGMENT
                                   pol
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  -------------------------
 1    0STIR           3.0
 2    SMDE                 Drop size         4
 3    DPMODE               U.ampl          -50 mV     t.meas         30.0 ms
                           t.step         0.60 s      t.pulse        40.0 ms
 4    SWEEP         42.0   U.start        -500 mV     U.step            6 mV
                           U.end          -900 mV     Sweep rate       10 mV/s
 5    STIR                 Rot.speed      2000 /min
 6    0MEAS                U.standby           mV
 7    END
```

Report for the example determination of sulfite according to method 2

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : Ad1dmeso             User:  zu                  Date: 1993-05-23
 Modified    : 1993-05-23 14:00:50  Run :  0                   Time: 13:59:08
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        Standard                                                        1 mL
--------------------------------------------------------------------------------
 Method  :  A199SOA1
 Title   :  Bestimmung von Sulfit an der DME mittels Std.Add.
 Remark1 :  Bestimmung von Sulfit mittels Standardaddition
 Remark2 :  Auswertung linear
--------------------------------------------------------------------------------

  Substance : Sulfit                                          Comments
  Mass conc.:    3.227 mg/L            Mass     : 3.227 ug   ------------------
  MC.dev.   :    0.123 mg/L (3.82%)    Add.mass :     2 ug
  Cal.dev.  :    -                     V0.sample:     1 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -597   -18.92  -18.92
              10   -597   -30.29  -30.29            -11.37
              20   -597   -42.11  -42.11            -11.83

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Sulfit       std.add.     -1.883e-08   -6.421e-05                 2.027e-10

Final results                        +/- Res.dev.   %      Comments
 --------------------------------     ----------------     ------------------
     Sulfit =   3.2266 mg/L              0.123    3.82
```

Method print for the determination of sulfite according to method 2

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0100) ==================
 Method: AB199_2 .mth         OPERATION SEQUENCE
 Title : Determination of Sulfite with DME. AB199 Part 2
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    DOS/M                V.added      10.000 mL
 2    REM                  10 mL buffer (0.2 mol/L NaOH,0.4 mol/L acetic acid)
 3    PURGE
 4    STIR          300.0  Rot.speed      2000 /min
 5    0PURGE
 6    SMPL>M               V.fraction          mL     V.total              L
 7    (ADD
 8      NOP         10.0
 9      SEGMENT            Segm.name   pol
10      ADD>M              Soln.name   SO3-Std        V.add         0.020 mL
11    ADD)2
12    END

 Method: AB199_2               SEGMENT
                                    pol
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    0STIR
 2    DME
 3    DPMODE               U.ampl          -50 mV     t.meas         20.0 ms
                           t.step         0.40 s      t.pulse        40.0 ms
 4    SWEEP         31.2   U.start        -400 mV     U.step            6 mV
                           U.end          -850 mV     Sweep rate       15 mV/s
 5    STIR                 Rot.speed      2000 /min
 6    0MEAS                U.standby           mV
 7    END
```