
Application Bulletin

Of interest to: General analytical laboratories, Pharmacy, Photoindustry
Environmental protection

B 1, 2, 4, 6

Polarographic determination of sulphide and sulphite

Summary

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

Apparatus and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
 - 757 VA Computrace
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Literature

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Direct determination of sulfide by rapid direct current polarography.
Anal. Chem. 45, (1973), 2414-2417
- Canterford, D.R.
Simultaneous determination of cyanide and sulfide with rapid direct current polarography.
Anal. Chem. 47, (1975), 88-92
- Leppingen, J. / Vahtila, S.
Differential pulse polarographic determination of Thiol flotation collectors and sulfide in waters.
Talanta 33, (1986), 795-799
- Blasius, E. / Schreiner, C. / Ziegler, K.
Polarographische Bestimmung von Schwefelverbindungen nebeneinander in wässrigen Lösung.
Arch. Eisenhüttenwes. 45/7, (1974), 441-444
- Cheshchevoi, V.N. / Polushkin, V.A. / Slovetskii, V.L.
Analysis of the mixture of sulphur containing ions in water solutions by polarography.
Zavodsk. Lab. 51 (1985), 16-17
- Donahue, J.J. / Oliveri- Vigh, S.
Simultaneous polarographic determination of bisulfite and iproniazid in gel formulations.
J. Pharm. Sci. 62, (1973), 1990-1992
- Garber, R.W. / Wilson, C.E.
Determination of atmospheric sulfur dioxide by differential pulse polarography
Anal. Chem. 44, (1972), 1357-1360

- Holak, W. / Patel, B.
Differential pulse polarographic determination of sulfites in food: Collaborative study.
J. Assoc. Off. Anal. Chem. 70, (1987), 572-578
- Holak, W. / Specchio, J.
Determination of sulfites in foods by simultaneous nitrogen purging and differential pulse polarography.
J. Assoc. Off. Anal. Chem. 72, (1989), 476-480
- Smyth, W.F. / Vaneesorn, Y.
Recent applications of polarography and voltammetry to environmental and pharmaceutical analysis.
International Labmate 1986, 41-46, ISSN - 0143-5140

Method 1: Sulphide determination

Reagents

All of the used reagents must be of purest quality possible (analytical grade or suprapur). Only ultrapure water should be used.

- Sodium hydroxide, suprapur, w(NaOH) = 30 %
- Na₂S, CAS 27610-45-3

Ready-to-use solutions:

- Diluted sodium hydroxide solution, c(NaOH) = 0.1 mol/L
5 mL sodium hydroxide is made up to 500 mL with ultrapure water.
- Sulphide standard: β(Sulfide) = 1 g/L
The standard solution is prepared from Na₂S with oxygen free sodium hydroxide solution c(NaOH) = 0.1 mol/L.

Analysis

Measuring solution:

10 mL diluted sodium hydroxide solution
purge for 5 minutes with nitrogen

+ 10 mL (diluted) sample
mix while stirring (without nitrogen).

The polarogram is recorded with the following parameters:

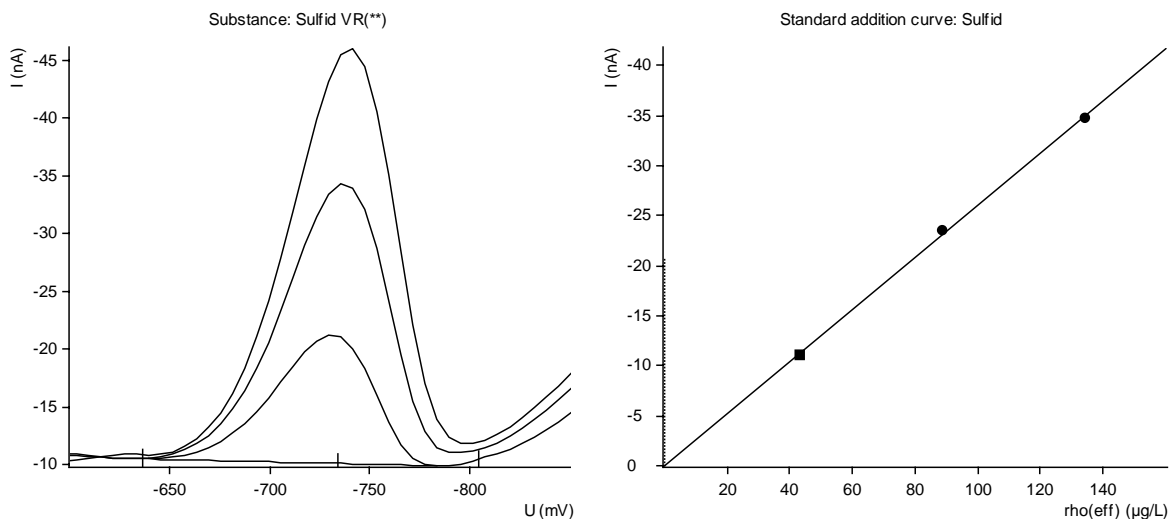
Working electrode	SMDE
Stirrer/RDE	2000
Measurement mode	DP
Purge time (ohne Probe)	10 s
Pulse amplitude	50 mV
Equilibration time	3 s
Start potential	- 0.50 V
End potential	- 0.90 V
Voltage step	6 mV
Voltage step time	0.6 s
Sweep rate	10 mV/s
Peak potential (sulphide)	- 0.75V

The concentration is determined by standard addition.

Remarks

- When the 757 VA Computrace is used the deaeration has to be done prior to the start of the method.
- After the addition of a sample solution or standard solutions, deaeration with nitrogen may no longer be performed, otherwise loss of sulphide 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 sulphide determination is linear up to 1.6 mg/L.
- The determination limit for sulphide lies by 20 µg/L.

Figures



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===== 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: -
    
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Pos.	Ident.1/S1 Standard	Ident.2/S2	Ident.3/S3	Method.call	Sample size/S0 1 mL
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Method      : A199S_A2
Title       : Bestimmung von Sulfid an der DME mittels Std.Add.
Remark1    : Bestimmung von Sulfid mittels Standardaddition
Remark2    :
    
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Substance   : Sulfid
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	

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===== METROHM 746 VA TRACE ANALYZER (5.746.0100) =====
Method: AB199_1 .mth          OPERATION SEQUENCE
Title : Determination of Sulphide 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	OPURGE				
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
    
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	Instructions	t/s	Main parameters	Auxiliary parameters	
1	OSTIR	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	OMEAS		U.standby mV		
7	END				

Fig. 1 Sulphide: determination and parameters on the 746 VA Trace Analyzer

Method 2: Sulphite determination

Reagents

All of the used reagents must be of purest quality possible (analytical grade or suprapur). Only ultrapure water should be used.

- Sodium hydroxide, suprapur, $w(\text{NaOH}) = 30\%$
- Acetic acid, suprapur, $w(\text{CH}_3\text{COOH}) = 100\%$
- Na_2SO_3 , CAS 7757-83-7

Ready-to-use solutions:

- Acetate buffer pH 4.6: $c(\text{NaOH}) = 0.2\text{ mol/L}$, $c(\text{CH}_3\text{COOH}) = 0.4\text{ mol/L}$
10 mL sodium hydroxide and 11.1 mL acetic acid are made up to 500 mL with ultrapure water.
- Sulphite standard: $\beta(\text{Sulfite}) = 1\text{ g/L}$
The standard solution is prepared from Na_2SO_3 with oxygen free ultrapure water.

Analysis

10 mL acetate buffer
deaerate 5 minutes with nitrogen.

+ 10 mL (diluted) sample
without degasing with nitrogen, stir for 10 seconds.

The polarogram is recorded with the following parameters:

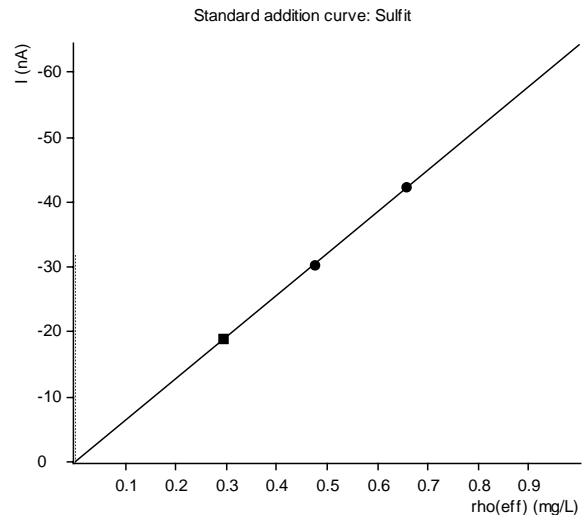
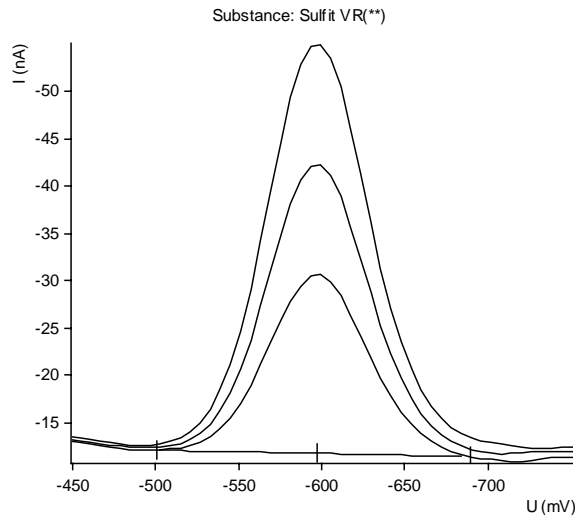
Working electrode	DME
Stirrer/RDE	2000
Measurement mode	DP
Purge time	10 s
Pulse amplitude	50 mV
Equilibration time	3 s
Start potential	- 0.40 V
End potential	- 0.85 V
Voltage step	6 mV
Voltage step time	0.4 s
Sweep rate	15 mV/s
Peak potential (sulphite)	- 0.60 V

The concentration is determined by standard addition.

Remarks

- At the 757 VA Computrace the deaeration has to be done before the start of the method
- After addition of a sample solution or standard solution, deaeration with nitrogen may no longer be performed, otherwise sulphur dioxide can escape. (mix only with stirring).
- In the presence of sulphide, a peak appears at -0.45 V. This can not be used for quantitative analyses. (Acidic medium - high volatility of hydrogen sulphide).
- Sulphite can also be determined in 1 mmol/L hydrochloric acid as supporting electrolyte.
- Should sulphide and sulphite be determined together in the same sample, the sulphide must first be polarographed in alkaline solution, and after addition of 250 µL 50% acetic acid/ 10 mL acetate buffer, sulphite can be analyzed.
- In the presence of thiosulphate, two overlapping peaks can be observed between - 0.14 V and - 0.28 V.
(With thiosulphates 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 sulphite should be performed immediately upon taking the sample, because sulphite solutions are not stable.

Figures



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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Determ.      : Adldmeso          User: zu          Date: 1993-05-23
Modified     : 1993-05-23 14:00:50 Run : 0          Time: 13:59:08
Sample table: -
    
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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

```

===== METROHM 746 VA TRACE ANALYZER (5.746.0100) =====
Method: AB199_2 .mth                OPERATION SEQUENCE
Title : Determination of Sulphite 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	OSTIR				
2	DME				
3	DPMODE		U.ampl	-50	mV
			t.step	0.40	s
4	SWEEP	31.2	U.start	-400	mV
			U.end	-850	mV
5	STIR		Rot.speed	2000	/min
6	OMEAS		U.standby	mV	
7	END				

Fig. 2 Sulphite: determination and parameters on the 746 VA Trace Analyzer