Metrohm

Application Bulletin 192/2 e

Determination of thiourea in the lower mg/L and in the µg/L range by polarography and cathodic stripping voltammetry

Summary

Thiourea forms highly insoluble compounds with mercury. The resulting anodic waves are used for the polarographic determination of thiourea. For the analysis of very small quantities (µg/L), cathodic stripping voltammetry (CSV) is used. Differential Pulse measuring mode is used in both cases.

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

Reagents

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

- Sodium hydroxide, for trace analysis*, CAS 1310-73-2
- Thiourea, for analysis, CAS 62-56-6
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Solutions

Electrolyte solution	c(NaOH) = 2 mol/L

Standard solutions

Thiourea standard stock solution	β(Thiourea) = 100 mg/L in ultrapure water. More dilute solutions must be freshly prepared daily from the stock solution.

Method 1: Polarographic determination of thiourea concentrations 0.2 – 2 mg/L

Analysis

10 mL sample solution and 10 mL electrolyte solution are deaerated well with nitrogen in a polarographic vessel. The concentrations are determined by standard addition. After every standard addition purge well with nitrogen.

Measuring solution

10 mL sample solution

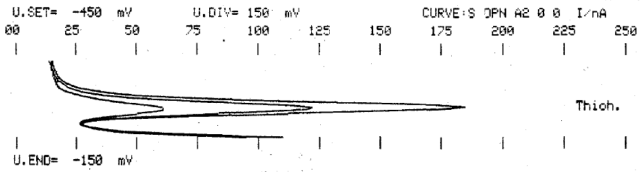
+ 10 mL electrolyte solution

Parameters

Voltammetric	
Electrode operating mode	DME
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Equilibration time	5 s
Sweep	
Start potential	-0.45 V
End potential	-0.15 V
Potential step	0.008 V
Potential step time	1.0 s
Sweep rate	0.008 V/s
Pulse amplitude	0.05 V

Substance	
Name	Thiourea
Characteristic potential	-0.26 V

Example



Result

β(thiourea)	0.31 mg/L

Method 2: Stripping voltammetric determination of thiourea concentrations 5 – 60 µg/L

Analysis

10 mL sample solution and 10 mL electrolyte solution are deaerated well with nitrogen in a polarographic vessel. The concentrations are determined by standard addition. After every standard addition purge well with nitrogen.

Measuring solution

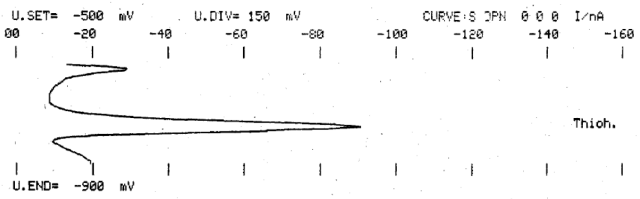
10 mL sample solution

+10 mL electrolyte solution

Parameters

Voltammetric	
Electrode operating mode	HMDE
Drop size	9
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	-0.2 V
Waiting time 1	150 s
Equilibration time	20 s
Sweep	
Start potential	-0.5 V
End potential	-0.9 V
Potential step	0.008 V
Potential step time	1.0 s
Sweep rate	0.008 V/s
Pulse amplitude	0.05 V
Substance	
Name	Thiourea
Characteristic potential	-0.75 V

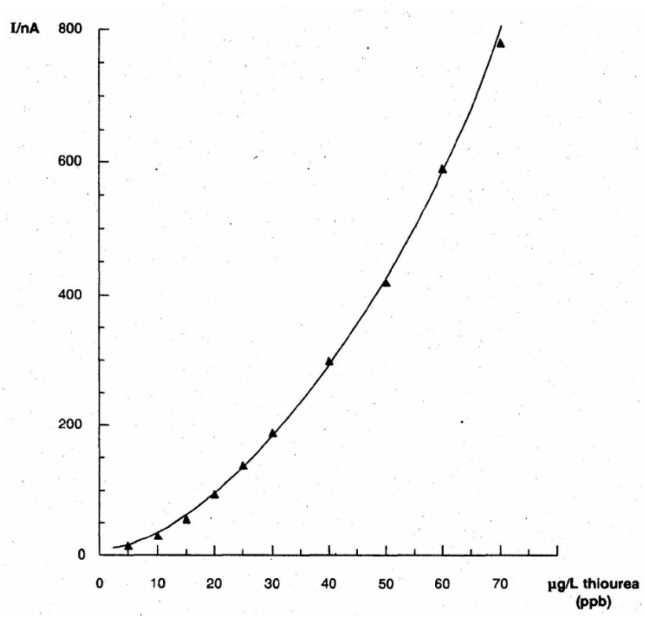
Example



Result (using a calibration curve)

β(thiourea)	16.5 µg/L

Calibration curve (stripping voltammetry)



Comments

- The largest possible mercury drops should be used
- Chloride ions up to a content of 10 mg/L do not interfere with the stripping voltammetry.

- If the sample contains more than 2 mg/L thiourea, it must be diluted for the polarographic determination (non-linear region).
- More dilute electrolyte solutions or smaller drop sizes restrict the working range. (Neutralize acidic sample solutions beforehand.)

References

- Arlt C., Naumann R.
  Vorschlag zur Bestimmung des Selens in Trinkwasser
  Z. Anal. Chem 282(1976), 463
- Stara V., Kopanica M.
  Adsorptive stripping voltammetric determination of thiourea and its thiourea derivatives. Anal. Chim. Acta 159, (1984), 105-110
- Kirchnerova J., Purdy C.
  A new simple voltammetric method for thiourea and thiourea dioxide determinations. Anal. Lett. 13/12, (1980), 1031-1040
- Smyth M. R., Osteryoung J. G.
  Determination of some thiourea-containing pesticides by pulse voltammetric methods of analysis. Anal. Chem. 49, (1977), 2310-2314

Appendix

Method print for the polarographic determination of thiourea (method 1)

```
   Thioharnstoff ppm-Bereich                          METHOD 18  PAGE 3
   MPL 1          EL.TYPE MME                         OPERATION SEQUENCE

   OPERATIONS/PARAMETERS
1  STIR  ;PURGE ;          300  s
2  0PURGE;0STIR ;
3  CADDL ;
4  STIR  ;PURGE ;          60  s
5  0STIR ;0PURGE;          5  s
6  DME   ;MEAS  ;          5  s
6a    M.MODE       DPN     50  mV
6b    T.STEP                1.0 s
6c    U.SET                -450  mV
7  SWP 0 ;                 37  s
7a    U.END                -150  mV
7b    U.STEP                8  mV
      SW.RATE               8.0 mV/  s
8  0MEAS ;ADD1)2;          5  s
9  BEEP  ;END   ;
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Method print for the stripping voltammetric determination of thiourea (method 2)

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   Thioharnstoff ppb-Bereich                          METHOD 30  PAGE 3
   MPL 1          EL.TYPE MME                         OPERATION SEQUENCE

   OPERATIONS/PARAMETERS
1  STIR  ;PURGE ;          300  s
2  BEEP  ;HOLD  ;
3  (REP  ;
4  PURGE ;STIR  ;          30  s
5  0PURGE;                 10  s
6  HMDE  ;MEAS  ;          120  s
6a    M.MODE       DPN    -50  mV
6b    T.STEP                1.0 s
6c    U.SET                -200  mV
7  0STIR ;                 30  s
8  MEAS  ;
8a    M.MODE       DPN    -50  mV
8b    T.STEP                1.0 s
8c    U.SET                -500  mV
9  SWP 0 ;                 50  s
9a    U.END                -900  mV
9b    U.STEP                8  mV

   OPERATIONS/PARAMETERS
      SW.RATE               8.0 mV/  s
10 0MEAS ;REP) 2;
11 BEEP  ;END   ;
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