Metrohm

Application Bulletin 207/3 e

Determination of silver by anodic stripping voltammetry at the carbon RDE

Summary

This Application Bulletin describes the stripping analysis of Ag at the rotating disk electrode (RDE) with glassy carbon tip (GC) or Ultra Trace graphite tip. In routine operation, the determination limit lies around 10 µg/L Ag, with careful work 5 µg/L Ag. After appropriate digestion, the silver determination is also possible with samples containing a relatively high proportion of organic substances (e.g. wine, foodstuffs etc.). The method has been developed primarily for water samples (well, ground and waste water, desilvering solutions of the photographic industry).

Instruments

VA instrument capable of operating a rotating disk electrode and supporting differential pulse (DP) measuring mode

Electrodes

WE	Glassy carbon electrode tip or Ultra Trace electrode tip Driving axle for RDE	6.1204.600 6.1204.180 6.1204.x10
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	Glassy Carbon rod Electrode holder	6.1247.000 6.1241.x20

Reagents

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

- Ethylenediaminetetraacetic acid disodium salt dihydrate, $Na_2EDTA \cdot 2H_2O$, for analysis, CAS 6381-92-6
- Potassium nitrate, for trace analysis*, CAS 7757-79-1
- Nitric acid, for trace analysis*, $w(HNO_3)$ = 65%, CAS 7697-37-2
- Ag stock solution, $\beta(Ag^+)$ = 1 g/L (commercially available)
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

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

Solutions

Na_2EDTA solution	$c(Na_2EDTA)$ = 0.2 mol/L in ultrapure water
Supporting electrolyte	$c(KNO_3)$ = 0.2 mol/L c(EDTA) = 0.004 mol/L Dissolve 20.2 g KNO_3 in high purity water. Add 20 mL $c(Na_2EDTA)$ = 0.2 mol/L and fill up to 1 L.

Standard solutions

Ag standard solution	$\beta(Ag)$ = 10 mg/L Diluted standard solutions are prepared by diluting with $c(HNO_3)$ = 0.1 mol/L.

Sample preparation

As traces of organic substances can also influence the silver determination, so-called pure waters must also be digested.

Digestion with the 909 UV Digester

Water with a slight to medium contamination with organic matter can be digested using the 909 UV Digester.

Add 50 µL hydrogen peroxide solution $w(H_2O_2)$ = 30% to 10 mL acidified water sample (pH = 2) and irradiate for 90 minutes at 90 °C. Allow to cool and transfer directly into the polarographic vessel.

Wet digestion with nitric acid/perchloric acid

Suitable for waters with a relatively high organic content.

Pipette 25 mL sample solution into a beaker and add 2 mL each of HNO_3 and $HClO_4$. The beaker is covered with a watch glass and carefully warmed. After 3 min, the solution is heated to boiling and evaporated until $HClO_4$ vapour appears. Continue heating until ca. 0.5 mL is left. Never evaporate to dryness!

After cooling, rinse the residue into a 25 mL volumetric flask with high purity water and fill up to the mark.

Digestion of photographic waste waters and desilvering solutions

Pipette 25 mL sample into a quartz dish and add 0.25 g sodium thiosulfate. Heat the solution to dryness at 120 °C in a drying oven. Then calcine the residue in a muffle furnace at 650 °C for 2h. After cooling, add 5 mL HNO_3 and 1 mL H_2SO_4 together with two glass beads. Heat until sulphuric acid vapour evolves, then cool. After a further addition of 5 mL HNO_3, the solution is heated again and evaporated almost to dryness. After cooling, add 25 mL high purity water and boil for 1 min. After cooling, add 0.4 mL of the EDTA solution c(Na_2EDTA) = 0.2 mol/L and adjust the pH value to 5.5 - 6.5 with w(NaOH) = 30%. Rinse the solution into a 50 mL volumetric flask with high purity water and fill up to the mark.

Analysis

Electrode pretreatment

- After a lengthy period of non-use or in daily routine operation before the first analysis, the glassy carbon electrode is mechanically cleaned with the polishing set and humidified aluminium oxide powder, then rinsed thoroughly with water and wiped with a soft cloth (Kleenex). The electrode is conditioned for 10 minutes in the polarographic measuring stand in HNO_3 (1:1) and rinsed again thoroughly with water.
- If the Ultra-Trace Electrode has not been used for a longer period or has been contaminated, it is cleaned off with a special trimming tool. Mount the electrode in the stand, turn on the stirrer and, putting slight pressure on the electrode tip, guide the tool back and forth. Rinse well with water afterwards and condition with HNO_3 1:1.
- An additional electrolytical cleaning is included in the program.

Measuring solution

10 mL diluted sodium hydroxide solution

(purge for 5 min with nitrogen)

10 mL (diluted) sample

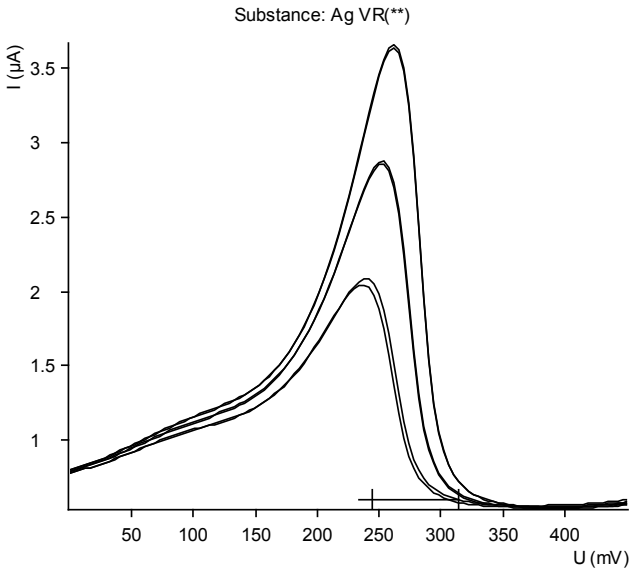
(mix while stirring without nitrogen)

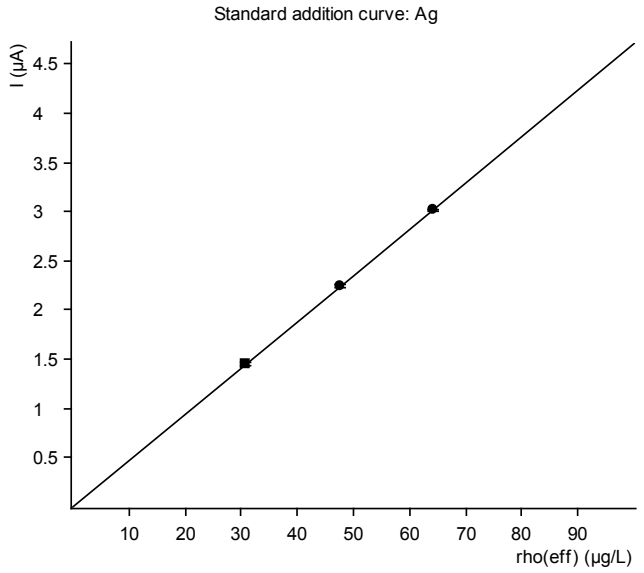
The concentration is determined by standard addition.

Parameters

Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	0.45 V
Waiting time 1	60 s
Potential 2	-0.4 V
Waiting time 2	120 s
Equilibration time	5 s
Sweep	
Start potential	0.0 V
End potential	0.45 V
Potential step	0.004 V
Potential step time	0.1 s
Sweep rate	0.04 V/s
Pulse amplitude	0.05 V
Substance	
Name	Ag
Characteristic potential	0.25 V

Example





Result

Sample	Ammonium thiosulfate
Sample size	2.0 mL
β(Ag)	2.3 mg/L

Comments

- With up to approx. 2.5 µg Ag in the polarographic vessel the standard addition curve is linear. Above this, non-linearity (flattering) of the curve appears owing to overloading of the electrode.
- All glassware and accessories that come into contact with the solutions must be cleaned for at least 2 h with HNO_3 1:1 and then rinsed thoroughly with high purity water.
- In the digestion of photographic waste waters, it is essential to add thiosulfate, otherwise silver will be lost.
- The peaks are very asymmetrical. It is important to set the foot point of the baseline at the rear side of the peak (rear half) and to evaluate with a slope = 0.

References

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Appendix

Report for the example determination of Ag in ammonium thiosulfate

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0100) ==================
 Determ.     :  06111406           User:                      Date:  98-06-11
 Modified    :  98-06-11 14:07:27   Run :  7                  Time:  14:06:55
 Sample table:  -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        (NH4)2S2O3                                                      2 mL
--------------------------------------------------------------------------------
 Method  :  AB207_Ag
 Title   :  Determination of Ag in (NH4)2S2O3 with RDE
 Remark1 :  UTGE
 Remark2 :  2 mL sample diluted to 50 mL, 5 mL used for determination
--------------------------------------------------------------------------------

  Substance : Ag                                                 Comments
  Mass conc.:    92.61 ug/L            Mass     :   463 ng   ----------------
  MC.dev.   :     1.82 ug/L (1.96%)    Add.mass :   250 ng
  Cal.dev.  :    -                     V0.sample:     5 mL

              VR   U/mV    I/uA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ----------------
              00   244     1.468   1.452   0.0233
              01   242     1.435
              10   257     2.249   2.242   0.0102   0.7906
              11   256     2.235
              20   265     3.013   3.005   0.0113   0.7631
              21   265     2.997

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Ag           std.add.     1.453e-06       0.04708                 1.784e-08


Final results                        +/- Res.dev.   %      Comments
 ---------------------------------     ----------------     ----------------
         Ag =   2.3151 mg/L              0.045    1.96
```

Method print for the determination of Ag

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB207   .mth         OPERATION SEQUENCE
 Title : Determination of Ag with RDE
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    DOS>M               Soln.name   KNO3EDTA      V.add        10.000 mL
 2    SMPL>M              V.fraction          mL    V.total             mL
 3    PURGE
 4    STIR          300.0  Rot.speed      2000 /min
 5    (ADD
 6      PURGE
 7      STIR        30.0   Rot.speed      2000 /min
 8      (REP
 9        SEGMENT          Segm.name   Silver
10      REP)1
11      ADD>M              Soln.name   std-Ag        V.add         0.025 mL
12    ADD)2
13    END


 Method: AB207                SEGMENT
                                Silver
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------ -----  ------------------------  ------------------------
 1    0PURGE
 2    RDE            5.0   Rot.speed      2000 /min
 3    DPMODE               U.ampl           50 mV    t.meas         20.0 ms
                           t.step         0.10 s     t.pulse        40.0 ms
 4    MEAS          120.0  U.meas         -400 mV
 5    0STIR
 6    MEAS           5.0   U.meas            0 mV
 7    SWEEP         11.6   U.start           0 mV    U.step            4 mV
                           U.end           450 mV    Sweep rate       40 mV/s
 8    PURGE
```

```
 9    RDE                  Rot.speed      2000 /min
10    MEAS          60.0   U.meas          450 mV
11    0MEAS                U.standby           mV
12    END
```

```
  Method: AB207                    SUBSTANCES
                                Ag       - Silver
-------------------------------------------------------------------------------

      Recognition                                Display / Plot
      -------------------------                  --------------------------
      U.verify           250 mV                  I.scale       auto
      U.tol (+/-)         50 mV                  U.div          50.00 mV/cm
      U.width min         10 mV                  U.begin              mV
      U.width max        200 mV                  U.end                mV
      I.threshold        200 pA


      Baseline                                   Evaluation
      -------------------------                  --------------------------
      Type           linear                      Mode          VA
      Scope          r.half                      Quantity      I.peak
      dU.front       auto                        Sign. digits     4
       S.front       auto
      dU.rear        auto
       S.rear          0.000


  Calibration   1998-06-11 14:32:03              Coefficients
  ---------------------------------              -------------------------
  Technique     std.add.                         Y.reg         1.453e-06
  Curve type    linear                           Slope           0.04708
                                                 Nonlin.
                                                 Mean dev.     1.784e-08

                Additions
                ------------------------------------------------------------
  Soln.name       std-Ag
  ----------
  Mass conc.         10 mg/L            g/L             g/L             g/L
  Range min              g/L            g/L             g/L             g/L
  Range max              g/L            g/L             g/L             g/L
  M.conc./cm             g/L            g/L             g/L             g/L


 Method: AB207                 CALCULATION
                              max. 15 lines
-------------------------------------------------------------------------------

 Quantity        Formula (R##, C##, A##)                   Res.unit   Sig.dig.
 ------------    ---------------------------------------   --------   --------
 Ag              R1000=MC:Ag                               #g/L          5
```