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# Application Bulletin

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Of interest to: General analytical laboratories, Waters, Metals,  
Foodstuffs, Photographic industry

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## Analysis of silver by stripping voltammetry

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### 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).

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### Apparatus and accessories

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

#### Electrodes

- Working electrode (WE)
  - Driving axle for RDE 6.1246.000
  - GC Tip 6.1204.110
  - or Ultra Trace Tip 6.1204.100
- Reference Electrode (RE)
  - Ag/AgCl Reference system 6.0728.020
  - Electrolyte vessel 6.1245.010
  - with outer electrolyte  $c(\text{KNO}_3) = 3 \text{ mol/L}$
- Auxiliary electrode (AE)
  - Electrode holder 6.1241.020
  - Glassy carbon tip 6.1247.000
- Stopper for MME 6.2709.040
- Polishing set 6.2802.000
- Trim tool 6.2827.000
- (only for Ultra Trace electrode)
- Measuring vessel 6.1415.210

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## Reagents

The reagents should be of the highest analytical quality (suprapur). Only high purity water should be used for the preparation of the solutions.

- Ethylenediaminetetraacetic acid disodium salt dihydrate, puriss.p.a., CAS 6381-92-6
- Potassium nitrate, suprapur, CAS 7757-79-1
- Nitric acid, suprapur,  $w(\text{HNO}_3) = 65\%$
- Ag stock solution,  $\beta(\text{Ag}^+) = 1 \text{ g/L}$  (commercially available)

### Ready-to-use solutions

- $c(\text{Na}_2\text{EDTA}) = 0.2 \text{ mol/L}$  in high purity water
- Supporting electrolyte:  $c(\text{KNO}_3) = 0.2 \text{ mol/L}$ ,  $c(\text{EDTA}) = 0.004 \text{ mol/L}$   
Dissolve 20.2 g  $\text{KNO}_3$  in high purity water. Add 20 mL  $c(\text{Na}_2\text{EDTA}) = 0.2 \text{ mol/L}$  and fill up to 1 L.
- Ag standard solution:  $\beta(\text{Ag}) = 10 \text{ mg/L}$   
More diluted standard solutions are prepared by diluting with  $c(\text{HNO}_3) = 0.1 \text{ mol/L}$ .

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## Electrode treatment

- 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 alox powder, then rinsed thoroughly with water and wiped with a soft cloth (Kleenex). The electrode is conditioned for 10 minutes in the polarographic stand in  $\text{HNO}_3$  (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  $\text{HNO}_3$  1:1.
- An additional electrolytical cleaning is included in the program.

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## Sample preparation

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

### Digestion with the 705 UV Digester

Water with a slight to medium contamination with organic matter can be digested using the UV Digester 705.

Add 50  $\mu\text{L}$  hydrogen peroxide solution  $w(\text{H}_2\text{O}_2) = 30\%$  to 10 mL acidified water sample ( $\text{pH} = 2$ ) and irradiate for 60 minutes at  $90^\circ\text{C}$ . 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  $\text{HNO}_3$  and  $\text{HClO}_4$ . The beaker is covered with a watch glass and carefully warmed. After 3 min, the solution is heated to boiling and evaporated until  $\text{HClO}_4$  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 thiosulphate. 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<sub>3</sub> and 1 mL H<sub>2</sub>SO<sub>4</sub> together with two glass beads. Heat until sulphuric acid vapour evolves, then cool. After a further addition of 5 mL HNO<sub>3</sub>, 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<sub>2</sub>EDTA) = 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

#### Measuring solution:

5 mL (diluted) sample  
+ 10 mL supporting electrolyte

The voltammogram is recorded with the following parameters:

Working electrode	RDE
Stirrer/RDE	2000
Measurement mode	DP
Purge time	300 s
Pulse amplitude	50 mV
Cleaning potential	0.45 V
Cleaning time	60 s
Deposition potential	-0.4 V
Deposition time	120 s
Equilibration time	5 s
Start potential	0 V
End potential	0.45 V
Voltage step	4 mV
Voltage step time	0.1 s
Sweep rate	40 mV/s
Peak potential (Ag)	0.25 V

The concentration is determined by standard addition.

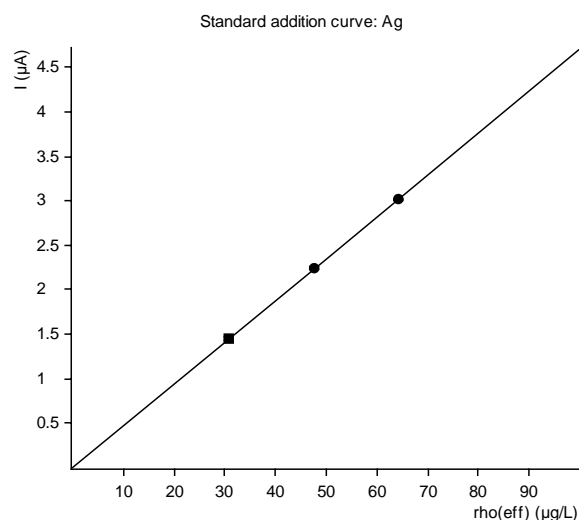
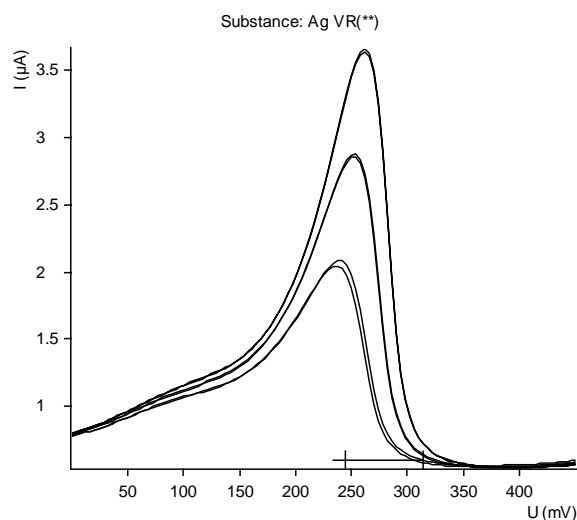
### Remarks

- 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<sub>3</sub> 1:1 and then rinsed thoroughly with high purity water.
- In the digestion of photographic waste waters, it is essential to add thiosulphate, 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.

## Literature

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Determination of trace amounts of silver with a chemically - modified carbon paste electrode.  
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Voltammétrie de l'argent par redissolution du carbon vitreux et application au dosage de l'argent dans l'uranium et le plutonium.  
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The application of stripping analysis to the determination of silver using graphite electrodes  
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## Figures



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===== 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: -
    
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Pos.  Ident.1/S1  Ident.2/S2  Ident.3/S3  Method.call  Sample size/S0
      (NH4)2S2O3
-----
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
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Substance : Ag
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
Comments  : -----
    
```

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

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Final results
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Ag = 2.3151 mg/L          +/- Res.dev.  %      Comments
                          0.045  1.96
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**Fig. 1** Stripping voltammetric analysis of silver at the Ultra Trace RDE Result report and curves at the 746 VA Trace Analyzer

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB207 .mth          OPERATION SEQUENCE
Title : Determination of Ag with RDE
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	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	OPURGE					
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	OSTIR					
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	OMEAS		U.standby	mV		
12	END					

Method: AB207

 SUBSTANCES  
Ag - Silver

## Recognition

U.verify	250 mV
U.tol (+/-)	50 mV
U.width min	10 mV
U.width max	200 mV
I.threshold	200 pA

## Display / Plot

I.scale	auto
U.div	50.00 mV/cm
U.begin	mV
U.end	mV

## Baseline

Type	linear
Scope	r.half
dU.front	auto
S.front	auto
dU.rear	auto
S.rear	0.000

## Evaluation

Mode	VA
Quantity	I.peak
Sign. digits	4

Calibration 1998-06-11 14:32:03

 Technique std.add.  
Curve type linear

## Coefficients

Y.reg	1.453e-06
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

**Fig. 2** Stripping voltammetric analysis of silver at the Ultra Trace RDE Method at the 746 VA Trace Analyzer