

Application Bulletin



Of interest for:
General laboratories
Environment protection, toxicology, food analysis

No. 96/4 e
B 1 2 4 7 9

Stripping voltammetry analysis of mercury

<p>Summary</p>	<ul style="list-style-type: none"> ▶ This Bulletin describes the stripping voltammetry analysis of Hg at the rotating gold electrode (RDE-Au). The limit of detection is 1 µg/L Hg. ▶ After appropriate digestion, the Hg determination is possible even in samples with a relatively high proportion of organic substances (wastewater, foodstuffs, products such as tea, coffee, tobacco, biological fluids, pharmaceuticals). The method has been developed primarily for the investigation of water samples. ▶ UV-Photolysis with the 705 UV-digester is a method to eliminate low to moderate contents of these organic compounds, which often severely disturb the Trace Analysis.
<p>Apparatus and accessories</p>	<ul style="list-style-type: none"> ▶ 2.646.003X VA Processor with 2.647.0020 VA Stand ▶ 6.1246.000 Driving Axle for RDE and 6.1204.070 Gold tip ▶ 6.0728.000 + 6.1245.000 Reference electrode: Ag / AgCl / c(LiCl) = 3 mol/L in H₂O (internal system) // Primary solution (external system) ▶ Auxiliary electrode: 6.1247.000 Glassy Carbon with electrode holder 6.1241.020 ▶ 6.2709.040 Stopper ▶ 6.2802.010 Polishing Set
<p>Reagents</p>	<p>These should be of the highest analytical quality. Digestion chemicals are described in the corresponding section.</p> <ul style="list-style-type: none"> ▶ Ultrapure water Free from organic residues. Twice-distilled water can also be used. ▶ Primary solution NaCl (0.351 g) and 1.50 g Na₂H₂EDTA · 2H₂O are dissolved in 500 mL ultrapure water. After addition of 22 mL 60% HClO₄ (or 18.8 mL 70% HClO₄), the solution is made up to 1 L with ultrapure water. This solution is stable for about 1 week. ▶ Hg standard, stock solution Commercial Hg standard solution in c(HNO₃) = 2 mol/L containing 1000 mg/L Hg(II) or: 1.078 g HgO are dissolved in 10 mL conc. HNO₃ and the solution made up to 1 L with ultrapure water. ▶ Hg standard, working solution Prepared daily from the stock solution. It contains 1 mg/L Hg(II) in c(HNO₃) = 0.01 mol/L.
<p>Pretreatment of the gold electrode</p>	<ul style="list-style-type: none"> ▶ Before first-time use or if not used for a lengthy period, but also if the electrode has been contaminated with relatively large amounts of Ag, Hg or Se, its surface must be regenerated or reactivated as follows: With the 646/647 "stirring speed" set at 5, the surface is polished for at least 60 s using the polishing kit and moistened aluminum oxide powder. The polishing process is repeated, again for 60 s, but this time with just the polishing cloth and ultrapure water without aluminum oxide. The electrode is then rinsed thoroughly with ultrapure water. ▶ To reactivate the surface, 10 mL primary solution and 10 mL ultrapure water are added to a polarographic vessel and deaeration performed with nitrogen for 5 min. The reactivation program (<i>Fig. 1</i>) is now run. On its completion, the polarographic vessel is removed and the electrode and vessel rinsed with ultrapure water.
<p>Method</p>	<ul style="list-style-type: none"> ▶ Primary solution (10 mL) and 10 mL ultrapure water are pipetted into the polarographic vessel. After deaeration, the reactivation program (<i>Fig. 1</i>) is run. When this is complete, the electrode and the vessel are rinsed with ultrapure water. ▶ Sample solution (1 to 10 mL) containing maximum 400 ng Hg is now pipetted into the polarographic vessel. The volume is made up to 20 mL with primary solution, deaeration performed with nitrogen for 5 min and the program started (<i>Figs 2 and 3</i>).

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	<p>▶ Figs 4 and 5 show the mercury determination in a synthetic water sample with a content of ca. 5 ppb Hg. Two standard additions.</p>								
Linearity	<p>▶ Fig. 6 shows a standard addition curve for the mercury determination.</p> <p>▶ With up to ca. 600 ng Hg in the polarographic vessel, the curve is a straight line. Above this, non-linearity (flattening) of the curve appears owing to overloading of the electrode surface. It must thus be ensured that not more than 400 ng Hg are added with the sample to the polarographic vessel. The remaining, permissible 200 ng Hg are intended for the standard additions, and naturally these must also lie within the linear range.</p>								
Remarks	<p>▶ The electrodes and the polarographic vessel must be cleaned with HNO₃/ultrapure water 1:1 before and in between the determinations. This is best achieved by filling the polarographic vessel with this solution and then rinsing with ultrapure water.</p> <p>▶ Ultrapure water is a must! Normal, deionised water contains residual organic components from the ion exchanger that can disturb the Hg determination (baseline, peak height, peak width).</p> <p>▶ Samples that contain more than 400 ng Hg/sample mass must be appropriately diluted or less sample used.</p> <p>▶ The primary solution contains EDTA to suppress disturbing influences due to metal ions as far as possible. In some cases, an increase in the EDTA content can help to increase the size of the Hg peak and make it easier to evaluate. To avoid disturbances, the maximum excess of the following elements over Hg may be:</p> <table style="margin-left: 40px;"> <tr> <td>Pb, Cd, Bi, Mn</td> <td>1000 fold</td> </tr> <tr> <td>Cu</td> <td>250 fold</td> </tr> <tr> <td>Se</td> <td>25 fold</td> </tr> <tr> <td>Ag</td> <td>8 fold</td> </tr> </table> <p>▶ The primary solution is only stable for about 1 week. An alternative would be to take 20 mL of sample solution and add 1 mL NaCl 0.1 mol/L, 400 µL EDTA 0.1 mol/L and 200 µL HClO₄ suprapure 70 %.</p>	Pb, Cd, Bi, Mn	1000 fold	Cu	250 fold	Se	25 fold	Ag	8 fold
Pb, Cd, Bi, Mn	1000 fold								
Cu	250 fold								
Se	25 fold								
Ag	8 fold								
Digestions	<p>As mercury is a highly volatile element, appropriate attention must be paid to the digestion procedures. Only chemicals of the highest purity may be used.</p> <p>▶ Open digestions with H₂SO₄/HNO₃ or H₂O₂ To avoid evaporation of Hg, some thiourea is added to the sample. It forms the practically insoluble HgS, which is not destroyed until the end of the digestion. Never evaporate to dryness!</p> <p>▶ Closed digestions The best method has proved to be the microwave digestion with nitric acid/perchloric acid or sulphuric acid/nitric acid. This digestion needs an aftertreatment with UV. Digestions under pressure can also be used, some of which also require UV aftertreatment.</p> <p>▶ UV digestion with the 705 UV Digester This is used primarily for waters containing slight amounts of organic impurities and for aftertreatment of the above-mentioned digestions. But it can also be employed for the digestion of clear beverages and filtered wastewaters containing no suspended matter after appropriate dilution (1:10). The 705 UV Digester allows the simultaneous digestion of 12 samples. Sample (10 mL) (with wine, e.g. 1 mL sample + 10 mL ultrapure water) and 50 µL 30% H₂O₂ are added to the digestion vessels. The cover is put on and digestion performed for 30 ... 200 min (typically 60 min), depending on the organic fraction. (The samples should be acidified for the digestion, pH = 1 ... 2, preferably with HCl.) The digestion samples can be transferred directly to the polarographic vessel.</p>								

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Literature

- ▶ Sipos, L. / Golimowski, J. / Valenta, P. / Nürnberg, H.W.
New voltammetric procedure for the simultaneous determination of copper and mercury in environmental samples.
Fresenius, Z. Anal. Chem. 298 (1979) 1–8
- ▶ Kapel, M. / Komaitis, M.E.
Polarographic determination of trace elements in food from a single digest.
Analyst 104 (1979) 124–135
- ▶ Nürnberg, H.W. / Valenta, P. / Sipos, L. / Branica, M.
The reliable determination of mercury traces in sea water by subtractive differential pulse voltammetry at the twin gold electrode.
Anal. Chim. Acta 115 (1980) 25–42
- ▶ Ahmed, R. / Valenta, P. / Nürnberg, H. W.
Voltammetric determination of mercury levels in tuna fish.
Mikrochim. Acta (1981) 171–184
- ▶ Ireland-Ripert, J. / Bermond, A. / Ducauze, C.
Determination of methylmercury in the presence of inorganic mercury by anodic stripping voltammetry.
Anal. Chim. Acta 143 (1982) 249–254
- ▶ Golimowski, J. / Gustavsson, I.
Determination of mercury in fish using differential pulse anodic stripping voltammetry.
Fresenius, Z. Anal. Chem. 317 (1984) 481
- ▶ Leu, M. / Seiler, H.
AC-2 Invers-voltammetrische Bestimmung von Quecksilber in Harn.
Fresenius, Z. Anal. Chem. 321 (1985) 479–482 (in German)
- ▶ Seritti, A. / Morelli, E. / Orsini, F. / Nannicini, L.
Heavy metals in seawater in front of chlor-alkali plant.
Marine Pollution Bulletin 18/8 (1987) 461–463

Fig. 1 Operation Sequence and segment on the 693 for the electrode activation

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===== METROHM 693 VA PROCESSOR (5.693.0021) =====
Method: AB96_2 .mth OPERATION SEQUENCE
Title : Preparation of Au-Electrode for Hg-Determ. AB96
  
```

	Instructions	t/s	Main parameters	Auxiliary parameters
1	DOS/M		V.added	21.600 mL
2	REM		20 mL H2O, 1 mL NaCl, 400 uL EDTA, 200 uL HClO4	
3	PURGE			
4	STIR	90.0	Rot. speed	2000 /min
5	ØPURGE			
6	<REP			
7	SEGMENT		Segm. name	Au_Prep
8	SEGMENT		Segm. name	Au_Prep
9	REP>8			
10	ØMEAS			
11	BEEP			
12	END			

```

Method: AB96_2 SEGMENT
Au_Prep
  
```

	Instructions	t/s	Main parameters	Auxiliary parameters
1	<REP			
2	RDE		Rot. speed	2000 /min
3	DCTMODE		t. step	0.10 s
4	MEAS	10.0	U. meas	0 mV
5	MEAS	30.0	U. meas	1500 mV
6	REP>8			
7	END			

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Fig. 4 Curves of the mercury determination 693 VA Processor

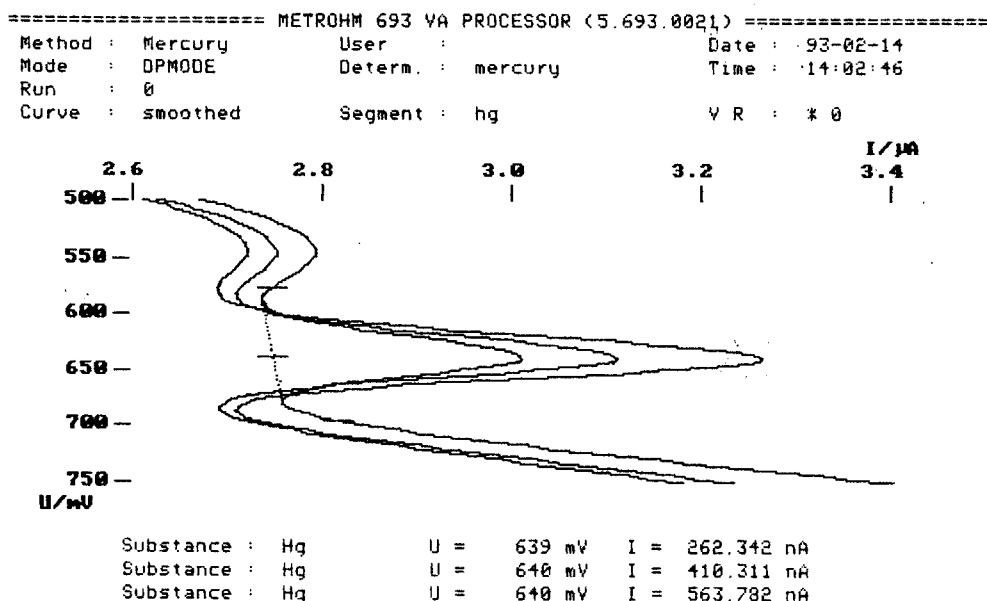


Fig. 5 Full report

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===== METROHM 693 VA PROCESSOR (5.693.0021) =====
Determ. : mercury      User      :      Date : 93-02-14
Modified : 93-04-10 09:56:17 Run : 0      Time  : 14:02:46
Sample table: -
    
```

Pos.	Ident.1/S1	Ident.2/S2	Ident.3/S3	Method.call	Sample size/S0
	NaOH-1mol/L	pH 1.3			500 µL

```

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Method : Mercury
Title  : Determination of Mercury in Sodium Hydroxyde
Remark1 : Determination of Mercury
Remark2 :
    
```

Substance	Mass conc.	MC.dev.	Cal.dev.	Mass	Add.mass	V0.sample	Comments
Hg	34.16 µg/L	0.699 µg/L (2.05%)	-	17.08 ng	10 ng	500 µL	

VR	U/mV	I/nA	I.mean	Std.dev.	1.delta	Comments
00	639	262.3	261.9	0.6835		
01	639	261.4				
10	640	410.3	415.2	6.916	153.3	
11	639	+20.1				
20	640	563.8	567.9	5.849	152.7	
21	640	572.1				

Substance	Techn.	Y.reg/offset	Slope	Nonlin.	Std.add.mass
Hg	std.add.	2.619e-07	0.3+04		10 ng

SOLUTIONS
max. +0

Soln.name	Pos.	Std.subst.	Mass conc.	Remark
SeIsol	Do.1	Sele	0.010 g/L	from: Sele
Mo-std	-	Mo	100 µg/L	from: Mo
PbStd	-	Pb	1 g/L	from: Pb

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Fig. 6 Standard addition calibration curve 693 VA Processor

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===== METROHM 693 VA PROCESSOR (5.693.0021) =====
Method : Mercury      User      :                               Date : 93-02-14
Mode   : DPMODE      Determ. : mercury          Time : 14:02:46
Run    : 0           Sample   : NaOH-1mol/L
  
```

```

Standard addition curve
Curve type : lin      Slope   : 3.404e-01   Mean.dev. : 3.534e-09
Mode       : const    Y.reg   : 2.619e-07
  
```

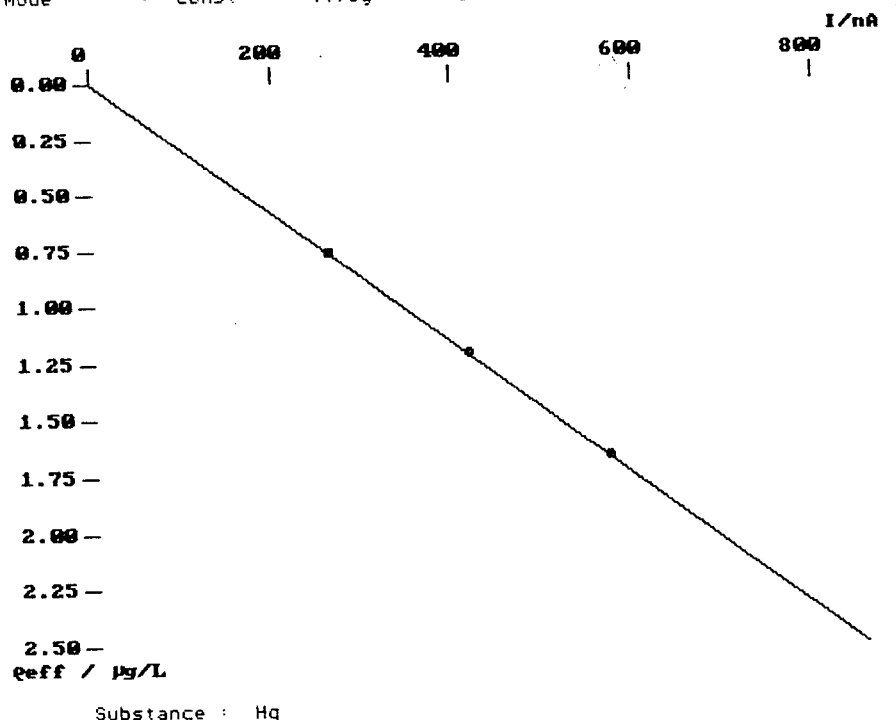


Fig. 7 Program page 3, 646 VA Processor. Electrode activation

Gold RDE - Surface Preparation Procedure
MPL 1 EL.TYPE RDE

METHOD 4 PAGE 3
OPERATION SEQUENCE

```

OPERATIONS/PARAMETERS
1 PURGE ;STIR ;          10 s
2 OPURGE;                5 s
3 <CYC ;
4 RDE ;
5 MEAS ;                 10 s
5a M.MODE                DCT
5b T.STEP                 800 ms
5c U.SET                  0.000 V
6 MEAS ;                 30 s
6a M.MODE                DCT
6b T.STEP                 800 ms
6c U.SET                  1.500 V
7 CYC> 0;
8 OMEAS ;
9 BEEP ;END ;
  
```

OPERATIONS/PARAMETERS

Stripping voltammetry analysis of mercury

Fig. 8 Program page 2, 646 VA Processor

1	Gold RDE - Surface Preparation Procedure	METHOD 4 PAGE 2
2	MPL 1 EL.TYPE RDE	GEN.SPECIFICATIONS
PARAMETERS		
3	IR.MODE N	
4	SPEED 5	
5	D.SIZE 5	
6	N.DROPS 5	
RECOGNITION		
7	SPIKE THRESH 4	
8	H.THRESH 3	
9	U.TOL 7	
10	W.TOL 6	
11	ASYM.TOL 6	

Fig. 9 Program page 3, 646 VA Processor. Hg determination

	Detn. of Hg in Waters and Extracts of Solids	METHOD 3 PAGE 3
	MPL 1 EL.TYPE RDE	OPERATION SEQUENCE
OPERATIONS/PARAMETERS		
1	PURGE ;STIR ; 5 s	9c U.SET 370 mV
2	[ADDL ;OPURGE; 5 s	10 OSTIR ; 10 s
3	RDE ;	11 MEAS ; 10 s
4	MEAS ;	11a M.MODE DPN 50 mV
4a	M.MODE DPN 50 mV	11b T.STEP 800 ms
4b	T.STEP 800 ms	11c U.SET 500 mV
4c	U.SET 200 mV	12 SWP 0 ; 68 s
5	DSWP ; 104 s	12a U.END 840 mV
5a	U.END 1.500 V	12b U.STEP 4 mV
5b	U.STEP 10 mV	SW.RATE 5.0 mV/ s
	SW.RATE 12.5 mV/ s	13 STIR ;
6	OMEAS ;	14 MEAS ; 30 s
7	STIR ;PURGE ; 30 s	14a M.MODE DPN 50 mV
8	OPURGE;	14b T.STEP 800 ms
9	MEAS ; 120 s	14c U.SET 1.500 V
9a	M.MODE DPN 50 mV	15 OMEAS ;PURGE ;STIR ;
9b	T.STEP 800 ms	16 BEEP ;ADD1]2; 30 s
Detn. of Hg in Waters and Extracts of Solids		
	MPL 1 EL.TYPE RDE	METHOD 3 PAGE 3
		OPERATION SEQUENCE
OPERATIONS/PARAMETERS		
17	OMEAS ;OPURGE;OSTIR ;	
18	BEEP ;END ;	

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Fig. 10 Program page 4, 646 VA Processor

Detn. of Hg in Waters and Extracts of Solids				METHOD 3 PAGE 4	
MPL 1	EL.TYPE RDE			ALLOCATIONS	
a	b	c	d	e	f
SOLUTE	U.VERIF	DOS	V.SOLN	m.CONC	m.BLANK
Subst	Ux	SoIn	c, v	rho.x	bx
1 Hg	660 mV	1	c 50 uL	1.000 mg/L	0.000 g
2					
3					
4					
5					
6					
7					
8					
9	SUPP.ELEC	NaCl/EDTA/HClO4			
10	V.MEAS	20.000 mL			
11	ALIQOT	1.000			
12	DATE	91-01-25			
13	TIME	13:04			

Fig. 11 Curves 5 ppb Hg in water sample with two standard additions

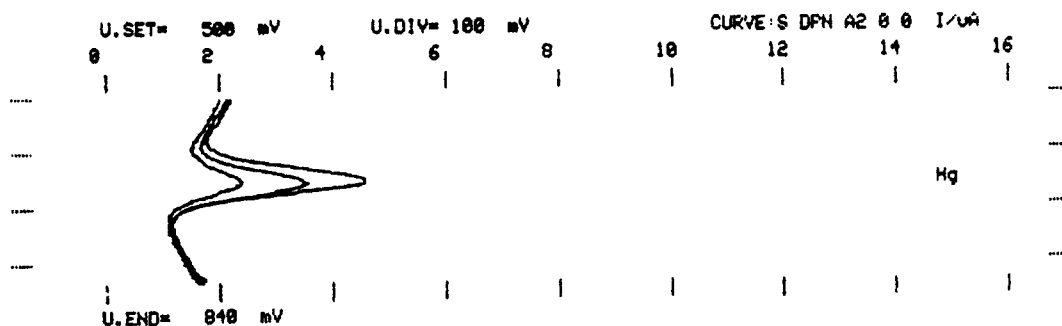


Fig. 12 Full Report of the determination from Fig. 11

METROHM 646 VA-PROCESSOR (5.646.6041)

Detn. of Hg in Waters and Extracts of Solids				METHOD 3	
MPL 1	EL.TYPE RDE				
SUPP.ELEC	NaCl/EDTA/HClO4				
V.MEAS	20.000 mL				
ALIQOT	1.000				
REMARK	Linear & LOD tests				
	Ag/AgCl (supp.elec.filled) reference electrode				
NAME	Prof.J.G.Dick				
RUN#	2				

ANALYTE	L R S	U.SUBST	EV.VALUE	DELTA	m.ANALYTE
Vit.B1	A0 0 0	654 mV	1.047 uA		
	A1 0 0	656 mV	2.081 uA	1.034 uA	
	A2 0 0	651 mV	3.083 uA	1.001 uA	
m.STD	50.00 ng	SLOPE	49.10 ng/uA		51.69 ng
rho(Hg)	=	5.16	ug/L		

SMPL.V,m 10.0000 mL IDENT 10mLSE + 10mL Sp1.2
 DATE 91-01-25 TIME 11:52