Application Bulletin

Metrohm

Of interest for:
Trace analysis, environmental analysis

No. 147/1 e

Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

Summary

The metals Cd, Co, Cu, Fe, Ni, Pb and Zn are determined in the sub-ppb range (limit of detection 0.05 µg/L) by means of stripping voltammetry. The DP-ASV method is used for Cd, Cu, Pb and Zn whereas Co, Ni and Fe are determined by means of the DP-CSV method (dimethylglyoxime or catechol complexes).

Use of the VA Processor and the sample changer allows automatic determination of the above metal ions in one solution. The method has been specially developed for trace analysis in the manufacture of semiconductor chips based on silicon. It can naturally also be employed successfully in environmental analysis.

Instruments

- VA Processor 646 with VA Stand 647 and, depending on the degree of automation required, VA Sample Changer 675 and Multi-Dosimats 665.

Reagents

All reagents used must be of at least purity grade puriss. p.a.. The solution must be prepared with ultrapure water (≤ 0.1 µS/cm 20°C).

- **Acetate buffer**
  pH = 4.6 with $c(CH_3COOH)$ = 2 mol/L and $c(NH_3)$ = 1 mol/L.

- **Ammonium chloride buffer**
  26 mL $w(HCl)$ = 0.32 and 44 mL $w(NH_3)$ = 0.25 are made up to 100 mL with ultrapure water.

- **Catechol solution:** c(Catechol) = 1 mol/L
  Catechol (5.5 g) is dissolved in 50 mL oxygen-free ultrapure water under a stream of nitrogen. The solution must be tightly stoppered and stored in the dark. The stability of the solution varies between 1 day and up to 3 weeks, depending on the purity of the catechol. (Allow to stand 1 h before use.)

- **Pipes Buffer:** c(Pipes) = 1 mol/L
  1,4-bis(2-ethanesulfonic acid) piperazine (6.047 g) is mixed with 1 mL $w(NaOH)$ = 0.3 and a little ultrapure water. After adjustment of the pH to 8.0 with $w(NH_3)$ = 0.25, the solution is made up to 20 mL with ultrapure water.

- **Dimethylglyoxime in triethanolamine**
  Dimethylglyoxime (0.5 g) is mixed with 100 mL triethanolamine/ultrapure water (1:1) over a period of 1 h using a magnetic stirrer. The insoluble components are then filtered off using a fluted filter and the clear filtrate stored in a dark bottle.

- **Standard solutions**
  Solutions weaker than ρ(Me) = 100 mg/L are stored in plastic bottles and should be prepared every week as follows: The concentrated standard solution is diluted with ultrapure water and acidified with 0.4 mL/100 mL conc. HNO_3.

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Sample preparation

- One drop $w(HF) = 0.4$ (40%) is placed on the chip and evaporated by warming. A white, powdery residue is formed. This is dissolved in a drop of conc. nitric acid and rinsed into the polarographic vessel with ultrapure water. A blank is prepared using the same reagents.

Method setup

- The first step involves simultaneous determination of the metals Zn, Pb, Cd, and Cu at pH = 5.0 according to the DP-ASV method.
- In the second step, iron is determined in the pipes buffer in the form of a catechol complex at pH = 7.0...7.2 using the DP-CSV method.
- Finally, Co and Ni are determined as their dimethylglyoxime complexes in NH_3/NH_4Cl buffer at pH = 9.1.

Determination

- Acetate buffer (50 µL) is added to the sample solution and the pH adjusted to 5.0 with $w(NH_3) = 0.1$. Duplicate determinations of Zn, Cd, Pb and Cu each with two standard additions are now performed (PAGE 3, lines 1...10).
- Catechol solution (100 µL) and pipes buffer (300 µL) are now added. Iron is also determined in a duplicate analysis with two standard additions (PAGE 3, lines 11...19). The pH value of the solution should be 7.0...7.2.
- Finally, the pH value is adjusted to 9.1...9.2 by addition of 500 µL ammonium chloride buffer. After addition of 100 µL triethanolamine/dimethylglyoxime solution, duplicate determinations of Co and Ni each with two standard additions are performed (PAGE 3, lines 20...27). A determination requires approx. 100 min when in this form.

- ***Fig. 1*** *shows the operation sequence of the method on PAGE 3.*

Zn,Cd,Pb,Cu,Fe,Ni und Co im sub-ppb-Bereich — METHOD 4 PAGE 3
MFL 1 EL.TYPE MME — OPERATION SEQUENCE

	OPERATIONS/PARAMETERS		
1	PURGE ;STIR ;CADDL ;	300	s
2	PURGE ;STIR ;	30	s
3	@PURGE;CREP ;	10	s
4	HMDE ;STIR ;MEAS ;	120	s
4a	M.MODE	DPN	
4b	T.STEP	600	ms
4c	U.SET	-1.109	V
5	@STIR ;	10	s
6	SWP 0 ;	53	s
6a	U.END	-750	mV
6b	U.STEP	4	mV
	SW.RATE	6.6	mV/ s
7	SWP 1 ;	45	s
7a	U.END	-450	mV
7b	U.STEP	4	mV
	SW.RATE	6.6	mV/ s
8	SWP 2 ;	36	s

	OPERATIONS/PARAMETERS		
8a	U.END	-210	mV
8b	U.STEP	4	mV
	SW.RATE	6.6	mV/ s
9	SWP 3 ;	61	s
9a	U.END	200	mV
9b	U.STEP	4	mV
	SW.RATE	6.6	mV/ s
10	REP) 1;BEEP ;ADDI32;		
11	BEEP ;PURGE ;STIR ;	30	s
12	HOLD ;CADDL ;		
13	PURGE ;STIR ;	30	s
14	@PURGE;CREP ;	10	s
15	HMDE ;STIR ;MEAS ;	120	s
15a	M.MODE	DPN	
15b	T.STEP	600	ms
15c	U.SET	-250	mV
16	@STIR ;	15	s

Zn,Cd,Pb,Cu,Fe,Ni und Co im sub-ppb-Bereich — METHOD 4 PAGE 3
MFL 1 EL.TYPE MME — OPERATION SEQUENCE

	OPERATIONS/PARAMETERS		
17	SWP 4 ;	60	s
17a	U.END	-650	mV
17b	U.STEP	4	mV
	SW.RATE	6.6	mV/ s
18	REP) 1;BEEP ;ADD2I32;		
19	BEEP ;PURGE ;STIR ;	30	s
20	HOLD ;CADDL ;		
21	PURGE ;STIR ;	30	s
22	@PURGE;CREP ;		
23	HMDE ;STIR ;MEAS ;	30	s
23a	M.MODE	DPN	
23b	T.STEP	600	ms
23c	U.SET	-700	mV
24	@STIR ;MEAS ;	10	s
24a	M.MODE	DPN	
24b	T.STEP	600	ms
24c	U.SET	-800	mV

	OPERATIONS/PARAMETERS		
25	SWP 5 ;	60	s
25a	U.END	-1.000	V
25b	U.STEP	2	mV
	SW.RATE	3.3	mV/ s
26	SWP 6 ;	37	s
26a	U.END	-1.250	V
26b	U.STEP	4	mV
	SW.RATE	6.6	mV/ s
27	REP) 1;BEEP ;ADD3I32;		
28	@MEAS ;BEEP ;END ;		

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Determination *(continued)*

- For automation with the sample changer, the following additional instruments are needed:

  Seven Dosimats with the solutions:

  1. Dosimat for the standard addition of Zn, Cd, Pb and Cu
  2. Dosimat for the standard addition of Fe
  3. Dosimat for the standard addition of Co and Ni
  4. Dosimat for the addition of catechol solution (brown glass)

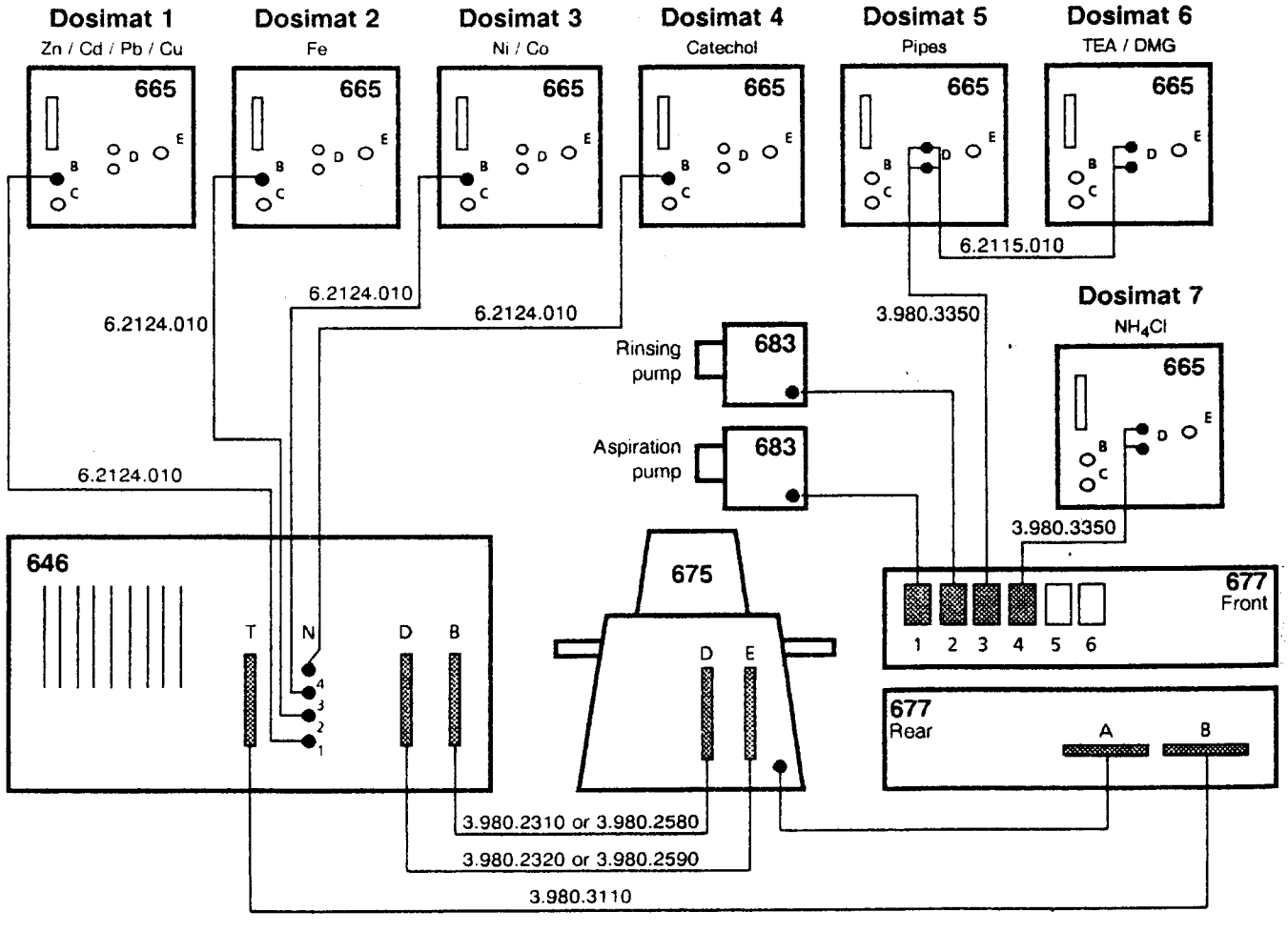
  The Dosimats 1...4 are controlled via PAGE 4 (2.665.0010).

  5. Dosimat for the addition of pipes buffer
  6. Dosimat for the addition of triethanolamine/dimethylglyoxime
  7. Dosimat for the addition of ammonium chloride buffer

  The Dosimats 5...7 (as well as the two 683 Pump Units – siphoning and rinsing polarographic vessel/electrodes) are controlled via the 677 Drive Unit. The volume to be dispensed is stored in the burette and the addition triggered by a control pulse. Two special 3.980.3350 cables and one 6.2115.010 cable are needed for the connection to the 677 Drive Unit. The ammonium chloride and triethanolamine buffer solutions are controlled via a single cable and are thus both added at the same time.

- Additionally are needed:
  - 3×6.182.010 Capillary tubing for the three auxiliary Dosimats
  - 1×A.403.009 Stopper
    (3 holes of Ø = 1.5 mm must be drilled by the customer).

Fig. 2 *Interconnection of the instruments with the cable connections*



Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

Illustrations

The following Figures provide an overview of the determination of the 7 elements using the sample changer:

Fig. 3 *PAGE 2 of the 646 VA Processors. Note particularly items 7...11.*

```
 1  Zn,Cd,Pb,Cu,Fe,Ni,Co mit Probenwechsler          METHOD  5  PAGE 2
 2  MPL 1          EL.TYPE MME                      GEN.SPECIFICATIONS

    PARAMETERS
 3  IR.MODE              N
 4  SPEED                5
 5  D.SIZE               7
 6  N.DROPS              5

    RECOGNITION
 7  SPIKE THRESH         5
 8  H.THRESH             2
 9  U.TOL                7
10  W.TOL                9
11  ASYM.TOL             8
```

Fig. 4 *PAGE 3, now completely filled for work with the sample changer (35 itetms)*

```
Zn,Cd,Pb,Cu,Fe,Ni,Co mit Probenwechsler          METHOD  5  PAGE 3
MPL 1          EL.TYPE MME                       OPERATION SEQUENCE

   OPERATIONS/PARAMETERS                          OPERATIONS/PARAMETERS
 1 PURGE ;STIR  ;CADDL ; 30  s                 8a   U.END            -210  mV
 2 PURGE ;STIR  ;        60  s                 8b   U.STEP             4  mV
 3 0PURGE;(REP  ;        10  s                      SW.RATE           6.6 mV/  s
 4 HMDE  ;STIR  ;MEAS  ; 120  s                 9 SWP 3 ;              61  s
 4a   M.MODE      DPN    50  mV                9a   U.END             200  mV
 4b   T.STEP             600  ms               9b   U.STEP              4  mV
 4c   U.SET             -1.109 V                    SW.RATE           6.6 mV/  s
 5 0STIR ;               10  s                10 REP) 1;BEEP  ;ADD1]2;
 6 SWP 0 ;               53  s                11 PURGE ;STIR  ;DOS4  ; 120  s
 6a   U.END             -750  mV               12 CTRL 3;0CTRL3;PURGE ; 60.0 s
 6b   U.STEP              4  mV               13 PURGE ;STIR  ;CADDL ; 60  s
      SW.RATE            6.6 mV/  s          14 PURGE ;STIR  ;        120  s
 7 SWP 1 ;               45  s                15 0PURGE;(REP  ;        10  s
 7a   U.END             -450  mV               16 HMDE  ;STIR  ;MEAS  ; 120  s
 7b   U.STEP              4  mV               16a   M.MODE      DPN    -50  mV
      SW.RATE            6.6 mV/  s          16b   T.STEP             600  ms
 8 SWP 2 ;               36  s                16c   U.SET              -250  mV

Zn,Cd,Pb,Cu,Fe,Ni,Co mit Probenwechsler          METHOD  5  PAGE 3
MPL 1          EL.TYPE MME                       OPERATION SEQUENCE

   OPERATIONS/PARAMETERS                          OPERATIONS/PARAMETERS
17 0STIR ;              15  s                25c   U.SET             -800  mV
18 SWP 4 ;              60  s                26 SWP 5 ;              63  s
18a   U.END            -650  mV               26a   U.END             -1.010 V
18b   U.STEP             4  mV               26b   U.STEP              2  mV
      SW.RATE            6.6 mV/  s                SW.RATE           3.3 mV/  s
19 REP) 1;BEEP  ;ADD2]2;                      27 SWP 6 ;              36  s
20 CTRL 4;0CTRL4;       20.0 s                27a   U.END             -1.250 V
21 PURGE ;STIR  ;CADDL ; 120  s               27b   U.STEP              4  mV
22 PURGE ;STIR  ;        120  s                     SW.RATE           6.6 mV/  s
23 0PURGE;(REP  ;        10  s                28 REP) 1;BEEP  ;ADD3]2;
24 HMDE  ;STIR  ;MEAS  ; 30  s                29 0MEAS ;STIR  ;CTRL 1; 12.0 s
24a   M.MODE      DPN    -30  mV               30 (REP  ;
24b   T.STEP             600  ms               31 0CTRL1;CTRL 2;       20.0 s
24c   U.SET             -700  mV               32 0CTRL2;CTRL 1;REP) 3; 40.0 s
25 0STIR ;MEAS  ;         10  s                33 0CTRL1;0STIR ;
25a   M.MODE      DPN    -30  mV               34 CHANGE;PURGE ;STIR  ;
25b   T.STEP             600  ms               35 BEEP  ;END   ;
```

Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

Illustrations (continued)

Fig. 5 *PAGE 4. Please note that minimum 80 µL are dispensed. Only burette cylinders of 1 mL and 5 mL should be employed.*

Zn,Cd,Pb,Cu,Fe,Ni,Co mit Probenwechsler — METHOD 5 PAGE 4
MPL 1 — EL.TYPE MME — ALLOCATIONS

	a SOLUTE Subst	b U.VERIF Ux	c DOS Soln	d V.SOLN c, v	e m.CONC rho.x	f m.BLANK bx
1	Zn	-998 mV	1	c 80 uL	500.0 ug/L	0.000 g
2	Cd	-560 mV	1	c 80 uL	100.0 ug/L	0.000 g
3	Pb	-340 mV	1	c 80 uL	1.000 mg/L	0.000 g
4	Cu	30 mV	1	c 80 uL	100.0 ug/L	0.000 g
5	Fe	-450 mV	2	c 100 uL	500.0 ug/L	0.000 g
6	Ni	-934 mV	3	c 100 uL	1.000 mg/L	0.000 g
7	Co	-1.100 V	3	c 100 uL	40.00 ug/L	0.000 g
8	Catech		4	c 100 uL	110.0 g/ L	0.000 g
9	SUPP.ELEC	c(HNO 3)=0.01 mol/L				
10	V.MEAS	20.000 mL				
11	ALIQUOT	1.000				
12	DATE	87-01-12				
13	TIME	11:09				

Fig. 6 *PAGE 5*

Zn,Cd,Pb,Cu,Fe,Ni,Co mit Probenwechsler — METHOD 5 PAGE 5
MPL 1 — EL.TYPE MME — DATA OUTPUT

	SEGMT	a Y.AXIS/L	b Y.AXIS/R	c X.AXIS/DIV	d	e
1	SWP 0	0.00 A	300 nA	100 mV		
2	SWP 1	0.00 A	25.0 nA	100 mV		
3	SWP 2	0.00 A	160 nA	100 mV		
4	SWP 3	0.00 A	160 nA	100 mV		
5	SWP 4	0.00 A	-160 nA	100 mV		
6	SWP 5	0.00 A	-400 nA	50.0 mV		
7	SWP 6	-6.00 nA	-20.0 nA	100 mV		
8						
9	RECORD	FR	SXXX			
10						
11	SEND					
12						

Fig. 7 *PAGE 6 with the calculation principles*

Zn,Cd,Pb,Cu,Fe,Ni,Co mit Probenwechsler — METHOD 5 PAGE 6
MPL 1 — EL.TYPE MME — RES.CALCULATION

	ANALYTE	a EVAL	b R.QUANT	c R.UNIT	d SIGNIF.DIG
1	Zn	N	rho(Zn)	ug/L	4
2	Cd	N	rho(Cd)	ug/L	4
3	Pb	N	rho(Pb)	ug/L	4
4	Cu	N	rho(Cu)	ug/L	4
5	Fe	N	rho(Fe)	ug/L	4
6	Ni	N	rho(Ni)	ug/L	4
7	Co	N	rho(Co)	ug/L	4
8					
		(EV.QUANT	+ ADDEND)	* FACTOR	/ DIVISOR
11	Zn	A	0.00000	1.00000 E+ 6	1.00000
12	Cd	A	0.00000	1.00000 E+ 6	1.00000
13	Pb	A	0.00000	1.00000 E+ 6	1.00000
14	Cu	A	0.00000	1.00000 E+ 6	1.00000
15	Fe	A	0.00000	1.00000 E+ 6	1.00000
16	Ni	A	0.00000	1.00000 E+ 6	1.00000
17	Co	A	0.00000	1.00000 E+ 6	1.00000
18					

Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

Illustrations (continued)

Fig. 8 *Result block of a blank value determination*

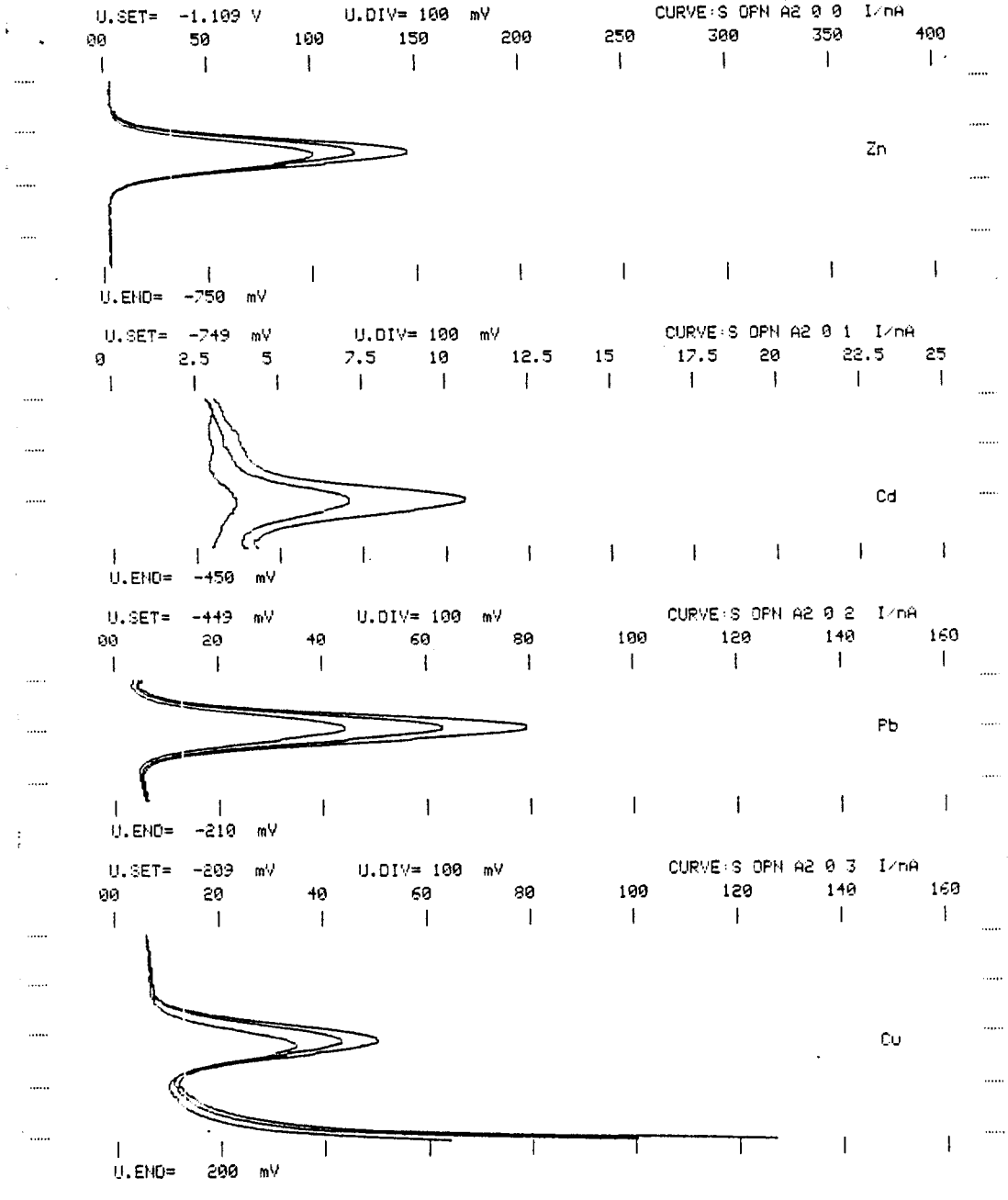
```
METROHM 646 VA-PROCESSOR  (5.646.5041)
Zn,Cd,Pb,Cu,Fe,Ni,Co mit Probenwechsler              METHOD   5
MPL  1          EL.TYPE    MME

SUPP.ELEC       c(HNO 3)=0.01 mol/L
V.MEAS           20.000 mL
ALIQUOT          1.000

REMARK          Halbleiter - Analytik
                7 Elemente in einer Methode; Blindw.HNO3 0.01m/L
NAME            Wittmann
RUN#            -1

    ANALYTE     L R S        U.SUBST      EV.VALUE     DELTA        m.ANALYTE
    Zn          A0 0 0       -962  mV     101.5 nA
                A0 1 0       -966  mV     104.4 nA
                A1 0 0       -966  mV     124.0 nA
                A1 1 0       -966  mV     124.0 nA     21.05 nA
                A2 0 0       -966  mV     150.3 nA
                A2 1 0       -966  mV     156.9 nA     29.55 nA
               m.STD    40.00 ng      SLOPE    1.580 ug/uA          160.5 ng
    Cd          A0 0 1       -551  mV   ! 792.4 pA
                A0 1 1       -544  mV   ! 816.3 pA
                A1 0 1       -545  mV     3.525 nA
                A1 1 1       -544  mV     3.525 nA     2.751 nA
                A2 0 1       -545  mV     6.649 nA
                A2 1 1       -545  mV     6.898 nA     3.213 nA
               m.STD    8.000 ng      SLOPE    2.680 ug/uA          1.947 ng
    Pb          A0 0 2       -351  mV     41.50 nA
                A0 1 2       -352  mV     43.90 nA
                A1 0 2       -351  mV     60.84 nA
                A1 1 2       -351  mV     61.67 nA     18.55 nA
                A2 0 2       -351  mV     78.20 nA
                A2 1 2       -351  mV     81.18 nA     18.43 nA
               m.STD    80.00 ng      SLOPE    4.325 ug/uA          184.8 ng
    Cu          A0 0 3        15   mV     25.33 nA
                A0 1 3        15   mV     27.07 nA
                A1 0 3       7.3   mV     35.17 nA
                A1 1 3       6.7   mV     34.64 nA     8.705 nA
                A2 0 3       6.7   mV     43.63 nA
                A2 1 3       5.9   mV     44.21 nA     9.018 nA
               m.STD    8.000 ng      SLOPE    902.7 ng/uA          23.60 ng
    Fe          A0 0 4       -451  mV     16.42 nA
                A0 1 4       -454  mV     16.51 nA
                A1 0 4       -451  mV     24.87 nA
                A1 1 4       -452  mV     24.71 nA     8.325 nA
                A2 0 4.      -445  mV     32.59 nA
                A2 1 4       -446  mV     33.53 nA     8.275 nA
               m.STD    50.00 ng      SLOPE    6.023 ug/uA          99.24 ng
    Ni          A0 0 5       -948  mV     105.3 nA
                A0 1 5       -948  mV     109.5 nA
                A1 0 5       -948  mV     114.9 nA
                A1 1 5       -948  mV     137.3 nA     18.67 nA
                A2 0 5       -947  mV     136.3 nA
                A2 1 5       -947  mV     159.7 nA     21.94 nA
               m.STD    100.0 ng      SLOPE    4.923 ug/uA          526.3 ng
    Co          A0 0 6       -1.089 V     3.047 nA
                A0 1 6       -1.089 V     3.464 nA
                A1 0 6       -1.087 V     6.766 nA
                A1 1 6       -1.087 V     8.159 nA     4.207 nA
                A2 0 6       -1.086 V     11.32 nA
                A2 1 6       -1.085 V     13.43 nA     4.916 nA
               m.STD    4.000 ng      SLOPE    876.8 ng/uA          2.751 ng
```

Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

Illustrations *(continued)*

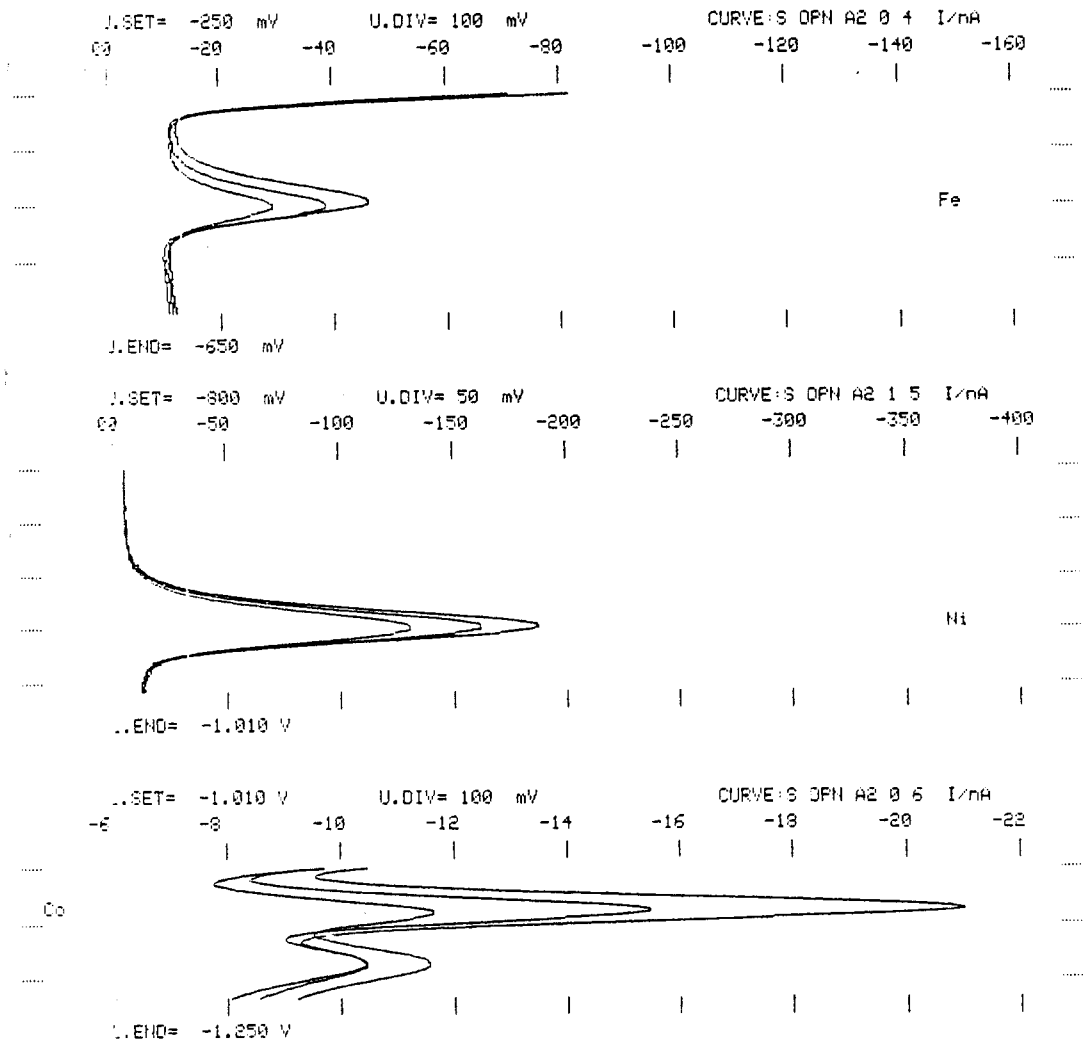
```
rho(Zn)    =    8.029        ug/L
rho(Ni)    =    -----        ug/L
rho(Co)    =    -----        ug/L
rho(Cd)    =  ! 97.36   E- 3 ug/L
rho(Fe)    =    -----        ug/L
rho(Pb)    =    9.242        ug/L
rho(Cu)    =    1.180        ug/L
rho(Cd)    =    -----        ug/L
rho(Pb)    =    -----        ug/L
rho(Fe)    =    4.362        ug/L
rho(Zn)    =    -----        ug/L
rho(Ni)    =    26.31        ug/L
rho(Co)    =    .1375        ug/L

SMPL.V.m          20.0000 mL          IDENT Test mit Probenw.
DATE  87-01-09  TIME   12:37
```

Fig. 9 *Voltammograms for the data in Figure 8*



Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

Illustrations *(continued)*



Remarks

- The electrodes and polarographic vessels are stored in $w(HNO_3) = 0.08$ (8%) and also rinsed with this solution.
- The addition of triethanolamine increases the sensitivity of the Co determination. At the same time, it suppresses possible interferences due to relatively large Zn contents. The Ni peak is somewhat attenuated.
- In the standard additions, the peak potential of the iron-catechol complex is shifted slightly. This is due to the acidic standard addition solution. With this shift, which is dependent on pH, interferences caused by relatively large amounts of Cu can also be eliminated. (Cu also forms catechol complexes with peak potentials around –250 mV. For the iron complexes, the following dependences apply: pH = 6.9 –0.40 V // pH = 7.2: –0.45 V.)
- Pipes has a limited storage life. We found that the substance had decomposed after two years in a broached reagent bottle and was thus unfit for use. Pipes itself also shows a peak which moreover lies near that of the iron-catechol complex. Since this peak is small and flat, however, it can be subtracted as a blank value on PAGE 4 (e.g. 2 ng/20 mL).
  If buffer solutions are prepared using decomposed pipes, the base peak is steep and large. The blank value is increased by a factor 10 and makes evaluation of the iron impossible (**Fig. 10 and 11**).

Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

Remarks
(continued)

Fig. 10

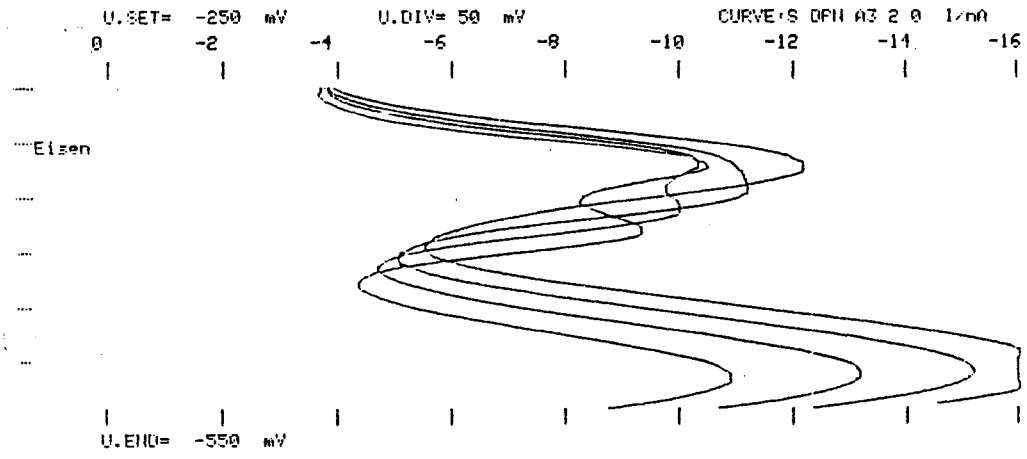
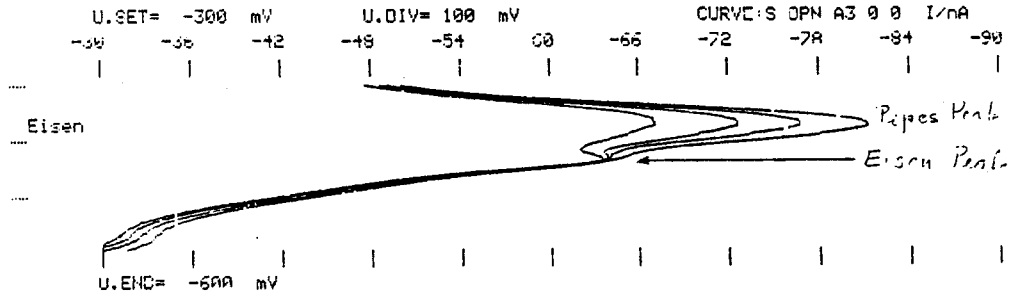
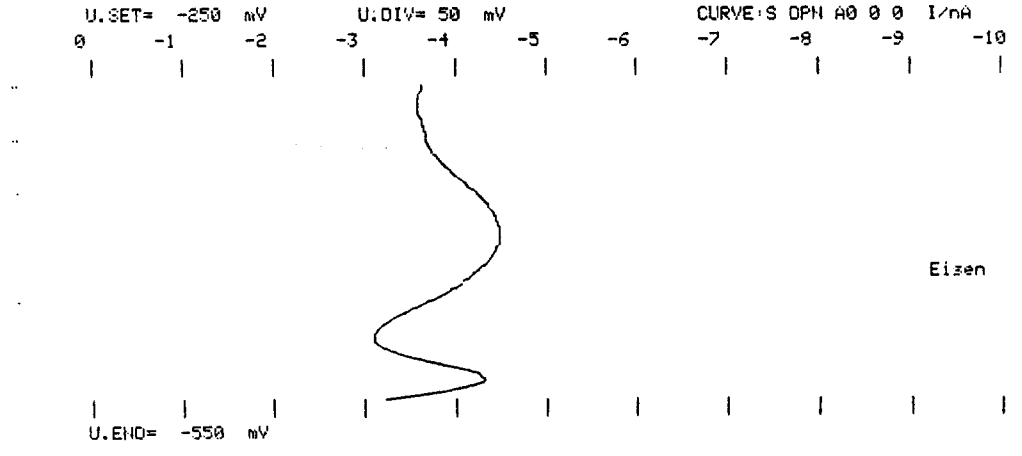


Fig. 11



- The following method can be very useful to check the quality of the pipes:
  Pipes buffer (100 µL) is added to 20 mL ultrapure water, the solution deaerated with nitrogen and a voltammogram recorded in the same manner as in the iron determination (without catechol addition). **Fig. 12** shows a good, **Fig. 13** a poor, decomposed pipes buffer.

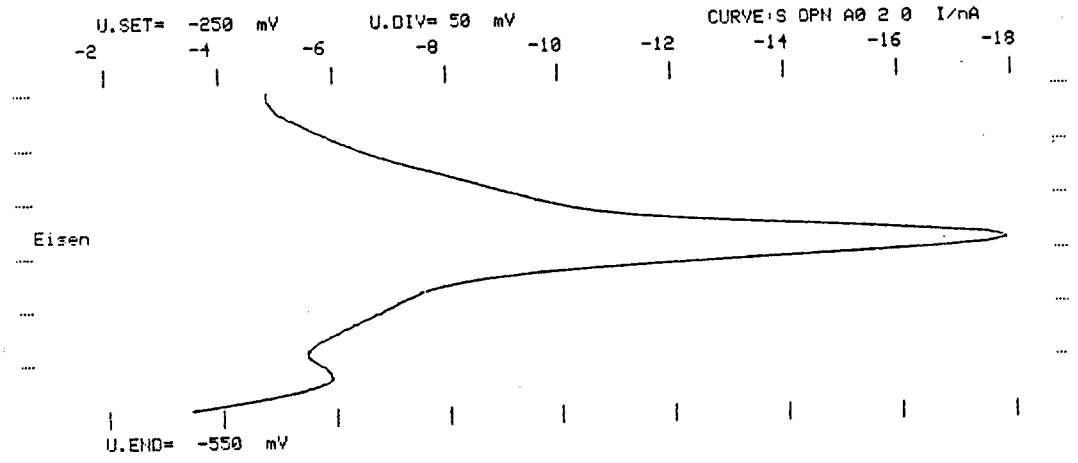
Fig. 12



Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

Remarks *(continued)*

Fig. 13

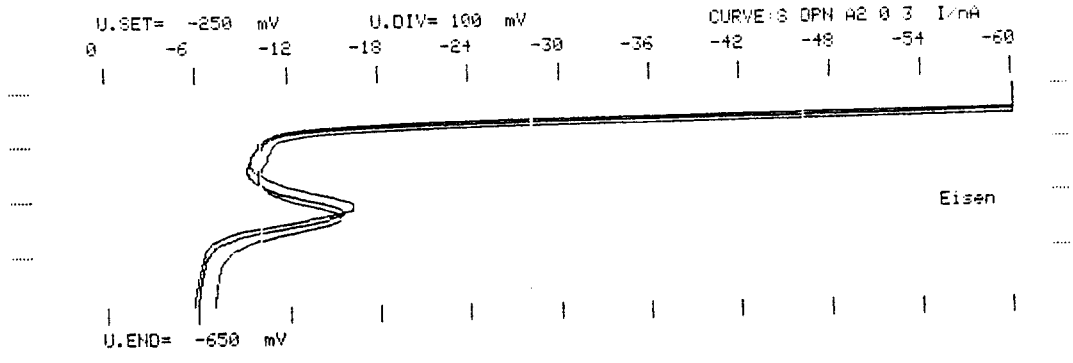


- The catechol solution should be prepared using pure, undecomposed catechol. If this solution has a brownish colour from the very start, filtration (fluted filter) is usually useful to enable the solution to be kept for 3...4 days.

  Recrystallization from hot toluene followed by vacuum drying is better. Solutions prepared from catechol purified in this manner can be stored for up to 20 days.

  Catechol solutions undergoing decomposition and which are thus unfit for use show the following behaviour: the peaks are shifted and become smaller. Furthermore, the standard additions are no longer linear and the baseline is highly distorted. **Fig. 14** shows an example of such a curve.

Fig. 14



Simultaneous trace determination of 7 metal ions in "electronic grade" materials with the aid of stripping voltammetry

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