Monograph

Voltammetric analysis methods in electroplating

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1 Introduction

The generic term voltammetry is used for an analytical procedure based on current-potential measurements in an electrochemical cell. The analytical signal evaluated is the faradaic current that flows through the cell when the analyte reacts at a working electrode (WE). Possible analytes are an anion, a cation or an electrochemically active group of a molecule. The methods used today, for example differential pulse (DP), generally yield peak-shaped current signals; the peak height being proportional to the analyte concentration within certain limits. The peak potential allows to draw qualitative conclusions.

According to the IUPAC rules, the term **polarography** is to be used whenever the current-potential curve is recorded at a liquid working electrode whose surface is periodically renewed. Examples are the classical **DME (**Dropping Mercury Electrode) and the **SMDE** (Static Mercury Drop Electrode).

The term **voltammetry** is short for «voltamperometry» (not used in English) and comprises the two terms voltametry and amperometry. Voltammetry uses stationary, often solid working electrodes. The classical working electrode for voltammetric methods is the HMDE (Hanging Mercury Drop Electrode). Solid electrode materials used are a mercury film, gold, bismuth and different types of carbon such as graphite, coal paste or glassy carbon.

To enhance the sensitivity and selectivity, so-called pulse methods are generally used, the most applied being the DP method (differential pulse).

Compared to other analytical methods, voltammetric methods have some substantial advantages:

- relatively modest purchase and maintenance costs
- high selectivity, also in complex matrices
- samples with a high salt content pose no problem
- often multi-element analysis and/or speciation are possible
- high sensitivity, low determination limits

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- Introduction to polarography and voltammetry
- Practical voltammetry

Metrohm also puts at your disposal, free of charge, a large number of **Application Bulletins** and **Application Notes.** Please find a list with a selection of these documents in the Appendix.

Meaning of acronyms used:

Acronym	Meaning
AdSV	adsorptive stripping voltammetry
ASV	anodic stripping voltammetry
CSV	cathodic stripping voltammetry
CVS	cyclic voltammetric stripping
DC	direct current
DME	dropping mercury electrode
DP	differential pulse
HMDE	hanging mercury drop electrode
SMDE	static mercury drop electrode

1.1 Instruments and accessories used

- 797 VA Computrace with 800 Dosino
- 705 UV Digester

1.2 Determination of contents

In voltammetric analyses, the standard addition technique is used for determining contents. This means that a voltammetric run is carried out with the sample solution, generally followed by two standard additions with the species concerned, whose content in the sample is then calculated from the differences of the measured signals.

Most standard solutions are commercially available with a metal ion concentration of ρ(Me) = 1 g/L. In a first step, these solutions are diluted with ultrapure water and acidified.

These dilute solutions are then used in a preliminary experiment. Based on the peak heights obtained with and without spiking, the concentration of the standard solution to be used is then calculated. The most accurate results are obtained if the first standard addition doubles the sample peak concerned.

1.3 Determination of blank value

The majority of VA analyses are trace analyses. The blank values of the reagents needed for digestion and for preparing the background electrolyte are not always equal to zero. Especially Co, Cr, Fe, Ni and Zn are ubiquitous and can, if disregarded, cause erroneous, high-bias results. Correct results are only obtained if the blank value of the reagents is taken into account.

The procedure is exactly the same as with the sample solution: same reagent quantities, same conditions, same instrument parameters as far as possible. Instead of the sample, however, ultrapure water is used. The blank value of the species is then subtracted from the sample content, for example in µg/L.

1.4 Determination of organic additives

The determination of organic additives in galvanic baths using cyclic voltammetric stripping (CVS) is a special application of voltammetric analysis. The additives, called suppressors, levelers or brighteners, are determined indirectly by means of their effect on the deposition rate of the main bath component. Cyclic voltammetry is the current measuring technique used. Quantification of the components is done by applying special calibration techniques: Dilution Titration (DT), Linear Approximation Technique (LAT), Modified Linear Approximation Technique (MLAT) and Response Curve Technique (RC).

2 Effluents of the electroplating industry

2.1 General

Most countries have official regulations concerning effluents, be it for their discharge into the sewage system or directly into a water course. The latter usually demands lower limiting values, i.e. lower concentrations. The valency or form of bonding of the element concerned may also be important. Thus, for example, Cr(VI) is much more toxic than Cr(III). The same applies for free and complexed cyanide, $K_4[Fe(CN)_6]$ being an example of a compound containing cyanide in complexed form.

Thanks to their selectivity and low limits of detection, stripping-voltammetric methods are ideal for the analysis of electroplating effluents. Their only drawback are interferences by organic compounds that are generally present in effluents. We therefore recommend to digest the effluents before analyzing them. Different methods are available for sample digestion. The best method certainly is UV digestion with the 705 UV Digester. It has the following advantages:

- The blank values are practically zero as only small amounts of chemicals have to be added.
- No losses as digestion is performed at temperatures below 100 °C.
- Up to 12 samples can be digested in one run.
- Environment-friendly as there are no noxious acid fumes.
- Complete digestion, no more interfering organic compounds such as complexing agents.

2.2 UV digestion

2.2.1 Digestion reagents

- Nitric acid; $w(HNO_3)$ = 65%, or hydrochloric acid; $w(HCl)$ = 30%, e.g. «suprapur»
- Hydrogen peroxide; $w(H_2O_2)$ = 30%, e.g. «suprapur»

2.2.2 General digestion procedure

Acidify the solution by adding HNO_3, bringing it to a pH value of 2. As a rule, 100 µL $w(HNO_3)$ = 65% is sufficient for 100 mL water sample. If the sample solution is alkaline and/or buffered, more acid has to be added.

Transfer 1...10 mL acidified effluent sample (make up to 10 mL with ultrapure water as required) into a quartz vessel, add 100 µL $w(H_2O_2)$ = 30% and treat in the UV Digester for 60 min at 90 °C.

2.2.3 Oxidation of Cr(III) to Cr(VI)

Adjust the sample solution to a pH value of 5...7[1] with NaOH or HNO_3. Transfer 1...10 mL of this solution (make up to 10 mL with ultrapure water as required) into a quartz vessel, add 100 µL $w(H_2O_2)$ = 30% and treat in the UV Digester for 60 min at 90 °C. Add another 10 µL $w(H_2O_2)$ = 30% and digest for another 30 min.

2.3 Chromium by means of DP polarography

ρ(Cr) ≥10 µg/L

2.3.1 Reagents

All reagents have to be of the highest possible purity. Use only ultrapure water.

- Cr(VI) standard: $\rho(Cr^{6+})$ = 100 mg/L
  Measure 10.0 mL $\rho(Cr^{6+})$ = 1 g/L (ready-for-use commercial reagent) into a 100-mL volumetric flask, make up to the mark with ultrapure water and mix.
- Potassium hydroxide solution: w(KOH) = 45%
- Ammonia: $w(NH_3)$ = 5%
- Acetic acid: $w(CH_3COOH)$ = 98%
- Ethylenediamine: puriss. p.a. (CAS 107-15-3)

2.3.2 Analysis

The Cr(VI) determination is carried out directly with the sample solution whereas the digestion solution is used for determining the total Cr.

Transfer 10 mL sample solution or the digestion solution into the polarographic vessel and preneutralize to pH = 7...8 with KOH solution. Add 20 µL ethylenediamine, 150 µL acetic acid, 300 µL KOH solution and 200 µL ammonia 5% and (if necessary) adjust the pH value to 9.5 with KOH solution or acetic acid. Deaerate with nitrogen and record the DP polarogram under the following conditions:

[1] The pH value has to be >5 to ensure that all the chromium is present in its hexavalent form.

Working electrode	DME	Start potential	–0.08 V
Stirrer speed	2000 rpm	End potential	–0.4 V
Mode	DP	Voltage step	0.006 V
Purge time	600 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Cr(VI)	approx. –0.25 V
Pulse time	0.04 s		

The Cr content is determined according to the standard addition method (e.g., two additions of 50 µL Cr standard, ρ = 100 mg/L

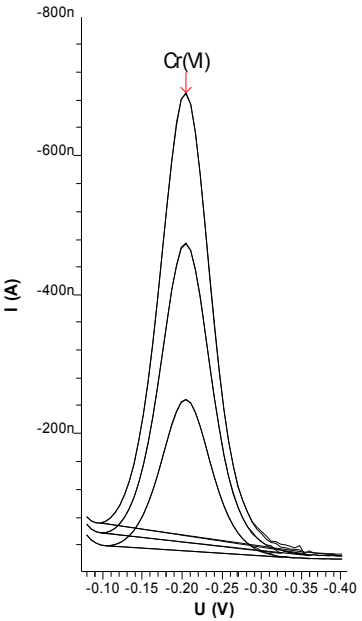

Fig. 1 Polarographic determination of 1 mg/L Cr(VI) in waste water

2.4 Cyanide

2.4.1 Methods of sample preparation

If only the free cyanide is of interest, the samples can be used directly.

Otherwise one distinguishes between the easily releasable cyanides (e.g. from KCN) and the total cyanide content (includes also CN complexes of heavy metals). The decomposition and separation is carried out according to DIN 38405 D13/14 and is described in detail in the Application Bulletin no. 46 «Potentiometric determination of cyanide». In this voltammetric procedure, the supporting electrolyte is used instead of NaOH as the absorption solution.

In the following, two analyses methods are described:

- By means of DP polarography for cyanide contents of 0.1...10 mg/L and
- By means of DP stripping voltammetry for cyanide contents of 10...100 µg/L.

2.4.2 Reagents

All reagents have to be of the highest possible purity. Use only ultrapure water.

- Cyanide standard: $\rho(CN^-)$ = 100 mg/L
  First dissolve 0.6 g KOH and then 0.2503 g KCN in ultrapure water, make up to 1 liter and mix.
- Cyanide standard solution: $\rho(CN^-)$ = 10 mg/L
  In a 100-mL volumetric flask, dissolve 0.6 g KOH in approx. 50 mL ultrapure water. Leave to cool down, then add 10.0 mL $\rho(CN^-)$ = 100 mg/L, make up to the mark with ultrapure water and mix. This standard solution must be prepared daily.
- Supporting electrolyte:
  Dissolve 100 g KOH and 123 g H_3BO_3 in approx. 750 mL ultrapure water. Leave to cool down, then make up to 1 liter with ultrapure water and mix.

2.4.3 Polarographic analysis

Transfer 10 mL absorption solution or 1...10 mL sample solution plus 10 mL supporting electrolyte into the polarographic vessel and deaerate with nitrogen, then record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.05 V
Stirrer speed	2000 rpm	End potential	–0.4 V
Mode	DP	Voltage step	0.004 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	5 s	Sweep rate	0.0067 V/s
Pulse amplitude	0.05 V	Peak potential CN^-	approx. –0.22 V
Pulse time	0.04 s		

The cyanide content is determined according to the standard addition method.

2.4.4 Stripping-voltammetric analysis

Transfer 10...20 mL absorption solution or 1...10 mL sample solution plus 10 mL supporting electrolyte into the polarographic vessel and deaerate with nitrogen, then record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.08 V
Mode	DP	End potential	–0.4 V
Purge time	300 s	Voltage step	0.004 V
Deposition potential	–0.08 V	Voltage step time	0.4 s
Deposition time	60 s	Sweep rate	0.01 V/s
Equilibration time	3 s	Peak potential CN^-	approx. –0.20 V
Pulse amplitude	0.05 V		

The cyanide content is determined according to the standard addition method.

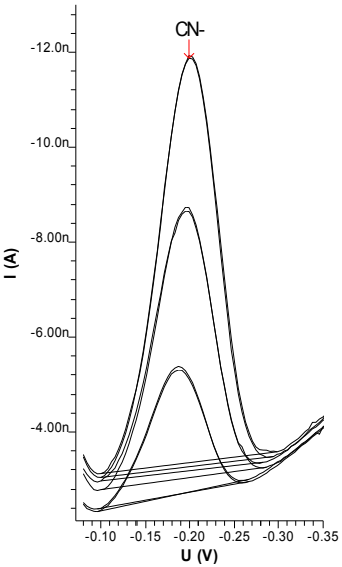

Fig. 2 Determination of 44 µg/L CN^- in waste water by means of CSV (cathodic stripping voltammetry).

2.5 Nickel and cobalt

2.5.1 Reagents

The reagents have to be of the highest possible purity. Use only ultrapure water.

- Supporting electrolyte: NH_3-NH_4Cl buffer, pH = 10
  Under stirring add 53 mL *w*(HCl) = 30% and 112.5 mL *w*(NH_3) = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime, Na salt: (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every day.
- Standards: ρ(Me) = 1 g/L (Me = Ni, Co)
  These are commercially available ready for use.

- Standard solution: ρ(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Me) = 1 g/L and 0.1 mL w(HNO_3) = 65%, fill up to the mark with ultrapure water and mix.

2.5.2 Analysis

Rinse the sample digestion solution into the polarographic vessel with ultrapure water, add 0.5 mL supporting electrolyte and 100 µL DMG solution (the pH value of the mixture should be between 8.5 and 9). Deaerate with nitrogen, then record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.80 V
Stirrer speed	2000 rpm	End potential	–1.25 V
Mode	DP	Voltage step	0.004 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.0067 V/s
Pulse amplitude	0.05 V	Peak potential Ni	approx. –0.95 V
Pulse time	0.04 s	Peak potential Co	approx. –1.10 V

The nickel and cobalt contents are determined according to the standard addition method.

2.6 Zinc, cadmium, lead and copper

2.6.1 Reagents

The reagents have to be of the highest possible purity. Use only ultrapure water.

- Supporting electrolyte: Ammonium acetate / acetic acid buffer pH = 4.6
  Add 60 mL *w*(CH_3COOH) = 96% and 37.5 mL *w*(NH_3) = 25% to approx. 300 mL ultrapure water. Leave to cool down and then make up to 500 mL with ultrapure water and mix.
- Potassium chloride solution: *c*(KCl) = 3 mol/L
  Dissolve 60 g KCl in ultrapure water, make up to 250 mL and mix.
- Standards: *ρ*(Me) = 1 g/L (Me = Zn, Cd, Pb, Cu)
  These are commercially available ready for use.

- Standard solution: ρ(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Me) = 1 g/L and 0.1 mL w(HNO_3) = 65%, fill up to the mark with ultrapure water and mix.

2.6.2 Analysis

Rinse the sample decomposition solution into the polarographic vessel with ultrapure water, add 1 mL supporting electrolyte (pH = 4.6) and deaerate with nitrogen. If the solution contains chloride, add 0.5 mL KCl solution. Record the DP polarogram under the following conditions:

Working electrode	DME	End potential	–1.1 V
Stirrer speed	2000 rpm	Voltage step	0.006 V
Mode	DP	Voltage step time	0.6 s
Purge time	300 s	Sweep rate	0.01 V/s
Equilibration time	3 s	Peak potential Cu	approx. –0.1 V
Pulse amplitude	0.05 V	Peak potential Pb	approx. –0.4 V
Pulse time	0.04 s	Peak potential Cd	approx. –0.6 V
Start potential	–0.05 V	Peak potential Zn	approx. –0.96 V

The metal contents are determined according to the standard addition method.

2.6.3 Remark

If only the content of Zn has to be determined, work is preferably carried out in an NH_3/NH_4Cl electrolyte (see below – Ni/Co). The peak potential of Zn is then approx. –1.2 V.

2.7 EDTA and/or NTA

2.7.1 General

The procedure described allows the determination of EDTA and NTA in effluents in concentrations of 0.05...25 mg/L. With the addition of Bi(III) ions EDTA and NTA are transferred at a pH value of 2.0 to the corresponding Bi complexes. As their peak potentials differ clearly, they can be determined simultaneously by means of DP polarography.

The interfering anions nitrite, sulfide and sulfite are eliminated from the sample by acidifying and blowing out. Interfering cations are eliminated by cation exchange

(which also decomposes heavy metal ion complexes involving EDTA and NTA). Interfering organic constituents (e.g. surfactants) are eliminated from the sample with an apolar adsorber resin.

2.7.2 Reagents

All reagents have to be of the highest possible purity. Use only ultrapure water.

- Nitric acid: $w(HNO_3)$ = 65% and $c(HNO_3)$ = 2 mol/L
- Alkaline Bi(III)nitrate: $Bi(OH)_2NO_3$ (CAS 1304-85-4)
- Potassium nitrate: KNO_3
- Methanol: CH_3OH
- Ascorbic acid: Vitamin C (CAS 50-81-7)
- NTA: nitrilotriacetic acid (CAS 139-13-9)
- EDTA: ethylenediaminetetraacetic acid disodium salt, dihydrate Na_2EDTA x 2 H_2O (CAS 6381-96-6)
- Caustic soda solution: c(NaOH) = 0.1 mol/L and c(NaOH) = 2 mol/L
- Hydrochloric acid: c(HCl) = 0.1 mol/L
- Strongly acidic cation exchanger in the Na^+ form: 300…1000 µm (20…50 mesh), e.g. Amberlite IR 120
- Apolar adsorber resin: on the basis of polystyrene for analytical purposes: 300...1000 µm (20...50 mesh), e.g. XAD 2
- Bi(III) nitrate solution: ρ(Bi) = 2000 mg/L
  2.8 g $Bi(OH)_2NO_3$ is dissolved in 25 mL $w(HNO_3)$ = 65% and made up to 1 liter with ultrapure water.
- Bi/NTA stock solution: ρ(NTA) = 1000 mg/L
  a) 4.5 g $Bi(OH)_2NO_3$ is dissolved in 30 mL $w(HNO_3)$ = 65% and diluted to approx. 400 mL with ultrapure water.

  b) 1.000 g NTA is dissolved in 20 mL c(NaOH) = 2 mol/L and diluted to approx. 400 mL with ultrapure water.

  Both solutions are mixed, left to cool down and then made up to 1 liter with ultrapure water and mixed. This stock solution can be stored for approx. 1 month.
- Bi/NTA standard solution: ρ(NTA) = 100 mg/L
  In a 100-mL volumetric flask, add 15 mL $c(HNO_3)$ = 2 mol/L to 10.0 mL Bi/NTA stock solution, make up to the mark with ultrapure water and mix. This standard solution can be used for 1 week.
- Bi/EDTA stock solution: ρ(EDTA) = 1000 mg/L
  a) 3.1 g $Bi(OH)_2NO_3$ is dissolved in 30 mL $w(HNO_3)$ = 65% and diluted to approx. 400 mL with ultrapure water.

  b) 1.2740 g Na_2EDTA x 2 H_2O is dissolved in 20 mL c(NaOH) = 2 mol/L and diluted to approx. 400 mL with ultrapure water.

Both solutions are mixed, left to cool down and then made up to 1 liter with ultrapure water and mixed. This stock solution can be stored for approx. 1 month.

- Bi/EDTA standard solution: ρ(EDTA) = 100 mg/L
  In a 100-mL volumetric flask, add 15 mL c(HNO_3) = 2 mol/L to 10.0 mL Bi/EDTA stock solution, make up to the mark with ultrapure water and mix. This standard solution can be used for 1 week.

2.7.3 Column preparation for solid phase extraction

Glass columns are used with an inner diameter of 8 mm and a disposable cock (boring 2.5 mm), e.g. according to DIN analysis EHB 3 NS.

2.7.3.1 Cation exchanger

Add the five-fold volume of *c*(HCl) = 0.1 mol/L to the cation exchanger resin and stir for at least 2 h. Rinse acid-free with ultrapure water, decant the excess water and convert the resin to the Na^+ form with the five-fold amount of *c*(NaOH) = 0.1 mol/L. Subsequently, rinse to neutral with ultrapure water.

Provide the column with a glass fiber stopper. Suspend 5 mL cation exchanger resin in ultrapure water and fill bubble-free into the column (the filling height is approx. 100 mm). Rinse with 20 mL ultrapure water and keep the water level always 2...3 mm above the packing. Discard the resin after use.

2.7.3.2 Apolar adsorber resin

Provide the column with a glass fiber stopper. Suspend 5 mL adsorber resin in methanol and fill bubble-free into the column. Rinse with 10 mL methanol and subsequently with 20 mL ultrapure water, keeping the water level 2...3 mm above the packing. Discard the adsorber resin after use.

2.7.4 Sampling and sample preparation

Adjust the water sample to pH 2.0 by adding *w*(HNO_3) = 65% (usually, the addition of 1 mL HNO_3 per liter waste water is sufficient). Eliminate undissolved substances from the sample by filtration through a membrane filter (pore size 0.45 µm). The sample stabilized in this way can be stored in the refrigerator at 4 °C for approx. 1 week.

Dissolve 20 g KNO_3 in 100 mL of the prepared water sample. This solution is passed through the adsorber resin at a rate of 5 mL/min. The initial 20 mL is discarded, the remaining 80 mL is passed through the cation exchanger (also at the rate of 5 mL/min). Again, the initial 20 mL is discarded so that 60 mL sample remains for the polarographic analysis.

2.7.5 Analysis

Pipet 10 mL sample solution into the polarographic vessel, add 400 mg ascorbic acid and deaerate for 5 min with nitrogen, then record the DP polarogram between +0.1 V and –0.6 V. The resulting polarogram must not show any peak at the peak potentials of Bi/NTA (approx. –0.23 V) and Bi/EDTA (approx. –0.44 V).

Now add 25 µL Bi(III) nitrate solution (at higher contents correspondingly more) and deaerate for 5 min with nitrogen. Record another DP polarogram under the same conditions as above. The Bi peak situated at approx. +0.02 V should be about twice as large as the peaks of the corresponding EDTA or NTA complexes. If this is not the case, add more Bi(III) nitrate solution.

The NTA and/or EDTA concentrations are determined by means of standard additions using the corresponding standard solutions.

Working electrode	DME	Start potential	+0.1 V
Stirrer speed	2000 rpm	End potential	–0.6 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	10 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Bi-NTA	approx. –0.22 V
Pulse time	0.04 s	Peak potential Bi-EDTA	approx. –0.44 V

2.7.6 Remarks

To avoid errors in sample preparation, the recovery rate *W* of each measurement series has to be determined. For this purpose, 100 mL NTA or EDTA standard solution are subjected to the complete analysis procedure (including resins). The recovery rate must be >90% and has to be taken into account for the content calculation. If the recovery rate is <90% the quality of the cation exchanger must be checked. The following calculations are applied:

W in % = A x 100 / B

A = mg/L NTA or EDTA found

B = mg/L NTA or EDTA added

Taking into account W, the result of the analysis is calculated as follows:

D = C x 100 / *W*

C = mg/L NTA or EDTA found

D = mg/L NTA or EDTA corrected

2.8 Tin

2.8.1 Reagents

All reagents used have to be of the highest possible purity. Use only ultrapure water.

- Supporting electrolyte: citrate / oxalate / hydrochloric acid buffer
  Dissolve 29.4 g trisodium citrate dihydrate (CAS 6132-04-03), 12.6 g oxalic acid dihydrate (CAS 6153-56-6) and 21.2 mL *w*(HCl) = 30% in approx. 600 mL ultrapure water, make up with it to 1 liter and mix.
- CTAB solution: *c*(CTAB) = 0.005 mol/L
  Dissolve 182 mg cetyl-(hexadexyl) trimethylammonium bromide (CAS 57-09-0) in ultrapure water, make up with it to 100 mL and mix.
- Standard: $\rho(Sn^{2+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Sn) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 0.5 mL *w*(HCl) = 30% and 1.0 mL $\rho(Sn^{2+})$ = 1 g/L, make up to the mark with ultrapure water and mix.

2.8.2 Analysis

Transfer 5.0 mL sample digestion solution into the polarographic vessel and add 5 mL supporting electrolyte. Add 50 µL CTAB solution, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.80 V
Mode	DP	End potential	–0.30 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.75 V	Voltage step time	0.1 s
Deposition time	180 s	Sweep rate	0.06 V/s
Equilibrium time	5 s	Peak potential Sn	approx. –0.51 V
Pulse amplitude	0.05 V		

The tin content is determined according to the standard addition method.

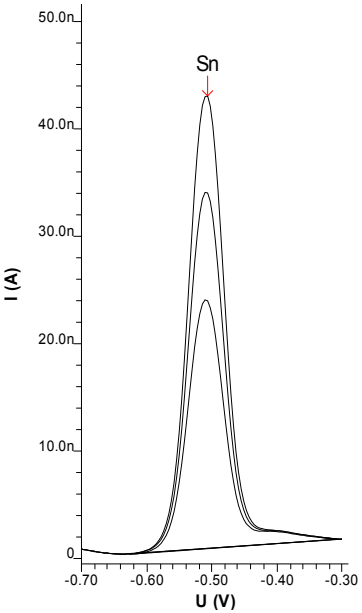

Fig. 3 Determination of 235 µg/L Sn in waste water by means of ASV (anodic stripping voltammetry).

3 Electroplating baths

3.1 General

The determination of the main constituents of electroplating baths is described in detail in «Plate PAC – Plating Baths Potentiometric Analysis Collection» (order no. 6.6044.00X). This compilation contains 76 proven titration methods for precise routine bath control.

Titrimetric methods are often less suitable for secondary constituents or contaminants as time-consuming sample preparation steps are usually required. This is, however, a typical application area for voltammetry. Whereas in many baths voltammetric analysis can take place directly or after dilution, in some baths, especially **cyanide baths**, a decomposition has to be carried out beforehand. Acidic decomposition is mostly used, which has to be carried out in the **fume hood because of the formation of toxic gases.**

The reagents used in the analyses must be of the highest purity. Use only ultrapure water.

The composition of electroplating baths depends on the application and therefore varies greatly. For this reason, a few bath types are mentioned at the beginning of the sub-chapters. However, only a selection can be given. Some of the described analysis methods may not be suitable for all bath types or may have to be modified slightly.

3.2 Silver baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Bright silver baths	Ag, AgCN, KCN, K_2CO_3	Cu, Co, Cr, Fe, Ni, Sb, Se	Sulfonates
High-speed baths	Ag, AgCN, KCN, K_2CO_3, KNO_3, KOH	Cu, Co, Cr, Fe, Ni, Sb, Se	Sulfonates
Electroless baths	$AgNO_3$, NH_3, $Na_2S_2O_3$		

3.2.1 Sample preparation

Cyanide interferes with the voltammetric determination of metal ions and has to be eliminated from the sample solution. The procedure for **Fe, Co, Cr, Cu, Ni and Se** is as follows:

Work in the fume hood, toxic HCN is formed!

Pipet 2.0 mL bath sample into a Kjeldahl flask. Add dropwise 2 mL $w(HNO_3)$ = 65% (caution, violent reaction – **work in the fume hood!!**) and heat to boiling until the precipitate has dissolved. Add 10 mL ultrapure water, heat to boiling once more and leave to cool. Then rinse quantitatively with ultrapure water into a 50 mL volumetric flask, make up with it to the mark and mix.

For Sb the following procedure is applied:

Pipet 5.0 mL bath sample into a Kjeldahl flask. Carefully, add 10 mL w(HCl) = 17% (caution, fierce reaction – **work in the fume hood!!**) and heat to boiling. Leave to cool down, add 25 mL ultrapure water, filtrate through a paper filter into a 100-mL volumetric flask, rinse with ultrapure water, make up with it to the mark and mix.

3.2.2 Antimony(III)

3.2.2.1 Reagents

- Supporting electrolyte: c(HCl) = 1 mol/L
- Standard: ρ(Sb) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Sb) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1 mL each ρ(Sb) = 1 g/L and w(HCl) = 30%, make up to the mark with ultrapure water and mix. This solution can be used for one week.

3.2.2.2 Analysis

Transfer 10 mL supporting electrolyte and 5.0 mL sample digestion solution (corresponding to 0.25 mL original bath) into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.3 V
Mode	DP	End potential	–0.07 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.3 V	Voltage step time	0.6 s
Deposition time	60 s	Sweep rate	0.01 V/s
Equilibration time	5 s	Peak potential Sb	approx. –0.13 V
Pulse amplitude	0.01 V		

The antimony content is determined according to the standard addition method.

3.2.3 Chromium

3.2.3.1 Reagents

- Supporting electrolyte:
  Dissolve1.64 g sodium acetate, 1.96 g disodium diethylenetriamine pentaacetate (DTPA; CAS 87095-89-4) and 21.3 g $NaNO_3$ in ultrapure water, make up with it to 100 mL and mix.
- Cr(VI) standard solution: $\rho(Cr^{6+})$ = 100 mg/L
  Pipet 10.0 mL $\rho(Cr^{6+})$ = 1 g/L (ready-for-use commercial reagent) into a 100-mL volumetric flask, make up to the mark with ultrapure water and mix.
- Cr(VI) standard solution: $\rho(Cr^{6+})$ = 0.02 mg/L
  Pipet 2.0 mL $\rho(Cr^{6+})$ = 100 mg/L into a 100-mL volumetric flask, make up to the mark with ultrapure water and mix. Pipet 1.0 mL of the mixture into a second 100-mL volumetric flask, make up to the mark with ultrapure water and mix. Both dilutions have to be freshly prepared daily.

3.2.3.2 Analysis

Transfer 5.0 mL sample digestion solution (corresponding to 0.2 mL original bath) and 5 mL each of supporting electrolyte and ultrapure water into the polarographic vessel. Adjust the pH of the mixture to 6.8 ±0.1 with NaOH solution, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–1.0 V
Mode	DP	End potential	–1.45 V
Purge time	300 s	Voltage step	0.01 V
Deposition potential	–1.0 V	Voltage step time	0.3 s
Deposition time	60 s	Sweep rate	0.033 V/s
Equilibration time	5 s	Peak potential Cr	approx. –1.25 V
Pulse amplitude	0.05 V		

In order to determine the Cr content, 100 µL $\rho(Cr^{6+})$ = 0.1 mg/L is added twice. A blank value is also determined and taken into account for the calculation.

3.2.4 Cobalt and/or nickel

3.2.4.1 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer, pH = 10
  Under stirring add 53 mL $w(HCl)$ = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Ammonia: $w(NH_3)$ = 25%
- Dimethylglyoxime Na salt: (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standards: ρ(Me) = 1 g/L (Me = Ni, Co)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 10 mg/L
  Transfer 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Me) = 1 g/L and 0.1 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.2.4.2 Analysis

Transfer 10 mL ultrapure water, 0.1...1.0 mL sample digestion solution (corresponding to 4...40 µL original bath) and 0.5 mL supporting electrolyte into the polarographic vessel. Adjust the pH of the mixture to 8.5...9 with ammonia, add 100 µL DMG solution and deaerate with nitrogen, then record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.7 V
Mode	DP	End potential	–1.15 V
Purge time	300 s	Voltage step	0.004 V
Deposition potential	–0.7 V	Voltage step time	0.1 s
Deposition time	30 s	Sweep rate	0.04 V/s
Equilibration time	10 s	Peak potential Ni	approx. –0.95 V
Pulse amplitude	0.05 V	Peak potential Co	approx. –1.07 V

The metal contents are determined according to the standard addition method.

3.2.4.3 Remarks

With this method very low contents of Co or Ni can be determined. There is, however, an upper determination limit. Including the increments, not more than 100 µg/L Co or Ni should be present because at higher concentrations the surface of the HMDE will become overloaded by the accumulated DMG complex.

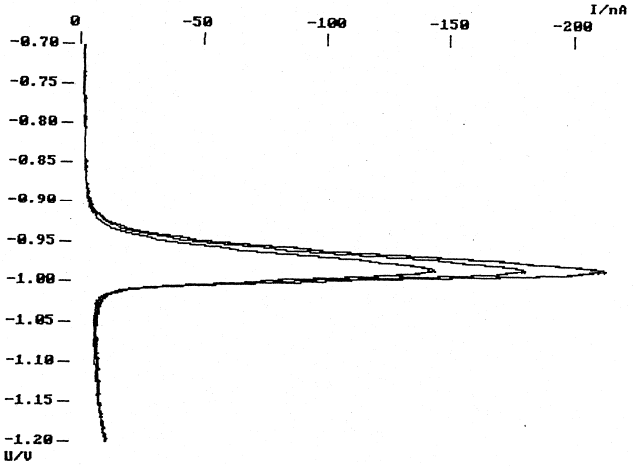

Fig. 4 Determination of 25.5 mg/L Ni in an Ag bath by means of AdSV (adsorptive stripping voltammetry)

3.2.5 Copper and iron

3.2.5.1 Reagents

- Pipes buffer:
  Dissolve 6.05 g piperazine-1,4-bis-2-ethanesulfonic acid (CAS 5625-37-6) in 1 mL w(NaOH) = 30% and 7 mL ultrapure water. Adjust the pH value to 7.0 with $w(NH_3)$ = 25%, make up to 20 mL with ultrapure water and mix.
- Catechol: 1,2-dihydroxybenzene (pyrocatechol; CAS 120-80-9) is purified through sublimation before use.
- Ammonia: $w(NH_3)$ = 10%
- Standards: ρ(Me) = 1 g/L (Me = Cu^{2+} and Fe^{3+})
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Me) = 1 g/L and 0.1 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.2.5.2 Analysis

Transfer 10 mL ultrapure water and 100 µL sample digestion solution (corresponding to 4 µL original bath) into the polarographic vessel and deaerate with nitrogen. Add a few catechol crystals and 0.2 mL pipes buffer and adjust the pH value to 7.0 with ammonia. Deaerate once more with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	0 V
Mode	DP	End potential	–0.5 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	0 V	Voltage step time	0.3 s
Deposition time	60 s	Sweep rate	0.02 V/s
Equilibration time	5 s	Peak potential Cu	approx. –0.17 V
Pulse amplitude	0.05 V	Peak potential Fe	approx. –0.325 V

The metal contents are determined according to the standard addition method.

3.2.5.3 Remarks

If only Cu is to be determined – especially if larger amounts are present in the bath sample – then DP polarography can be applied. For this, in a glass beaker add under stirring 0.5 mL w(HCl) = 30% to 10.0 mL decomposed bath sample. Filtrate through a paper filter into the polarographic vessel, rinse the filter with ultrapure water and adjust the pH value of the mixture to 9…9.5 with $w(NH_3)$ = 25%. Deaerate with nitrogen and record the DP polarogram at the DME between –0.1 V and –0.6 V. Peak potentials: Cu approx. –0.2 V and Fe approx. –0.46 V.

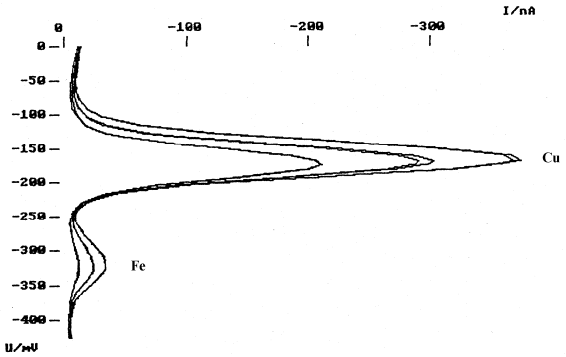

Fig. 5 Determination of 31.6 mg/L Cu and 162 µg/L Fe in an Ag bath by means of AdSV (adsorptive stripping voltammetry)

3.2.6 Selenium

3.2.6.1 Reagents

- Na_2EDTA: $c(Na_2EDTA)$ = 0.1 mol/L (CAS 6381-92-6)
  Dissolve 3.7 g Na_2EDTA x 2 H_2O in ultrapure water, make up with it to 100 mL and mix.
- Ammonium sulfate: $(NH_4)_2SO_4$ (CAS 7783-20-2)
- Copper sulfate solution: $c(CuSO_4)$ = 0.1 mol/L
  Dissolve 2.5 g $CuSO_4$ x 5 H_2O in ultrapure water, make up with it to 100 mL and mix.
- Sulfuric acid: $c(H_2SO_4)$ = 0.1 mol/L
- Se(IV) standard: $\rho(Se^{4+})$ = 1 g/L
  This standard is commercially available ready for use.
- Se(IV) standard solution: $\rho(Se^{4+})$ = 1 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 100 µL $\rho(Se^{4+})$ = 1 g/L and 0.1 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix. This solution has to be freshly prepared daily.

3.2.6.2 Analysis

Transfer 10 mL ultrapure water, 1 mL Na_2EDTA, 1 g $(NH_4)_2SO_4$, 1 mL $CuSO_4$ and 100 µL sample digestion solution (corresponding to 4 µL original bath) into the polarographic vessel. Adjust the pH of the mixture to 2.2 with H_2SO_4. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.45 V
Mode	DP	End potential	–0.75 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.4 V	Voltage step time	0.3 s
Deposition time	30 s	Sweep rate	0.02 V/s
Equilibration time	5 s	Peak potential Se(IV)	approx. –0.63 V
Pulse amplitude	0.05 V		

The selenium content is determined according to the standard addition method.

3.2.6.3 Remarks

Only Se(IV) is voltammetrically active. Any Se(VI) formed by the decomposition with HNO_3 has to be reduced before the determination.

3.3 Gold baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Alkaline cyanide baths	$KAu(CN)_2$, KCN, K_2CO_3, K_2HPO_4	Co, Cu, Fe, In, Ni, Pb, Sn, Zn	
Acidic cyanide baths	$KAu(CN)_2$, $CoSO_4$, citric acid, pH = 3.6…4.7	Cu, Fe, In, Ni, Pb, Sn, Zn	
Buffered citrate baths	$KAu(CN)_2$, K_2H citrate	Fe, Zn	
Buffered phosphate baths	$KAu(CN)_2$, KH_2PO_4, K_2HPO_4	Fe, Zn	
Cyanide-free baths	$NaAuCl_4$ x 2 H_2O, Na_2SO_3, $Na_2S_2O_3$, NaH_2PO_4, Tl_2SO_4	Cu, Ni, Pb, Zn	
Electroless baths	$KAu(CN)_2$, Au(I), Au(III), KCN, KOH, KBH_4 or dimethyl-amineborane or hypophosphite or hydrazine or hydroxylamine	Pb, Tl,	Ethyleneglycol, monoethylether, EDTA, NTA, thiourea

3.3.1 Sample preparation

Cyanide interferes with the voltammetric determination of the metal ions and has to be eliminated from the sample solution. The **decomposition procedure** depends on the metal ions to be determined and **must always be carried out in the fume hood as toxic HCN is given off.** The decomposition methods are listed with the particular metal ions.

3.3.2 Gold(I)

3.3.2.1 Sample preparation

No sample preparation is required.

3.3.2.2 Reagents

- Supporting electrolyte: KOH/EDTA, c = 1 mol/L or 0.05 mol/L
  Dissolve under stirring 7.31 g EDTA (CAS 60-00-4) and 28.1 g KOH (CAS 1310-58-3) in 300 mL ultrapure water, leave to cool and then make up to 500 mL with ultrapure water and mix.
- Standard solution: $KAu(CN)_2$, $\rho(Au^+)$ = 2 g/L
  Dissolve 0.1463 g $KAu(CN)_2$ and 0.5 g KCN in ultrapure water, make up with it to 50 mL and mix.

3.3.2.3 Analysis

Transfer 15 mL supporting electrolyte and 150...300 µL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.9 V
Stirrer speed	2000 rpm	End potential	–1.8 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.8 s
Equilibrium time	30 s	Sweep rate	0.0074 V/s
Pulse amplitude	0.05 V	Peak potential Au(I)	–1.1 V
Pulse time	0.04 s		

The gold(I) content is determined according to the standard addition method.

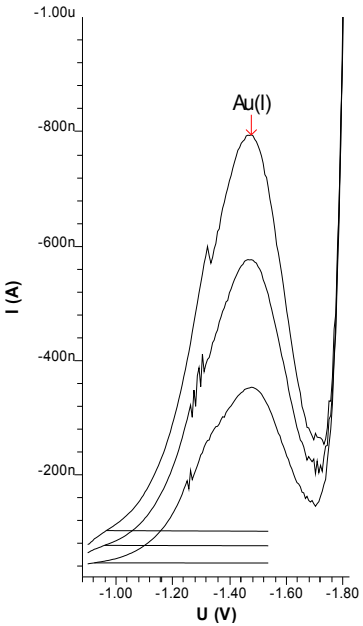

Fig. 6 Polarographic determination of 2 g/L Au(I) in an Au bath.

3.3.3 Cobalt and/or nickel

3.3.3.1 Sample preparation

Work in the fume hood!

Transfer 0.5 mL bath sample and approx. 10 mL ultrapure water into a Kjeldahl flask. Cautiously add 6 mL *w*(HCl) = 30%, heat and keep boiling for approx. 1 min. Leave to cool down, rinse the mixture quantitatively into a 100-mL volumetric flask with ultrapure water, make up to the mark and mix.

3.3.3.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Add under stirring 53 mL $w(HCl)$ = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime Na salt: (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standards: ρ(Me) = 1 g/L (Me = Ni and Co)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Me) = 1 g/L and 1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.3.3.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 50 µL original bath) and 2 mL supporting electrolyte into the polarographic vessel. Add 100 µL DMG solution and deaerate with nitrogen, then record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.8 V
Stirrer speed	2000 rpm	End potential	–1.25 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Ni	approx. –0.95 V
Pulse time	0.04 s	Peak potential Co	approx. –1.1 V

The nickel and cobalt contents are determined according to the standard addition method.

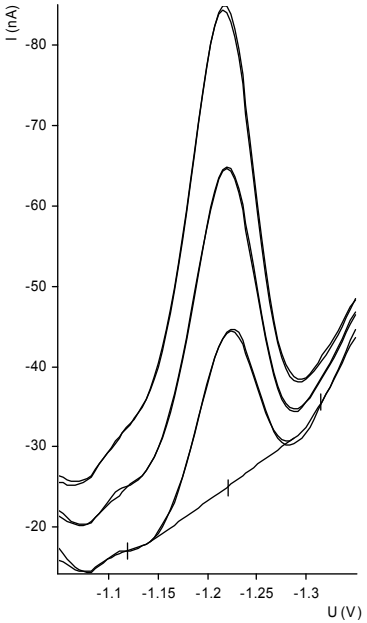

Fig. 7 Polarographic determination of 257.7 mg/L Co in a gold bath.

3.3.4 Copper

3.3.4.1 Reagents

- Supporting electrolyte: Ammonium citrate (CAS 3458-72-8)
  Dissolve 61 g citric acid triammonium salt in ultrapure water, make up with it to 250 mL and mix.
- Standard: ρ(Cu) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Cu) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Cu) = 1 g/L and 0.1 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.3.4.2 Sample preparation and analysis

Carry out the sample preparation in the fume hood!

Transfer 20.0 mL bath sample into a Kjeldahl flask and carefully add 1 mL $w(H_2SO_4)$ = 96% and 2 mL $w(HNO_3)$ = 65%. Heat and keep boiling for approx. 5 min. Leave to cool down, add 20 mL ultrapure water and 5 mL supporting electrolyte, heat to boiling and leave to cool down. Filtrate through a paper filter into a 100-mL volumetric flask, rinse with ultrapure water, make up to the mark and mix.

Transfer 10.0 mL prepared sample solution (corresponding to 2 mL original bath) into the polarographic vessel, deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	+0.1 V
Stirrer speed	2000 rpm	End potential	–0.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Cu	approx. 0.05 V
Pulse time	0.04 s		

The copper content is determined according to the standard addition method.

3.3.5 Iron

3.3.5.1 Sample preparation

Work in the fume hood!

Transfer 10.0 mL bath sample and 10 mL ultrapure water into a Kjeldahl flask. Carefully add 1 mL $w(H_2SO_4)$ = 96% and 2 mL $w(HNO_3)$ = 65%, heat and keep boiling for approx. 5 min. Leave to cool down, filtrate through a paper filter into a 50-mL volumetric flask, rinse with ultrapure water, make up to the mark and mix.

3.3.5.2 Reagents

- Sulfosalicylic acid solution (CAS 5965-83-3)
  Dissolve 10.17 g 5-sulfosalicylic acid dihydrate in ultrapure water, make up with it to 100 mL and mix.
- Phosphoric acid: $w(H_3PO_4)$ = 85%
- Ammonia: $w(NH_3)$ = 25%
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Fe^{3+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(Fe^{3+})$ = 1 g/L and 0.1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.3.5.3 Analysis

Transfer 5.0 mL prepared sample solution (corresponding to 1 mL original bath) into the polarographic vessel. Add 0.2 mL H_3PO_4 and 5 mL sulfosalicylic acid solution and adjust the pH to 9.5 with ammonia. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.3 V
Stirrer speed	2000 rpm	End potential	–1.6 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential	approx. –1.48 V
Pulse time	0.04 s		

The iron content is determined according to the standard addition method.

3.3.6 Indium

3.3.6.1 Reagents

- Supporting electrolyte:
  Dissolve 30 g glucose (CAS 14431-43-7) in 720 mL *w*(HCl) = 30%, make up to 1 liter with ultrapure water and mix.
- Methyl red solution:
  Dissolve 0.1 g methyl red (CAS 493-52-7) in ultrapure water, make up to 100 mL with ultrapure water and mix.
- In(III) standard: $\rho(In^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- In(III) standard solution: $\rho(In^{3+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(In^{3+})$ = 1 g/L and 1 mL *w*(HNO_3) = 65%, make up to the mark with ultrapure water and mix.

3.3.6.2 Sample preparation

Work in the fume hood!

Transfer 5.0 mL bath sample into a glass beaker and add under stirring 20 mL supporting electrolyte and 0.2 mL methyl red solution. Add 50 mL ultrapure water and deaerate by sparging nitrogen through the solution for 5 min to remove the cyanide. Make up to 100 mL with ultrapure water and mix.

3.3.6.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.5 mL original bath) into the polarographic vessel, deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.35 V
Stirrer speed	2000 rpm	End potential	–0.75 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential In	approx. –0.68 V
Pulse time	0.04 s		

The indium content is determined according to the standard addition method.

3.3.7 Lead and tin

3.3.7.1 Reagents

- Supporting electrolyte:
  Dissolve 29.5 g trisodium citrate dihydrate (CAS 6132-04-3), 12.6 g oxalic acid dihydrate (CAS 6153-56-6) and 25 mL *w*(HCl) = 30% in ultrapure water, make up with it to 1 liter and mix.
- CTAB solution: *c*(CTAB) = 0.005 mol/L
  Dissolve 0.46 g cetyltrimethylammonium bromide (hexadecyl-trimethylammonium bromide; CAS 57-09-0) in ultrapure water, make up with it to 250 mL and mix.
- Standards: *ρ*(Me) = 1 g/L (Me = Pb and Sn)
  These are commercially available ready for use.
- Standard solutions: *ρ*(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1 mL acid[2] and 1.0 mL *ρ*(Me) = 1 g/L, make up to the mark with ultrapure water and mix.

3.3.7.2 Sample preparation and analysis

Carry out the sample preparation in the fume hood!

Pipet 100 µL bath sample into the polarographic vessel, heat up and evaporate to dryness. Add 200 µL *w*(HCl) = 30% and 10 mL supporting electrolyte, heat and keep boiling for 30 s. Add another 10 mL supporting electrolyte and leave to cool. Add 200 µL CTAB solution, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.8 V
Mode	DP	End potential	–0.2 V
Purge time	300 s	Voltage step	0.004 V
Deposition potential	–0.8 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.02 V/s
Equilibration time	5 s	Peak potential Sn	approx. –0.54 V
Pulse amplitude	0.05 V	Peak potential Pb	approx. –0.42 V

The lead and tin contents are determined according to the standard addition method.

[2] For Pb: *w*(HNO_3) = 65%, for Sn: *w*(HCl) = 30%.

3.3.8 Thallium

(In electroless baths no sample preparation is required).

3.3.8.1 Reagents

- Standard: $\rho(Tl^+)$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Tl^+)$ = 5 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 0.50 mL $\rho(Tl^+)$ = 1 g/L and 1 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.3.8.2 Analysis

Transfer 10 mL ultrapure water and 100 µL sample solution into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.7 V
Mode	DP	End potential	–0.2 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.7 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Tl(I)	approx. –0.46 V
Pulse amplitude	0.05 V		

The thallium content is determined according to the standard addition method.

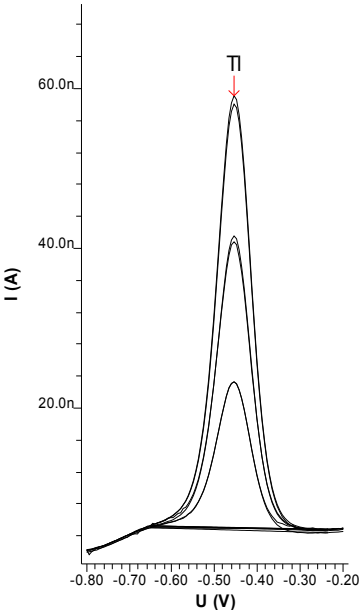

Fig. 8 Determination of 5.1 mg/L Tl in an Au bath by means of ASV (anodic stripping voltammetry).

3.3.9 Zinc

3.3.9.1 Sample preparation

Work in the fume hood!

Transfer 5.0 mL bath sample into a Kjeldahl flask. Carefully add 6 mL *w*(HCl) = 30%. Heat and keep boiling for 1 min. Leave to cool down, rinse the flask contents quantitatively into a 100-mL volumetric flask with ultrapure water, make up with it to the mark and mix.

3.3.9.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Dissolve 53.5 g NH_4Cl and 68 mL *w*(NH_3) = 25% in ultrapure water in a 1000-mL volumetric flask, make up to the mark and mix.
- Standard: *ρ*(Zn) = 1 g/L
  This standard is commercially available ready for use.

- Standard solution: ρ(Zn) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Zn) = 1 g/L and 1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.3.9.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.5 mL original bath) into the polarographic vessel and add 2 mL supporting electrolyte. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.1 V
Stirrer speed	2000 rpm	End potential	–1.45 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Zn	approx. –1.33 V
Pulse time	0.04 s		

The zinc content is determined according to the standard addition method.

3.3.10 NTA

3.3.10.1 Sample preparation

Depending on the expected NTA concentration, the bath sample is diluted at a ratio of 1:100 to 1:2000.

3.3.10.2 Reagents

- Ascorbic acid solution: ρ(ascorbic acid) = 40 g/L
  Dissolve 4 g L-ascorbic acid (CAS 50-81-7) in ultrapure water, make up with it to 100 mL and mix.
- Bi(III) solution: $\rho(Bi^{3+})$ = 2 g/L
  Transfer 0.465 g $Bi(NO_3)_3$ x 5 H_2O (CAS 10035-06-0) into a 100-mL volumetric flask and dissolve in 2.5 mL $w(HNO_3)$ = 65%. Make up to the mark with ultrapure water and mix.
- Bi/NTA standard: ρ(NTA) = 1 g/L
  a) Dissolve 0.254 g $Bi(NO_3)_3$ x 5 H_2O in 3 mL $w(HNO_3)$ = 65% and dilute to 40 mL with ultrapure water.

b) Dissolve100 mg nitrilotriacetic acid (NTA, CAS 139-13-9) in 2 mL c(NaOH) = 2 mol/L and dilute to 40 mL with ultrapure water.

Both solutions are brought together under stirring. Leave to cool down, dilute to 100 mL with ultrapure water and mix. The pH value should be approx. 0.7. This standard has a shelf life of approx. 1 month.

- Bi/NTA standard solution: ρ(NTA) = 100 mg/L
  Dilute 10.0 mL Bi/NTA standard with approx. 50 mL ultrapure water in a 100-mL volumetric flask. Add 15 mL $c(HNO_3)$ = 2 mol/L, make up to the mark with ultrapure water and mix. This solution has a shelf life of approx. 1 week.

3.3.10.3 Analysis

Transfer 10 mL ascorbic acid, 100 µL diluted sample solution and 50 µL[3] $\rho(Bi^{3+})$ = 2 g/L into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	0.1 V
Stirrer speed	2000 rpm	End potential	–0.4 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	10 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Bi/NTA	–0.22 V
Pulse time	0.04 s	Peak potential Bi(III)	0.02 V

The NTA content is determined according to the standard addition method.

3.3.10.4 Remarks

The Bi/NTA peak may show a shoulder at approx. –0.3 V that, however, does not interfere with the peak evaluation at –0.22 V.

To ensure that all the NTA has reacted to form the Bi(III) complex, the Bi(III) peak at 0.02 V should be about twice as high as the Bi/NTA peak. If this is not the case, add correspondingly more Bi(III) solution.

[3] This addition depends on the NTA content, if necessary add 75 µL.

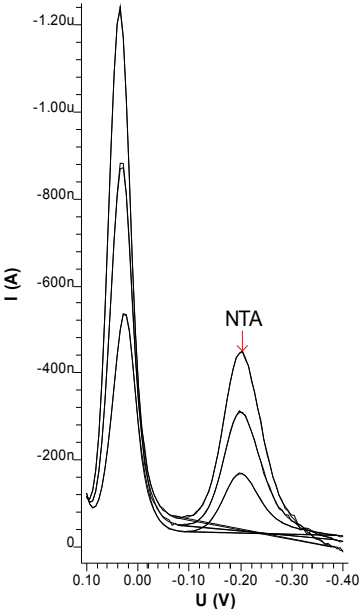

Fig. 9 Polarographic determination of 400 g/L NTA in a gold bath.

3.4 Cadmium baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Alkaline cyanide baths	Cd, KCN, K_2CO_3, KOH	Cu, Fe, Ni, Pb, Sb	

3.4.1 Antimony(III)

3.4.1.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 5.0 mL bath sample into a Kjeldahl flask. Carefully add (fierce reaction) 10 mL *w*(HCl) = 30% and heat to boiling. After 3 min leave to cool, rinse with ultrapure water into a 100-mL volumetric flask, make up with it to the mark and mix.

3.4.1.2 Reagents

- Supporting electrolyte: *c*(HCl) = 1 mol/L
- Standard: *ρ*(Sb) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: *ρ*(Sb) = 10 mg/L
  Transfer 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL *ρ*(Sb) = 1 g/L and *w*(HCl) = 30% each, make up to the mark with ultrapure water and mix.

3.4.1.3 Analysis

Transfer 10 mL ultrapure water and 10.0 mL prepared sample solution (corresponding to 0.5 mL original bath) into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.3 V
Mode	DP	End potential	–0.07 V
Purge time	300 s	Voltage step	0.004 V
Deposition potential	–0.3 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.02 V/s
Equilibration time	5 s	Peak potential Sb(III)	approx. –0.13 V
Pulse amplitude	0.01 V		

The antimony content is determined according to the standard addition method.

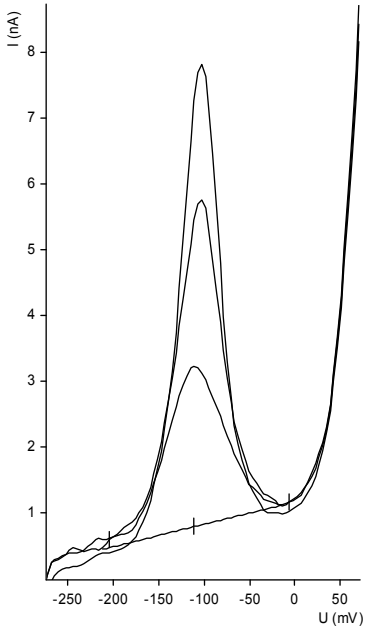

Fig. 10 Determination of 4.9 µg/L Sb(III) in a Cd bath by means of ASV (anodic stripping voltammetry).

3.4.2 Copper, nickel and zinc

3.4.2.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 2.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Carefully add 2 mL $w(H_2SO_4)$ = 96%, heat and keep boiling until SO_3 fumes appear. Leave to cool down, rinse the mixture with ultrapure water into a 100-mL volumetric flask, make up to the mark and mix.

3.4.2.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer, pH = 10
  Add under stirring 53 mL w(HCl) = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime Na salt: (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standards: ρ(Me) = 1 g/L (Me = Cu, Ni, Zn)
  These are commercially available ready for use.
- Standard solution: ρ(Me) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Me) = 1 g/L and 1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.4.2.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.2 mL original bath) and 5 mL supporting electrolyte into the polarographic vessel. Add 100 µL DMG solution and deaerate with nitrogen, then record the DP polarogram under the following conditions:

Working electrode	DME	End potential	–1.45 V
Stirrer speed	2000 rpm	Voltage step	0.006 V
Mode	DP	Voltage step time	0.6 s
Purge time	300 s	Sweep rate	0.01 V/s
Equilibration time	3 s	Peak potential Cu	approx. –0.25 V
Pulse amplitude	0.05 V	Peak potential Ni	approx. –0.95 V
Pulse time	0.04 s	Peak potential Zn	approx. –1.33 V
Start potential	–0.1 V		

The metal contents are determined according to the standard addition method.

3.4.3 Iron

3.4.3.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Place 2.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Carefully add 2 mL $w(H_2SO_4)$ = 96%, heat and keep boiling until SO_3 fumes appear. Leave to cool down, rinse the mixture with ultrapure water into a 100-mL volumetric flask, make up to the mark and mix.

3.4.3.2 Reagents

- Sulfosalicylic acid solution: (CAS 5965-83-3)
  Dissolve 10.17 g 5-sulfosalicylic acid dihydrate in ultrapure water, make up with it to 100 mL and mix.
- Phosphoric acid: $w(H_3PO_4)$ = 85%
- Ammonia: $w(NH_3)$ = 25%
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Fe^{3+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(Fe^{3+})$ = 1 g/L and 1 mL $w(HCl)$ = 30%, make up to the mark with ultrapure water and mix.

3.4.3.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 200 µL original bath) into the polarographic vessel. Add 0.2 mL H_3PO_4 and 5 mL sulfosalicylic acid solution and adjust the pH to 9.5 with ammonia. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.3 V
Stirrer speed	2000 rpm	End potential	–1.6 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Fe(III)	approx. –1.48 V
Pulse time	0.04 s		

The iron content is determined according to the standard addition method.

3.4.4 Lead

3.4.4.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 5.0 mL bath sample into a Kjeldahl flask and dilute with approx 10 mL ultrapure water. Carefully add 5 mL $w(H_2SO_4)$ = 96%, heat and keep boiling until SO_3 fumes appear. Leave to cool down, add cautiously approx. 50 mL ultrapure water and 5 g ammonium acetate (CAS 631-61-8), heat and keep boiling for approx. 5 min. The cooled solution is rinsed with ultrapure water into a 100-mL volumetric flask, made up with it to the mark and mixed.

3.4.4.2 Reagents

- Caustic soda solution: w(NaOH) = 30%
- Standard: ρ(Pb) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Pb) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Pb) = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.4.4.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.5 mL original bath) into the polarographic vessel and adjust the pH to 4...5 with caustic soda. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.55 V
Mode	DP	End potential	–0.3 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.55 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Pb	approx. –0.46 V
Pulse amplitude	0.05 V		

The lead content is determined according to the standard addition method.

3.5 Cobalt baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Sulfate/chloride baths	$CoSO_4$, $CoCl_2$, H_3BO_3	Ni, Pb, Zn	
Sulfamate baths	$Co(SO_3NH_2)_2$, formamide	Ni, Pb, Zn	
Fluoroborate baths	$Co(BF_4)_2$, H_3BO_3	Ni, Pb, Zn	
Electroless plating baths	$CoSO_4$, ($NiSO_4$), NaH_2PO_2, Na citrate, $(NH_4)_2$ SO_4, Na tartrate	Pb, Re, Zn	

3.5.1 Copper and lead

3.5.1.1 Reagents

- Hydrochloric acid: *w*(HCl) = 30%
- Standards: *ρ*(Me) = 1 g/L (Me = Cu, Pb)
  These are commercially available ready for use.
- Standard solutions: *ρ*(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL *ρ*(Me) = 1 g/L and 0.5 mL *w*(HNO_3) = 65%, make up to the mark with ultrapure water and mix.

3.5.1.2 Analysis

Transfer 10.0 mL sample solution and 1 mL hydrochloric acid into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.6 V
Mode	DP	End potential	–0.05 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.6 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Cu	approx. –0.22 V
Pulse amplitude	0.05 V	Peak potential Pb	approx. –0.44 V

The metal contents are determined according to the standard addition method.

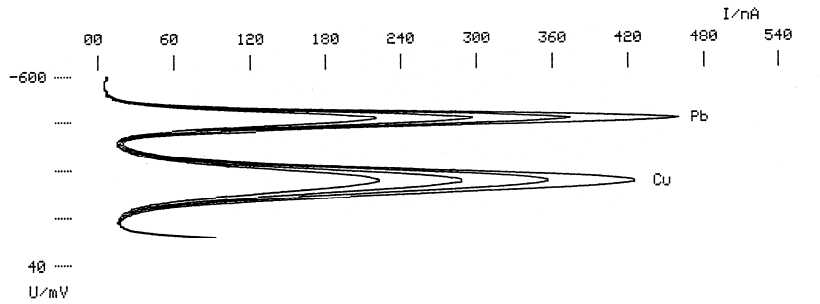

Fig. 11 Determination of 0.5 mg/L Cu and Pb each in a Co bath by means of ASV (anodic stripping voltammetry).

3.5.2 Nickel

3.5.2.1 Reagents

- Supporting electrolyte: *c*(pyridine) = 0.5 mol/L
  Transfer approx. 150 mL ultrapure water and 20 mL pyridine (CAS 110-86-1) into a 250-mL volumetric flask. Make up with ultrapure water to the mark and mix.
- Standard: ρ(Ni) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Ni) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Ni) = 1 g/L and 0.5 mL *w*(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.5.2.2 Analysis

Transfer 10 mL ultrapure water, 5 mL supporting electrolyte and 1.0 mL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.6 V
Stirrer speed	2000 rpm	End potential	–0.9 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.01 V	Peak potential Ni	approx. –0.78 V
Pulse time	0.04 s		

The nickel content is determined according to the standard addition method.

3.5.3 Zinc

3.5.3.1 Sample preparation

Transfer approx. 50 mL ultrapure water into a glass beaker and add 5.0 mL bath sample. Slowly add under stirring 7 mL *w*(NaOH) = 30%, leave to react under stirring for approx. 2 min. Filtrate through a paper filter in a 100-mL volumetric flask, rinse the glass beaker and filter with *c*(NaOH) = 0.1 mol/L, make up with it to the mark and mix.

3.5.3.2 Reagents

- Supporting electrolyte: NH_3-/NH_4Cl buffer
  Under stirring mix approx. 300 mL ultrapure water, 53 mL *w*(HCl) = 30% and 112.5 mL *w*(NH_3) = 25%. Leave to cool down, make up with ultrapure water to 500 mL and mix.
- Standard: ρ(Zn) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: *ρ*(Zn) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL *ρ*(Zn) = 1 g/L and 0.5 mL *w*(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.5.3.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.5 mL original bath) and 5 mL supporting electrolyte into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.0 V
Stirrer speed	2000 rpm	End potential	–1.45 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Zn	approx. –1.33 V
Pulse time	0.04 s		

The zinc content is determined according to the standard addition method.

3.6 Chromium baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Cr(VI)	CrO_3, H_2SO_4	Chloride, Cu, Fe, Ni, Se, Tl, Zn	
Cr(III)	NH_4-Cr(III) oxalate		Methanedisulfonic acid

3.6.1 General

In most cases the Cr(VI) present interferes with the voltammetric determination of the other species. Cr(VI) is therefore reduced to Cr(III) first. The corresponding procedure is described in the determinations concerned.

3.6.2 Copper, nickel and zinc

3.6.2.1 Sample preparation

Transfer approx. 30 mL ultrapure water into a glass beaker, add 2.0 mL bath sample and 0.5 mL $w(H_2SO_4)$ = 96%. After this add 15 mL $w(Na_2SO_3)$ = 5% (CAS 7757-83-7), heat and keep boiling for 2 min. Leave to cool down, rinse the solution with ultrapure water quantitatively into a 100-mL volumetric flask, make up to the mark with ultrapure water and mix.

3.6.2.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Add under stirring 53 mL w(HCl) = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime Na salt (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standards: ρ(Me) = 1 g/L (Me = Cu, Ni, Zn)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Me) = 1 g/L and 0.5 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.6.2.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.2 mL original bath) and 5 mL supporting electrolyte into the polarographic vessel. Add 100 µL DMG solution and deaerate with nitrogen, then record the DP polarogram under the following conditions:

Working electrode	DME	End potential	–1.45 V
Stirrer speed	2000 rpm	Voltage step	0.006 V
Mode	DP	Voltage step time	0.6 s
Purge time	300 s	Sweep rate	0.01 V/s
Equilibration time	3 s	Peak potential Cu	approx. –0.25 V
Pulse amplitude	0.05 V	Peak potential Ni	approx. –0.95 V
Pulse time	0.04 s	Peak potential Zn	approx. –1.33 V
Start potential	–0.1 V		

The metal contents are determined according to the standard addition method.

3.6.3 Iron

3.6.3.1 Sample preparation

- Reduction solution: *c*(oxalic acid) = 0.5 mol/L
  Dissolve 6.3 g $(COOH)_2$ x 2 H_2O (CAS 6153-56-6) in ultrapure water, make up with it to 100 mL and mix.

Transfer 250 µL bath sample and 25 mL reduction solution into a glass beaker. Heat slowly under stirring until the color changes to pure green, then keep boiling for 1 min. Leave to cool down, make up with ultrapure water to 50 mL in the volumetric flask and mix.

3.6.3.2 Reagents

- Supporting electrolyte:
  Transfer approx. 150 mL ultrapure water into a 250-mL volumetric flask. Dissolve in it 4.2 g $KBrO_3$ (CAS 7758-01-2), 4.3 g NaOH x H_2O (CAS 12200-64-5) and 1.86 g triethanolamine (CAS 102-71-6). Make up to the mark with ultrapure water and mix.
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Fe^{3+})$ = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL $\rho(Fe^{3+})$ = 1 g/L and 0.5 mL *w*(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.6.3.3 Analysis

Transfer 15 mL ultrapure water, 5 mL supporting electrolyte and 100 µL prepared sample solution (corresponding to 5 µL original bath) into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.7 V
Stirrer speed	2000 rpm	End potential	–1.3 V
Mode	DP	Voltage step	0.005 V
Purge time	300 s	Voltage step time	0.8 s
Equilibration time	5 s	Sweep rate	0.006 V/s
Pulse amplitude	0.05 V	Peak potential Fe(III)	approx. –1.0 V
Pulse time	0.04 s		

The iron content is determined according to the standard addition method. Using ultrapure water, the blank value of the supporting electrolyte is determined and subtracted from the result.

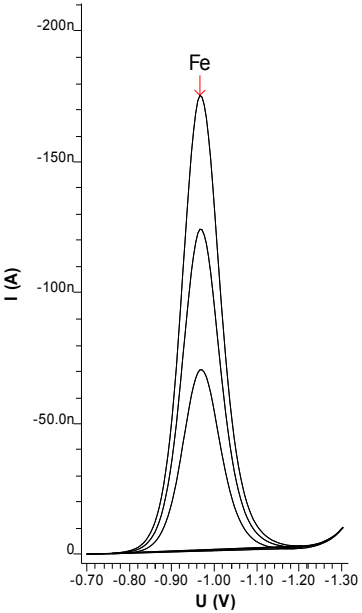

Fig. 12 Polarographic determination of 2.6 g/L Fe in a Cr bath.

3.6.4 Selenium

3.6.4.1 Sample preparation

Transfer approx. 30 mL ultrapure water into a glass beaker and add 2.0 mL bath sample and 0.5 mL $w(H_2SO_4)$ = 96%. Then add 15 mL $w(Na_2SO_3)$ = 5% (CAS 7757-87-7), heat and keep boiling for 2 min. Leave to cool down, rinse the solution quantitatively with ultrapure water into a 100-mL volumetric flask, make up to the mark with ultrapure water and mix.

3.6.4.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Mix under stirring approx. 300 mL ultrapure water, 53 mL $w(HCl)$ = 30% and 112.5 mL $w(NH_3)$ = 25%. Leave to cool down, make up with ultrapure water to 500 mL and mix.
- Standard: $\rho(Se^{4+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Se^{4+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(Se^{4+})$ = 1 g/L and 0.5 mL $w(HNO_3)$ 65%, make up to the mark with ultrapure water and mix.

3.6.4.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.2 mL original bath) and 5 mL supporting electrolyte into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.2 V
Stirrer speed	2000 rpm	End potential	–1.6 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.01 V	Peak potential Se(IV)	approx. –1.4 V
Pulse time	0.04 s		

The selenium content is determined according to the standard addition method.

3.6.5 Thallium

3.6.5.1 Sample preparation

Transfer approx. 10 mL ultrapure water into a glass beaker and add 10 mL bath sample and 0.5 mL $w(H_2SO_4)$ = 96%. Add under stirring ascorbic acid (CAS 50-81-7; vitamin C) until the solution turns clear and green (for the analysis only Cr^{3+} must be present). Rinse the solution quantitatively into a 50-mL volumetric flask with ultrapure water, make up to the mark with ultrapure water and mix.

3.6.5.2 Reagents

- Supporting electrolyte: acetate buffer
  In a 250-mL volumetric flask dissolve 9.6 g ammonium acetate (CAS 631-61-8) and 7.2 mL *w*(acetic acid) = 98% (CAS 64-19-7) in approx. 150 mL ultrapure water, make up to the mark and mix.
- Standard: $\rho(Tl^+)$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Tl^+)$ = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL $\rho(Tl^+)$ = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.6.5.3 Analysis

Transfer 5.0 mL prepared sample solution (corresponding to 1 mL original bath), 5 mL ultrapure water and 5 mL supporting electrolyte into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.6 V
Mode	DP	End potential	–0.2 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.6 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Tl(I)	approx. –0.45 V
Pulse amplitude	0.05 V		

The thallium content is determined according to the standard addition method.

Under the above conditions, lead emits a signal that overlies the thallium peak and thus interferes with the thallium determination. If the sample besides thallium also contains lead, an addition of EDTA for the complexation of lead is necessary. Usually, an addition of 0.5 mL of a 0.1 mol/L EDTA-Na_2 solution is sufficient.

3.7 Copper baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Electroless, A	$CuSO_4$, EDTA, formaldehyde, tetraethylammonium hydroxide		
Electroless, B	$CuSO_4$, EDTA, glycolic acid		2,2'-bipyridine
Electroless, C	$CuSO_4$, $NiSO_4$, H_3BO_3, NaH_2PO_2		Trisodiumcitrate, EDTA
Electroless, D	$CuSO_4$, NaOH, formaldehyde		Na/K tartrate Mercaptobenzothiazole
Sulfate baths, acidic	$CuSO_4$, H_2SO_4	NaCl, Cd, As, Fe, Sb, Sn, thiourea	Brightener, carrier, leveler, suppressor[4]
Fluoroborate baths, acidic	$Cu(BF_4)_2$, HBF_4, H_3BO_3	As, Fe, Sb, Sn	Brightener, carrier, leveler, suppressor[5]
Alkaline cyanide baths	CuCN, NaCN, (KCN), Na_2CO_3, NaOH, Na-K tartrate	Ni, Pb, Se, Sn, Zn	Formaldehyde, saccharin, polyethyleneglycol

3.8 Alkaline copper baths

3.8.1 General

This chapter treats chemical, cyanide-free copper baths. If baths containing cyanide have to be analyzed, it is necessary to destroy the cyanide by acidic decomposition under adequate precautions. Subsequently, the analyses can be carried out as described in the chapter *Au baths.*

[4] Most of these additives are patent-protected by the bath producers. A large variety of compounds is used for these applications (e.g., gelatin, polyethyleneglycols, anionic surfactants, mercaptoimidazole, acrylamine and sulfoalkylsulfide compounds, alkylated polyalkylenimides, etc.)

[5] See preceding footnote.

3.8.2 Cobalt and nickel

3.8.2.1 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Add under stirring 53 mL $w(HCl)$ = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime, Na salt: (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standards: ρ(Me) = 1 g/L (Me = Co, Ni)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Me) = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.8.2.2 Analysis

Transfer 10 mL ultrapure water, 3 mL supporting electrolyte and 100 µL bath sample into the polarographic vessel. Add 100 µL DMG solution, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.7 V
Mode	DP	End potential	–1.2 V
Purge time	300 s	Voltage step	0.004 V
Deposition potential	–0.7 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.02 V/s
Equilibration time	5 s	Peak potential Ni	approx. –0.95 V
Pulse amplitude	0.05 V	Peak potential Co	approx. –1.07 V

The metal contents are determined according to the standard addition method.

3.8.2.3 Remarks

With this method very small contents of Co or Ni can be determined. There is, however, an upper determination limit. Including the increments, not more than 100 µg/L Co or Ni should be present because at higher concentrations the surface of the HMDE will become overloaded by the accumulated DMG complex.

3.8.3 Formaldehyde

3.8.3.1 General

Formaldehyde can be reduced polarographically to methanol in alkaline solution. Larger amounts of sodium ions can interfere as sodium is reduced immediately after formaldehyde.

3.8.3.2 Reagents

- Supporting electrolyte: LiOH/EDTA
  Dissolve 9.15 g LiOH x H_2O (CAS 1310-66-3) and 7.44 g Na_2EDTA x 2 H_2O (CAS 6381-92-6) in ultrapure water, make up to 1 liter and mix.
- Standard solution: ρ(HCHO) = 1 g/L
  Start with a concentrated formaldehyde solution (CAS 50-00-0) whose content is determined by titration. Result (for example): w(HCHO) = 35.5%.

  Transfer approx. 200 mL ultrapure water into a 250-mL volumetric flask. Add 0.65 mL formaldehyde solution w = 35.5%, make up to the mark with ultrapure water and mix.

  Titration method

  Dilute 2...3 g formaldehyde solution with ultrapure water to 500 mL and mix. To 10.0 mL of this solution add 25.0 mL $c(I_2)$ = 0.05 mol/L and 2 mL c(NaOH) = 4 mol/L, mix and leave to react for 5 min. Then add 2 mL w(HCl) = 30% and titrate back the excess iodine with $c(Na_2S_2O_3)$ = 0.1 mol/L. The blank value of the iodine solution is determined the same way without formaldehyde. 6.0431.100 Pt Titrode; 1 mL $c(I_2)$ = 0.05 mol/L corresponds to 1.501 mg HCHO.

3.8.3.3 Analysis

Transfer 5 mL supporting electrolyte and 5.0 mL sample solution into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.4 V
Stirrer speed	2000 rpm	End potential	–1.8 V
Mode	DP	Voltage step	0.006 V
Purge time	600 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential HCHO	approx. –1.65 V
Pulse time	0.04 s		

The formaldehyde content is determined according to the standard addition method.

3.8.4 Lead and tin

3.8.4.1 Reagents

- Supporting electrolyte:
  Dissolve 29.5 g trisodium citrate dihydrate (CAS 6132-04-3), 12.6 g oxalic acid dihydrate (CAS 6153-56-6) and 25 mL *w*(HCl) = 30% in ultrapure water, make up with it to 1 liter and mix.
- CTAB solution: *c*(CTAB) = 0.005 mol/L
  Dissolve 0.46 g cetyltrimethylammonium bromide (hexadecyl-trimethylammonium bromide; CAS 57-09-0) in ultrapure water, make up with it to 250 mL and mix.
- Hydrochloric acid: *w*(HCl) = 30%
- Standards: *ρ*(Me) = 1 g/L (Me = Pb, Sn)
  These are commercially available ready for use.
- Standard solutions: *ρ*(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL acid[6] and 1.0 mL *ρ*(Me) = 1 g/L, make up to the mark with ultrapure water and mix.

[6] For Pb: *w*(HNO_3) = 65%, for Sn: *w*(HCl) = 30%.

3.8.4.2 Analysis

Transfer 10 mL supporting electrolyte, 200 µL *w*(HCl) = 30% and 100 µL bath sample into the polarographic vessel. Heat and keep boiling for 30 s. Add another 10 mL supporting electrolyte, leave to cool down, add 200 µL CTAB solution, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.8 V
Mode	DP	End potential	–0.2 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.8 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Sn	approx. –0.54 V
Pulse amplitude	0.05 V	Peak potential Pb	approx. –0.42 V

The lead and tin contents are determined according to the standard addition method.

3.8.5 Selenium

3.8.5.1 Sample preparation

Transfer 25.0 mL bath sample into a three-neck round-bottomed flask and connect a reflux condenser. Under swirling add dropwise 3 mL *w*(H_2SO_4) = 96%, heat and swirl from time to time until the white precipitate has dissolved. If the solution has a blackish coloring add *w*(HNO_3) = 65% until the solution is clear. Leave to cool, rinse the condenser with ultrapure water, heat again and keep boiling for approx. 3 min. Leave to cool down, rinse the flask contents with ultrapure water into a glass beaker and adjust the pH value to 7.0 with *w*(NaOH) = 30%. Filtrate through a paper filter into a 250-mL volumetric flask, rinse the filter with ultrapure water, make up with it to the mark and mix.

3.8.5.2 Reagents

- Na_2EDTA: *c*(Na_2EDTA) = 0.1 mol/L
  Dissolve 3.7 g Na_2EDTA x 2 H_2O (CAS 6381-92-6) in ultrapure water, make up with it to 100 mL and mix.

- Ammonium sulfate: $(NH_4)_2SO_4$ (CAS 7783-20-2)
- Copper sulfate solution: $c(CuSO_4)$ = 0.1 mol/L
  Dissolve 2.5 g $CuSO_4$ x 5 H_2O (CAS 7758-99-8) in ultrapure water, make up with it to 100 mL and mix.
- Se(IV) standard: $\rho(Se^{4+})$ = 1 g/L
  This standard is commercially available ready for use.
- Se(IV) standard solution: $\rho(Se^{4+})$ = 1 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 100 µL $\rho(Se^{4+})$ = 1 g/L and 0.1 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix. This solution has to be freshly prepared daily.

3.8.5.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 1 mL original bath), 1 mL each of $CuSO_4$ and Na_2EDTA solution and 1 g $(NH_4)_2SO_4$ into the polarographic vessel. Adjust the pH of the mixture to 2.2 with H_2SO_4, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.45 V
Mode	DP	End potential	–0.75 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.4 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Se(IV)	approx. –0.63 V
Pulse amplitude	0.05 V		

The selenium content is determined according to the standard addition method.

The decomposition with HNO_3 usually oxidizes Se(IV) to the voltammetrically inactive Se(VI), which must therefore be reduced to Se(IV) before the determination.

3.8.6 Zinc

3.8.6.1 Reagents

- Supporting electrolyte: acetate buffer
  In a 250-mL volumetric flask dissolve 9.6 g ammonium acetate (CAS 631-61-8) and 7.2 mL *w*(acetic acid) = 98% (CAS 64-19-7) in approx. 150 mL ultrapure water, make up with it to the mark and mix.
- Acetic acid: w(CH_3COOH) = 98%
- Caustic soda solution: w(NaOH) = 30%
- Standard: ρ(Zn) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Zn) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Zn) = 1 g/L and 1 mL *w*(CH_3COOH) = 98%, make up to the mark with ultrapure water and mix.

3.8.6.2 Analysis

Transfer 10 mL ultrapure water and 100 µL sample solution into the polarographic vessel. Add 1 mL supporting electrolyte and adjust the pH value to 5.0 with acetic acid or caustic soda solution (depending on the bath composition), deaerate with nitrogen, then record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–1.2 V
Mode	DP	End potential	–0.85 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–1.2 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Zn	approx. –1.01 V
Pulse amplitude	0.05 V		

The zinc content is determined according to the standard addition method.

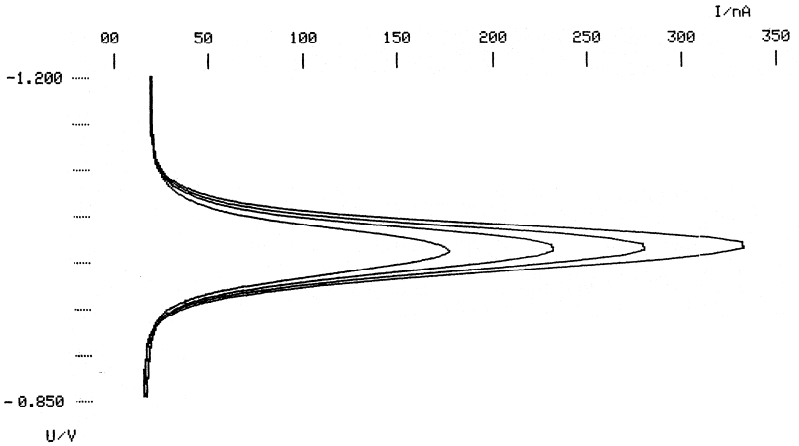

Fig. 13 Determination of 267 mg/L Zn in an alkaline Cu bath by means of ASV (anodic stripping voltammetry).

3.9 Acidic copper baths

3.9.1 Antimony(III)

3.9.1.1 Sample preparation

Make up 1 mL bath sample with ultrapure water in a 100-mL volumetric flask and mix (dilution 1:100).

3.9.1.2 Reagents

- Supporting electrolyte: c(HCl) = 1 mol/L
- Standard: ρ(Sb) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Sb) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL each of ρ(Sb) = 1 g/L and w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.9.1.3 Analysis

Transfer 15 mL supporting electrolyte and 150 µL diluted sample solution (corresponding to 1.5 µL original bath) into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.27 V
Mode	DP	End potential	–0.12 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.25 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Sb	approx. –0.20 V
Pulse amplitude	0.01 V		

The antimony content is determined according to the standard addition method.

3.9.2 Arsenic

3.9.2.1 Sample preparation

Transfer 200 µL bath sample and 10 mL ultrapure water into the reaction vessel. After the addition of 100 µL $w(H_2O_2)$ = 30%, decompose in the 705 UV Digester for 45 min at 90 °C. Leave to cool down, rinse with ultrapure water into a 20-mL volumetric flask, make up with it to the mark and mix. By this decomposition all As(III) is oxidized to As(V).

3.9.2.2 Reagents

- Cu standard solution: $\rho(Cu)$ = 1 g/L
  This standard is commercially available ready for use.
- Se(IV) standard: $\rho(Se^{4+})$ = 1 g/L
  This standard is commercially available ready for use.
- Se(IV) standard solution: $\rho(Se^{4+})$ = 100 mg/L
  Transfer 2.50 mL $\rho(Se^{4+})$ = 1 g/L and 0.1 mL $w(H_2SO_4)$ = 96% into a 25-mL volumetric flask. Make up to the mark with ultrapure water and mix.

- Supporting electrolyte:
  Weigh 4.0 g mannitol (CAS 69-65-8) into a 100-mL volumetric flask and add 40 mL $c(H_2SO_4)$ = 1 mol/L. After the addition of 70 µL $\rho(Se^{4+})$ = 100 mg/L and 1.0 mL ρ(Cu) = 1 g/L make up to the mark with ultrapure water and mix.
- Arsenic(V) standard: $\rho(As^{5+})$ = 1 g/L
  This standard is commercially available ready for use.
- Arsenic(V) standard solution: $\rho(As^{5+})$ =100 mg/L
  Transfer approx. 10 mL ultrapure water and 1 mL $w(HNO_3)$ = 65% into a 25-mL volumetric flask. After the addition of 2.50 mL $\rho(As^{5+})$ = 1 g/L make up to the mark with ultrapure water and mix.

3.9.2.3 Analysis

Transfer 5 mL ultrapure water and 10 mL supporting electrolyte into the polarographic vessel. Deaerate with nitrogen and record a DP stripping voltammogram as a blank run. Apply the same procedure, recording the DP stripping voltammogram (after deaeration) with the same (fresh) solutions plus 20 µL of the prepared sample solution (corresponding to 0.2 µL original bath). The following conditions apply to both voltammograms:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.5 V
Mode	DP	End potential	–0.9 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.65 V	Voltage step time	0.2 s
Deposition time	20 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential As(V)	approx. –0.72 V
Pulse amplitude	0.05 V		

The arsenic content in the blank and in the sample is determined according to the standard addition method. The blank value determined is subtracted from the measured sample concentration.

3.9.2.4 Remarks

As described above in the «Sample preparation» paragraph, this method determines the total arsenic content. It is also possible to determine the proportion of As(III). This determination is carried out in a supporting electrolyte that does not contain any mannitol, but otherwise has the same composition as the supporting electrolyte described above. The instrument parameters also remain the same. The standard additions, however, are carried out with $\rho(As^{3+})$ = 10 mg/L.

3.9.3 Iron

3.9.3.1 Reagents

- Supporting electrolyte:
  Dissolve 24 g citric acid (CAS 77-92-9), 9.3 g Na_2EDTA x 2 H_2O (CAS 6381-92-6) and 25.3 g KNO_3 (CAS 7757-79-1) in approx. 300 mL ultrapure water. Adjust the pH value with w(NaOH) = 30% to 5.0, leave to cool down, make up to 500 mL with ultrapure water and mix.
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Fe^{3+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 0.5 mL $w(H_2SO_4)$ = 96% and 5.0 mL $\rho(Fe^{3+})$ = 1 g/L, make up to the mark with ultrapure water and mix.

3.9.3.2 Analysis

Transfer 10 mL supporting electrolyte, 5 mL ultrapure water and 200 µL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	+0.1 V
Stirrer speed	2000 rpm	End potential	–0.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	5 s	Sweep rate	0.01 V/s
Pulse amplitude	0.01 V	Peak potential Fe(III)	approx. –0.08 V
Pulse time	0.04 s		

The iron content is determined according to the standard addition method.

3.9.4 Tin

3.9.4.1 Reagents

- Supporting electrolyte: *c*(HCl) = approx. 6 mol/L
  Mix 160 mL *w*(HCl) = 30% with ultrapure water and make up to 250 mL.
- Gelatin solution: *w*(gelatin) = 0.1%
  Heat 50 mL ultrapure water to boiling in a glass beaker. Add 0.1 g gelatin (CAS 9000-70-8) and stir until the gelatin has completely dissolved. Add 50 mL ultrapure water, mix and leave to cool. This solution has to be freshly prepared every other day.
- Tin(IV) standard: $\rho(Sn^{4+})$ = 1 g/L
  This standard is commercially available ready for use.
- Tin(IV) standard solution: $\rho(Sn^{4+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL each of $\rho(Sn^{4+})$ = 1 g/L and *w*(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.9.4.2 Analysis

Transfer 15 mL supporting electrolyte, 200 µL bath sample and 100 µL gelatin solution into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.52 V
Stirrer speed	2000 rpm	End potential	–0.75 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	5 s	Sweep rate	0.01 V/s
Pulse amplitude	0.01 V	Peak potential Sn(IV)	approx. –0.60 V
Pulse time	0.04 s		

The tin content is determined according to the standard addition method.

3.9.5 Thiourea

3.9.5.1 General

Chloride ions interfere strongly with the determination of thiourea or even make it impossible if no countermeasures are taken. To eliminate this interference the chloride ions are quantitatively precipitated by the addition of Hg(I) nitrate solution. This addition depends on the chloride ion concentration and can be optimized thus that the interfering peak disappears. Please note that also an excess in mercury nitrate interferes.

3.9.5.2 Reagents

- Hg(I) nitrate solution: ρ = 4 g/L
  Weigh 0.4 g $Hg_2(NO_3)_2$ x 2 H_2O (CAS 7782-86-7) into a 100-mL volumetric flask and add 100 µL $w(HNO_3)$ = 65%. Dissolve in ultrapure water, make up to the mark and mix.
- Gelatin solution: w(gelatin) = 0.1%
  Heat 50 mL ultrapure water to boiling in a glass beaker. Add 0.1 g gelatin (CAS 9000-70-8) and stir until the gelatin has completely dissolved. Add 50 mL ultrapure water, mix and leave to cool. This solution has to be freshly prepared every other day.
- Thiourea standard: ρ(thiourea) = 1 g/L
  Dissolve 100 mg thiourea (CAS 62-56-6) in deaerated ultrapure water, make up with it to 100 mL and mix. This solution has to be freshly prepared daily.
- Thiourea standard solution: ρ(thiourea) = 200 mg/L
  Transfer 20.0 mL ρ(thiourea) = 1 g/L into a 100-mL volumetric flask, make up to the mark with deaerated ultrapure water and mix. Also this solution has to be freshly prepared daily.

3.9.5.3 Analysis

Transfer 10.0 mL bath sample into the polarographic vessel. Add 0.8 mL Hg(I) nitrate solution and 100 µL gelatin solution, deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	+0.3 V
Stirrer speed	2000 rpm	End potential	+0.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	5 s	Sweep rate	0.01 V/s
Pulse amplitude	0.015 V	Peak potential thiourea	approx. +0.24 V
Pulse time	0.04 s		

The thiourea content is determined according to the standard addition method.

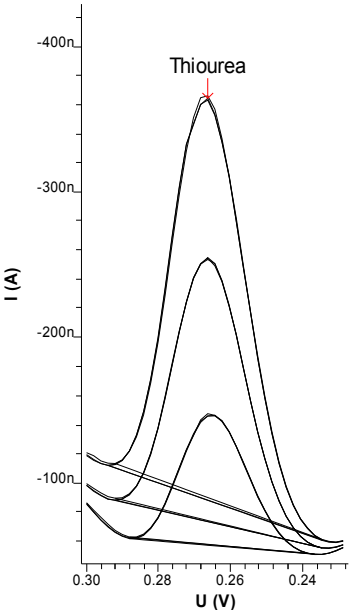

Fig. 14 Polarographic determination of 1.4 mg/L thiourea in an acidic Cu bath.

3.9.6 Suppressor with dilution titration (DT)

3.9.6.1 General

For acidic copper baths different organic additives are always used to adapt the properties of the copper deposit to the technical requirements. In many cases the determination can be carried out by cyclic voltammetry. The concentration of suppressors (also called carriers or levelers) is obtained by dilution titration (DT).

3.9.6.2 Reagents

The concentrations of $CuSO_4$, sulfuric acid and sodium chloride have to correspond to the concentrations in the bath to be analyzed. All the concentrations given are meant as examples.

- VMS – Virgin Make-Up Solution

  $\rho(CuSO_4 \times 5\ H_2O)$ = 60 g/L; w(H_2SO_4, 96%) = 130 mL/L; $\rho(Cl^-)$ = 50 mg/L

  Dissolve 60 g $CuSO_4 \cdot x\ 5\ H_2O$ and 82 mg NaCl in approx. 800 mL deionized water in a 1-L volumetric flask. Carefully add 130 mL H_2SO_4. Attention, the solution gets very hot! Leave to cool to room temperature and make up to the mark with deionized water.

- Suppressor concentrate solution, undiluted

  w(suppressor) = 1000 mL/L

  The suppressor concentrate is normally available ready for use from the manufacturer.

- Suppressor standard solution

  w(suppressor) = 10 mL/L

  Transfer approx. 40 mL VMS into a 50-mL volumetric flask. Add by pipetting 0.5 mL suppressor concentrate. Make up the solution to the mark with VMS. The suppressor concentrate is normally available ready for use from the supplier.

3.9.6.3 Calibration

Transfer 100 mL copper electrolyte without organic additives, the so-called virgin make-up solution (VMS), into a measuring vessel and record the signal of the copper deposition or dissolution, respectively, on the rotating platinum electrode (Pt RDE) by the cyclic voltammetric stripping technique (CVS). After this, several times add 15 µL suppressor standard solution, which causes the copper signal to gradually decrease. Continue the additions until a defined endpoint is reached, then calculate the calibration factor from the amount of suppressor added.

3.9.6.4 Analysis

To determine the suppressor concentration in the bath sample, again transfer 100 mL VMS into the measuring vessel and record the copper signal. Then successively add bath sample portions of 15 µL. The suppressor contained in the sample causes the copper signal to decrease. Continue adding sample portions until the defined endpoint is reached. The sample's suppressor concentration is calculated from the sample volume added and the calibration factor.

Working electrode	RDE
Initial mixing time	5 s
Pretreatment (electrode preparation)	
Equilibration Potential	1.625 V
Equilibration Time	5 s
Sweep	
Hydrodynamic measurement	Yes
Start potential	1.625 V
First vertex potential	–0.175 V
Second vertex potential	1.625 V
Voltage step	0.006 V
Sweep rate	0.1 V/s
No. of sweeps	3
Save last … sweeps	2

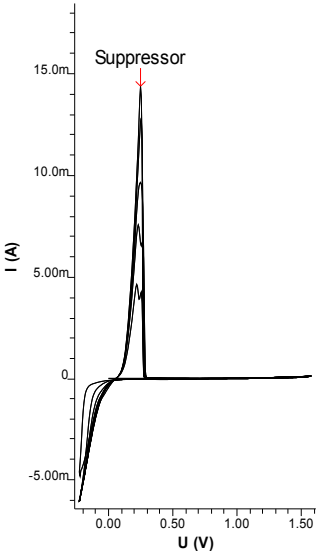

Fig. 15 Measuring curves for the determination of a suppressor in an acidic copper bath by means of CVS (cyclic voltammetric stripping).

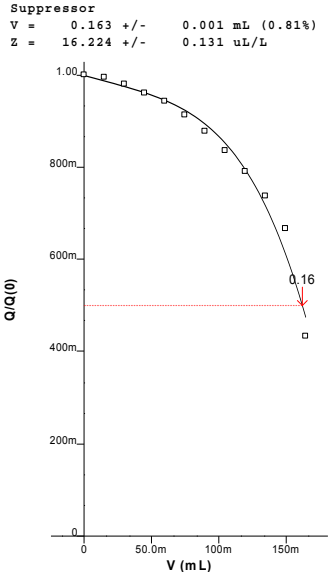

Fig. 16 Calibration curve for the determination of a suppressor in an acidic copper bath by means of dilution titration.

3.9.7 Brighteners with modified linear approximation technique (MLAT)

3.9.7.1 General

The determination of brighteners in acidic copper baths is performed by means of the Modified Linear Approximation Technique (MLAT). This technique is a modified standard addition method.

3.9.7.2 Reagents

The concentrations of $CuSO_4$, sulfuric acid and sodium chloride have to correspond to the concentrations in the bath to be analyzed. All concentration indications are to be regarded as examples.

- VMS – Virgin Make-Up Solution

  $\rho(CuSO_4 \times 5\ H_2O)$ = 60 g/L; c(H_2SO_4, 96%) = 130 mL/L; $\rho(Cl^-)$ = 50 mg/L

  Dissolve 60 g $CuSO_4 \cdot x\ 5\ H_2O$ and 82 mg NaCl in approx. 800 mL deionized water in a 1-L volumetric flask. Carefully add 130 mL H_2SO_4. Attention, the solution gets very hot! Leave to cool to room temperature and make up to the mark with deionized water.

- Suppressor concentrate solution, undiluted

  w(suppressor) = 1000 mL/L

  The suppressor concentrate is normally available ready for use from the manufacturer.

- Brightener standard solution, undiluted

  w(brightener) = 1000 mL/L

  The brightener solution is normally available ready for use from the manufacturer.

- Intercept solution

  $\rho(CuSO_4 \cdot x\ 5\ H_2O)$ = 60 g/L; c(H_2SO_4) = 130 mL/L; $\rho(Cl^-)$ = 50 mg/L; w(suppressor) = 40 mL/L

  Mix 30 mL VMS with 1.2 mL suppressor concentrate solution.

3.9.7.3 Analysis

To determine the intercept value, transfer 30 mL intercept solution into the measuring vessel and record the copper signal applying the parameter values listed below. After this, add 10 mL bath sample and another 0.2 mL suppressor concentrate to keep the suppressor concentration constant. Measure the sample signal. To determine the concentration, carry out two standard additions, each with 15 µL brightener standard solution.

Working electrode	RDE
Initial mixing time	5 s
Pretreatment (electrode preparation)	
Equilibration Potential	1.625 V
Equilibration Time	5 s
Sweep	
Hydrodynamic measurement	Yes
Start potential	1.625 V
First vertex potential	–0.25
Second vertex potential	1.625 V
Voltage step	0.006 V
Sweep rate	0.15 V/s
No. of sweeps	3
Save last … sweeps	2

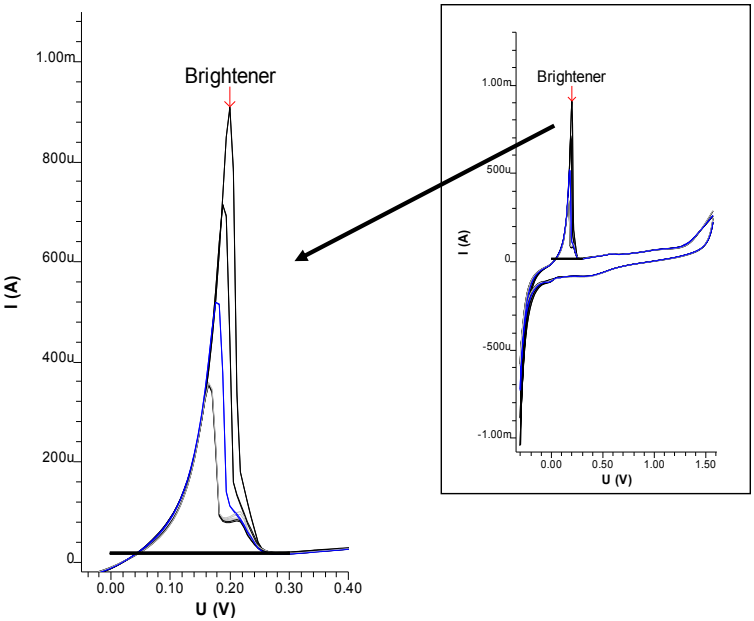

Fig. 17 Determination of 1.5 mL/L brightener in an acidic copper bath by means of CVS – MLAT (cyclic voltammetric stripping – modified linear approximation technique).

3.10 Brass baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Alkaline cyanide baths	Cu, Zn, NaCN, NaOH, Na_2CO_3, Na_2SO_3	Cd, Fe, Ni, Pb	

3.10.1 Cadmium and lead

3.10.1.1 General

What has been a disadvantage in the voltammetric analysis of cyanide baths here turns into an advantage in the analysis of Cd and Pt. The large amounts especially of Cu would strongly interfere with the determination. The cyano complexes of

both Cd and Pb are polarographically active and the peak potentials are displaced only by approx. 0.4 V towards the negative range compared to the free ions. The cyano complexes of Cu are polarographically inactive and those of Zn are displaced so strongly towards the negative voltage range that they do not interfere with the determination of Cu and Pb any more even if present at a large excess.

3.10.1.2 Reagents

- Supporting electrolyte: KCN / ethylenediamine
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Dissolve in it 3.26 g KCN (CAS 151-50-8) and 3.3 mL ethylenediamine (CAS 107-15-3), make up to the mark with ultrapure water and mix.
- Standards: ρ(Me) = 1 g/L (Me = Cd, Pb)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 50-mL volumetric flask. Add 5.0 mL ρ(Me) = 1 g/L and 0.1 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.10.1.3 Analysis

Transfer 15 mL ultrapure water, 1 mL supporting electrolyte and 1.0 mL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.55 V
Stirrer speed	2000 rpm	End potential	–1.3 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	5 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Pb	approx. –0.76 V
Pulse time	0.04 s	Peak potential Cd	approx. –1.1 V

The metal contents are determined according to the standard addition method.

3.10.2 Iron

3.10.2.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 2.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Then carefully add 2 mL $w(H_2SO_4)$ = 96%, heat to boiling and keep boiling until SO_3 fumes appear. Leave to cool down, transfer the decomposition solution quantitatively into a 100-mL volumetric flask with ultrapure water, make up to the mark with it and mix.

3.10.2.2 Reagents

- Supporting electrolyte:
  Dissolve 24 g citric acid (CAS 77-92-9), 9.3 g Na_2EDTA x 2 H_2O (CAS 6381-92-6) and 25.3 g KNO_3 (CAS 7757-79-1) in approx. 300 mL ultrapure water. Adjust the pH value to 5.0 with w(NaOH) = 30%, leave to cool down, make up to 500 mL with ultrapure water and mix.
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Fe^{3+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(Fe^{3+})$ = 1 g/L and 0.5 mL $w(H_2SO_4)$ = 96%, make up to the mark with ultrapure water and mix.

3.10.2.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.2 mL original bath) and 10 mL supporting electrolyte into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	+0.1 V
Stirrer speed	2000 rpm	End potential	–0.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	5 s	Sweep rate	0.01 V/s
Pulse amplitude	0.01 V	Peak potential Fe(III)	approx. –0.08 V
Pulse time	0.04 s		

The iron content is determined according to the standard addition method.

3.10.3 Nickel

3.10.3.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 2.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Then carefully add 2 mL $w(H_2SO_4)$ = 96%, heat to boiling and keep boiling until SO_3 fumes appear. Leave to cool down, transfer the decomposition solution quantitatively into a 100-mL volumetric flask with ultrapure water, make up with it to the mark and mix.

3.10.3.2 Reagents

- Sulfosalicylic acid solution: (CAS 5965-83-3)
  Dissolve 10.17 g 5-sulfosalicylic acid dihydrate in ultrapure water, make up with it to 100 mL and mix.
- Phosphoric acid: $w(H_3PO_4)$ = 85%
- Ammonia: $w(NH_3)$ = 25%
- Standard: ρ(Ni) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Ni) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Ni) = 1 g/L and 0.5 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.10.3.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.2 mL original bath) into the polarographic vessel. Add 0.2 mL H_3PO_4 and 5 mL sulfosalicylic acid and adjust the pH of the mixture to 9.5 with ammonia. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.8 V
Stirrer speed	2000 rpm	End potential	–1.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Ni	approx. –1.02 V
Pulse time	0.04 s		

The nickel content is determined according to the standard addition method.

3.11 Nickel baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Watts bath	$NiSO_4$, $NiCl_2$, H_3BO_3	Cd, Cr, Cu, Fe, Pb, Sb	Saccharin, thiourea
Sulfamate bath	$Ni(SO_3NH_2)_2$, $NiCl_2$, H_3BO_3	Cd, Cu, Pb, Sb	Saccharin, sulfonic acids, benzaldehyde derivatives
Electroless, acidic	$NiCl_2$, NaH_2PO_2, hydroxyacetic acid	Pb, Se, Sn	
Electroless, alkaline	$NiCl_2$, NaH_2PO_2, NH_4Cl, Na citrate	As, Mo, Pb, Se, Sn	Pyridine derivatives

3.11.1 Antimony (total)

3.11.1.1 Reagents

- Supporting electrolyte: *w*(HCl) = 10 %
  Transfer approx. 100 mL ultrapure water into a 250-mL volumetric flask. Add 83 mL *w*(HCl) = 30% make up to the mark with ultrapure water and mix.
- Standard: $\rho(Sb^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Sb^{3+})$ = 10 mg/L
  Transfer 60 mL *w*(HCl) = 30% into a 100-mL volumetric flask. Add 1.0 mL $\rho(Sb^{3+})$ = 1 g/L, make up to the mark with ultrapure water and mix. As the total amount of Sb is determined, the shelf life of the Sb(III) solution poses no problem.

3.11.1.2 Analysis

Transfer 15 mL supporting electrolyte and 20 µL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.3 V
Mode	DP	End potential	–0.1 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.45 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Sb	approx. –0.19 V
Pulse amplitude	0.01 V		

The antimony content is determined according to the standard addition method.

3.11.2 Butynediol (2-butyne-1,4-diol)

3.11.2.1 General

Butynediol is oxidized at 40 °C with periodic acid to a dialdehyde that can be determined polarographically after distillation.

3.11.2.2 Reagents

- Supporting electrolyte: *c*(TMAOH) = 0.5 mol/L
  In a 100-mL volumetric flask dissolve 18.1 g tetramethylammonium hydroxide pentahydrate ($C_4H_{13}NO$ x 5 H_2O, CAS 10414-65-4) in ultrapure water, make up with it to the mark and mix.
- Periodic acid:
  H_5IO_6 (CAS 10450-60-9)
- Butynediol standard: *ρ*(2-butyne-1,4-diol) = 1 g/L
  Dissolve 0.100 g 2-butyne-1,4-diol (CAS 110-65-6) in ultrapure water, make up with it to 100 mL and mix.
- Dialdehyde standard solution: *ρ*(dialdehyde) = 50 mg/L
  As described under sample preparation, 5.0 mL *ρ*(2-butyne-1,4-diol) = 1 g/L is oxidized, distilled, made up with ultrapure water to 100 mL and mixed.

3.11.2.3 Sample preparation

Into a distillation flask transfer 5.0 mL bath sample (or butynediol standard), 50 mL ultrapure water and 3 g periodic acid. Heat to 40 °C (not higher) and keep at this temperature for 10 min. Then distill into a 100-mL volumetric flask that contains 25 mL supporting electrolyte. After distillation make up to the mark with ultrapure water and mix.

3.11.2.4 Analysis

Transfer 20.0 mL prepared sample solution (corresponding to 1 mL original bath) into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.1 V
Stirrer speed	2000 rpm	End potential	–1.5 V
Mode	DP	Voltage step	0.006 V
Purge time	5 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential dialdehyde	approx. –1.37 V
Pulse time	0.04 s		

The butynediol content is determined according to the standard addition method.

3.11.3 Cadmium and lead

3.11.3.1 Reagents

- Supporting electrolyte: acetate buffer
  Dissolve 19.3 g ammonium acetate (CAS 631-61-8) and 14.5 mL *w*(acetic acid) = 96% (CAS 64-19-7) in ultrapure water, make up to 250 mL with it and mix.
- Standards: *ρ*(Me) = 1 g/L (Me = Cd, Pb)
  These are commercially available ready for use.
- Standard solutions: *ρ*(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL *ρ*(Me) = 1 g/L and 0.5 mL *w*(HNO_3) = 65%, make up to the mark with ultrapure water and mix.

3.11.3.2 Analysis

Transfer 10 mL ultrapure water, 5 mL supporting electrolyte and 0.50 mL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.7 V
Mode	DP	End potential	–0.25 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.9 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Pb	approx. –0.38 V
Pulse amplitude	0.05 V	Peak potential Cd	approx. –0.55 V

The metal contents are determined according to the standard addition method.

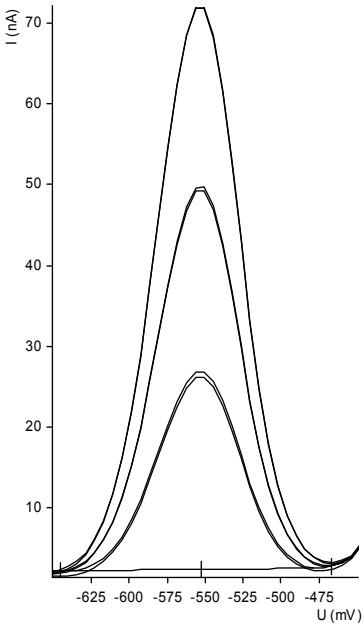

Fig. 18 Determination of 210 µg/L cadmium in a nickel bath by means of ASV (anodic stripping voltammetry).

3.11.4 Cobalt

3.11.4.1 Sample preparation

Depending on the expected Co content the bath sample is diluted with ultrapure water at a ratio of 1:100 to 1:1000.

3.11.4.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Add under stirring 53 mL $w(HCl)$ = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime Na salt: (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standard: $\rho(Co)$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Co)$ = 1 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 100 µL $\rho(Co)$ = 1 g/L and $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.11.4.3 Analysis

Transfer 10 mL ultrapure water, 1 mL supporting electrolyte and 10 µL diluted bath sample into the polarographic vessel. Add 100 µL DMG solution, deaerate with nitrogen and record the DP stripping polarogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.9 V
Mode	DP	End potential	–1.25 V
Purge time	300 s	Voltage step	0.004 V
Deposition potential	–1.0 V	Voltage step time	0.1 s
Deposition time	30 s	Sweep rate	0.04 V/s
Equilibration time	5 s	Peak potential Co	–1.1 V
Pulse amplitude	0.05 V		

The cobalt content is determined according to the standard addition method.

3.11.4.4 Remarks

With this method very low contents of Co can be determined. There is, however, an upper determination limit. Including the increments, not more than 100 µg/L Co should be present because at higher concentrations the surface of the HMDE will become overloaded by the accumulated DMG complex.

3.11.5 Copper

3.11.5.1 Reagents

- Supporting electrolyte: acetate buffer
  Dissolve 9.3 g ammonium acetate (CAS 631-61-8) and 14.5 mL *w*(acetic acid) = 96% (CAS 64-19-7) in ultrapure water, make up to 250 mL and mix.
- Potassium chloride solution: *c*(KCl) = 3 mol/L
  Dissolve 22.4 g KCl (CAS 7447-40-7) in ultrapure water, make up to 100 mL and mix.
- Standard: *ρ*(Cu) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: *ρ*(Cu) = 100 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 10.0 mL *ρ*(Cu) = 1 g/L and 0.5 mL *w*(HNO_3) = 65%, make up to the mark with ultrapure water and mix.

3.11.5.2 Analysis

Transfer 10 mL ultrapure water and 1 mL of each supporting electrolyte and KCl solution into the polarographic vessel. Add 0.50 mL bath sample, deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	+0.05 V
Stirrer speed	2000 rpm	End potential	–0.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Cu	approx. –0.1 V
Pulse time	0.04 s		

The copper content is determined according to the standard addition method.

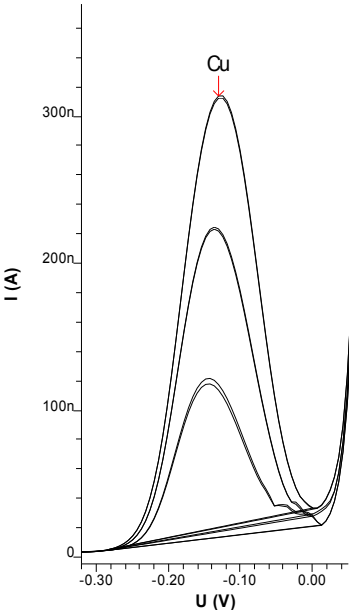

Fig. 19 Polarographic determination of 11.3 mg/L copper in a nickel bath.

3.11.6 Chromium – Cr(VI), Cr(III), Cr total

3.11.6.1 Reagents

- Ammonia: $w(NH_3)$ = 25%
- Ethylenediamine: (CAS 107-15-3)
- Acetic acid: $w(CH_3COOH)$ = 96…98% (CAS 64-19-7)
- Permanganate solution: $c(KMnO_4)$ = 0.02 mol/L
  This solution is commercially available ready for use.
- Standard: $\rho(Cr^{6+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Cr^{6+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(Cr^{6+})$ = 1 g/L and 0.2 mL $w(H_2SO_4)$ = 96%, make up to the mark with ultrapure water and mix.

3.11.6.2 Sample preparation and analysis

Transfer 1.0 mL bath sample and 15 mL ultrapure water into the polarographic vessel. Heat to boiling and dropwise add permanganate solution until the mixture stays pink. Leave to cool down, then add 10 µL ethylenediamine, 150 µL acetic acid and 200 µL ammonia. If necessary, adjust the pH value of the solution to 6.8 ±0.1 with KOH solution. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	+0.14 V
Stirrer speed	2000 rpm	End potential	–0.25 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Cr(VI)	approx. 0 V
Pulse time	0.04 s		

The chromium content is determined according to the standard addition method.

The method described determines the total chromium content – Cr(VI) plus Cr(III). If only the Cr(VI) content has to be determined, the sample preparation (oxidation with permanganate) can be dispensed with. To determine the Cr(III) content, two determinations are required (with and without sample preparation).

3.11.7 Iron

3.11.7.1 Sample preparation

Organic additives in Ni baths (e.g. surfactants) interfere with the Fe determination and have to be eliminated from the bath sample. This is best carried out by UV decomposition with the 705 UV Digester.

Transfer 10 mL ultrapure water, 100 µL bath sample and 50 µL each of w(HCl) = 30% and $w(H_2O_2)$ = 30% into the decomposition vessel. The mixture is then decomposed at 90 °C for 60 min.

3.11.7.2 Reagents

- Pipes buffer:
  Dissolve 6.05 g piperazine-1,4-bis(2-ethane sulfonic acid) (CAS 5625-37-6) in 1 mL $w(NaOH)$ = 30% and 7 mL ultrapure water. Adjust the pH value to 7.0 with $w(NH_3)$ = 25%, make up to 20 mL with ultrapure water and mix.
- Catechol: 1,2-dihydroxybenzene (pyrocatechol; CAS 120-80-9)
  Purify by sublimation before use.
- Ammonia: $w(NH_3)$ = 25%
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Fe^{3+})$ = 1 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 100 µL $\rho(Fe^{3+})$ = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.11.7.3 Analysis

Using a small amount of ultrapure water, transfer the digested sample solution (corresponding to 0.1 mL original bath) into the polarographic vessel and deaerate for 3 min with nitrogen. Add a few catechol crystals and 0.2 mL pipes buffer and adjust the pH value to 7.0 with ammonia. Deaerate once more with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.3 V
Mode	DP	End potential	–0.6 V
Purge time	180 s	Voltage step	0.006 V
Deposition potential	–0.3 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Fe(III)	approx. –0.45 V
Pulse amplitude	0.05 V		

The iron content is determined according to the standard addition method.

3.11.8 Saccharin

3.11.8.1 Reagents

- Supporting electrolyte:
  Transfer approx. 100 mL ultrapure water into a 250-mL volumetric flask. Dissolve in it 75 mL $w(NH_3)$ = 25%, 12.5 g NH_4Cl and 95 g Na_2EDTA x 2 H_2O (CAS 6381-92-6), make up to the mark with ultrapure water and mix.
- Sulfite solution: $w(Na_2SO_3)$ = 3%
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Dissolve in it 3 g Na_2SO_3 (CAS 7757-83-7), make up to the mark with ultrapure water and mix.
- Standard solution: ρ(saccharin) = 2 g/L
  Dissolve 200 mg saccharin (CAS 81-07-2) in c(NaOH) = 0.1 mol/L in a 100-mL volumetric flask, make up with it to the mark and mix.

3.11.8.2 Analysis

Transfer 20 mL supporting electrolyte, 1 mL sulfite solution and 1.0 mL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.5 V
Stirrer speed	2000 rpm	End potential	–1.85 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.01 V	Peak potential saccharin	approx. –1.74 V
Pulse time	0.04 s		

The saccharin content is determined according to the standard addition method.

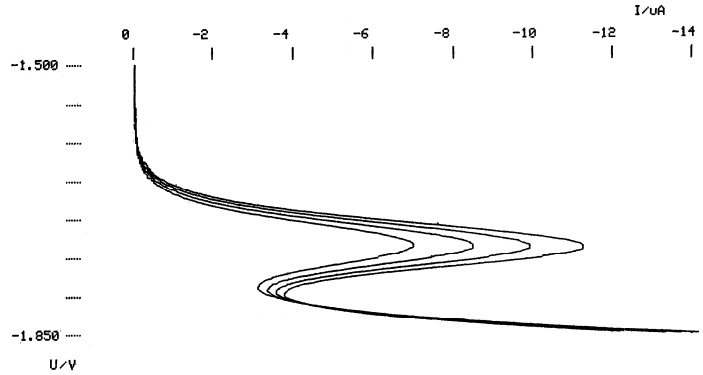

Fig. 20 Polarographic determination of 1.75 g/L saccharin in a nickel bath.

3.11.9 Thiourea

3.11.9.1 Reagents

- Ammonia buffer:
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Dissolve in it 5.4 g NH_4Cl and 15 mL $w(NH_3)$ = 25%, make up to the mark with ultrapure water and mix.
- Sodium acetate solution:
  Dissolve 8.2 g sodium acetate (CAS 127-09-3) in ultrapure water, make up with it to 100 mL and mix.
- Standard: ρ(thiourea) = 1 g/L
  Dissolve 100 mg thiourea (CAS 62-56-6) in deaerated ultrapure water, make up with it to 100 mL and mix. This standard solution must be freshly prepared daily.
- Standard solution: ρ(thiourea) = 1 mg/L
  Transfer approx. 90 mL deaerated ultrapure water into a 100-mL volumetric flask. Add 100 µL ρ(thiourea) = 1 g/L, make up to the mark with deaerated ultrapure water and mix. This solution must be freshly prepared before each sample series.

3.11.9.2 Analysis

Transfer 10 mL ultrapure water, 250 µL sodium acetate solution and 10 µL bath sample into the polarographic vessel. Adjust the pH value to exactly 8.9 by cautiously adding ammonia buffer (needs approx. 30 µL), deaerate with nitrogen, then record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	+0.1 V
Mode	DP	End potential	–0.6 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	+0.1 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential thiourea	approx. –0.38 V
Pulse amplitude	0.05 V		

The thiourea content is determined according to the standard addition method.

3.12 Lead and tin-lead baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Pb, acidic	Pb, methane-sulfonic acid	Cd, Cu, Zn	Patent-protected
Pb, alkaline	Pb, NaOH, Na acetate, Na tartrate	Cd, Cu, Zn	Colophony
Sn/Pb, acidic A	Pb, Sn, alkyl-sulfonic acid(s)	Cd, Cu, Fe, Ge, Ni, Zn	Cationic and/or non-ionic surfactants
Sn/Pb, acidic B	Pb, Sn, HBF_4	Cd, Cu, Fe, Ge, Ni, Zn	Resorcinol, gelatin

3.12.1 Cadmium, copper, nickel and zinc

3.12.1.1 Sample preparation

Work in the fume hood because of the formation of toxic acid fumes!

Transfer 5.0 mL sample into a Kjeldahl flask. Add 2 mL $w(H_2SO_4)$ = 96%, heat and keep boiling until SO_3 fumes appear. Leave to cool down, add approx. 50 mL ultrapure water, heat and keep boiling for approx. 3 min. Leave to cool down, filtrate the solution through a paper filter into a 100-mL volumetric flask, rinse the Kjeldahl

flask and filter with ultrapure water, make up to the mark with ultrapure water and mix.

3.12.1.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Under stirring add 53 mL w(HCl) = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime, Na salt: (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standards: ρ(Me) = 1 g/L (Me = Cd, Cu, Ni, Zn)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Me) = 1 g/L and 1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.12.1.3 Analysis

Transfer 20.0 mL prepared sample solution (corresponding to 1.0 mL original bath) and 5 mL supporting electrolyte into the polarographic vessel. Add 100 µL DMG solution and deaerate with nitrogen, then record the DP polarogram under the following conditions:

Working electrode	DME	End potential	–1.45 V
Stirrer speed	2000 rpm	Voltage step	0.006 V
Mode	DP	Voltage step time	0.6 s
Purge time	300 s	Sweep rate	0.01 V/s
Equilibration time	3 s	Peak potential Cu	approx. –0.25 V
Pulse amplitude	0.05 V	Peak potential Cd	approx. –0.62 V
Pulse time	0.04 s	Peak potential Ni	approx. –0.95 V
Start potential	–0.1 V	Peak potential Zn	approx. –1.33 V

The metal contents are determined according to the standard addition method.

3.12.2 Iron

3.12.2.1 Sample preparation

The sample preparation is the same as for the determination of Cd, Cu, Ni and Zn. For the determination of iron the same decomposition solution may be used.

3.12.2.2 Reagents

- Sulfosalicylic acid solution: (CAS 5965-83-3)
  Dissolve 10.17 g 5-sulfosalicylic acid dihydrate in ultrapure water, make up with it to 100 mL and mix.
- Phosphoric acid: $w(H_3PO_4)$ = 85%
- Ammonia: $w(NH_3)$ = 25%
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Fe^{3+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(Fe^{3+})$ = 1 g/L and 1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.12.2.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.5 mL original bath) into the polarographic vessel. Add 0.2 mL H_3PO_4 and 5 mL sulfosalicylic acid solution and adjust the pH to 9.5 with ammonia. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–1.3 V
Stirrer speed	2000 rpm	End potential	–1.6 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Fe(III)	approx. –1.48 V
Pulse time	0.04 s		

The iron content is determined according to the standard addition method.

3.12.3 Germanium

3.12.3.1 Reagents

- Supporting electrolyte: acetate buffer
  Dissolve 19.3 g ammonium acetate (CAS 631-61-8) and 14.5 mL *w*(acetic acid) = 96% (CAS 64-19-7) in ultrapure water, make up with it to 250 mL and mix.
- Catechol:
  1,2-dihydroxybenzene, p.a. (CAS 120-80-9)
- Standard: *ρ*(Ge) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: *ρ*(Ge) = 1 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 100 µL *ρ*(Ge) = 1 g/L and 0.5 mL *w*(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.12.3.2 Analysis

Transfer 10 mL ultrapure water, 1 mL supporting electrolyte, 100 µL bath sample and a few catechol crystals into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.5 V
Mode	DP	End potential	–0.9 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.5 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Ge	approx. –0.7 V
Pulse amplitude	0.05 V		

The germanium content is determined according to the standard addition method.

3.12.4 Organic additive with dilution titration – DT

3.12.4.1 General

The determination of organic additives in acidic tin and tin-lead baths can be carried out in many cases by cyclic voltammetry. In this example a methanesulfonic acid tin bath is used. Usually a mixture of additive solutions is applied whose content can be determined by dilution titration (DT).

3.12.4.2 Reagents

The concentrations of tin and methanesulfonic acid have to correspond to the concentrations in the bath to be analyzed. All concentration indications are meant as examples.

- VMS – virgin make-up solution

  ρ(Sn) = 15 g/L; ρ (Pb) = 2.7 g/L; c(MSA) ≈ 0.6 mol/L

  This solution can be set up only from a concentrated tin solution that contains pure Sn(II) at a defined concentration. Transfer 600 mL deionized water into a 1-L volumetric flask. Add 50 mL concentrated tin solution, 6 mL concentrated lead solution, 2 mL antioxidant solution and 65 mL methanesulfonic acid. Make up to the mark with deionized water.

- Additive concentrate solution, undiluted

  w(additive) = 1000 mL/L

  The additive concentrate is normally available ready for use from the manufacturer.

- Additive standard solution

  w(additive) = 40 mL/L

  Transfer 50 mL deionized water into a 100-mL volumetric flask. Add 10 mL concentrated tin solution, 0.2 mL antioxidant solution, 0.8 mL methanesulfonic acid and 4 mL concentrated additive. Make up to the mark with deionized water.

3.12.4.3 Calibration

Transfer 100 mL electrolyte without organic additives, the so-called virgin make-up solution (VMS), into the measuring vessel and record the signal of the tin deposition or dissolution on the rotating platinum disk electrode (Pt RDE) using the cyclic voltammetric stripping technique (CVS). Subsequently, add several times portions of 120 µL of additive standard solution, which causes the tin signal to decrease gradually. The additions are continued until a defined endpoint is reached. The calibration factor is then calculated from the quantities of additive added.

3.12.4.4 Analysis

To determine the additive concentration in the bath sample, again transfer 100 mL VMS into the measuring vessel and record the tin signal. Then successively add bath sample portions of 120 µL. The additive contained in the sample causes the tin signal to decrease. Continue adding sample portions until the defined endpoint is reached. The sample's additive concentration is calculated from the sample volume added and the calibration factor.

Working electrode	RDE
Initial mixing time	10 s
Pretreatment (electrode preparation)	
Cleaning potential	0.5 V
Cleaning time	10 s
Equilibration potential	0.475 V
Equilibration time	5 s
Sweep	
Hydrodynamic measurement	Yes
Start potential	0.475 V
First vertex potential	–0.625 V
Second vertex potential	0.475 V
Voltage step	0.006 V
Sweep rate	0.08 V/s
No. of sweeps	3
Save last … sweeps	2

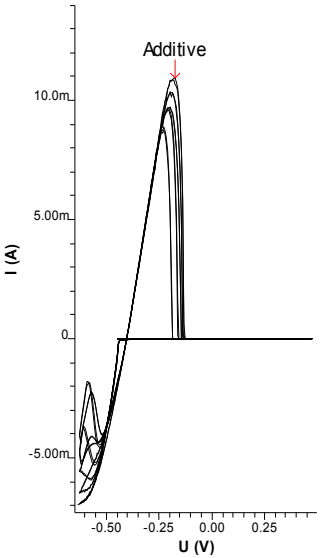

Fig. 21 Measurement curves for the determination of an additive in a tin/lead bath by means of CVS (cyclic voltammetric stripping).

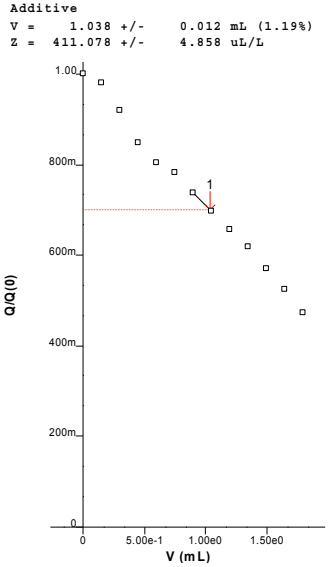

Fig. 22 Calibration curve for the determination of an additive in a tin/lead bath by means of dilution titration.

3.13 Palladium baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Alkaline baths	$PdCl_2$ or $Pd(NH_4)_2(NO_2)_2$, Na_2SO_4, NH_3	Ni, Se	
Acidic baths	$PdCl_2$ or H_2PdCl_4, NH_4Cl, HCl	Cr, Ni, Se	Saccharin, diamines

3.13.1 Chromium – Cr(VI) and total Cr

3.13.1.1 Sample preparation for total chromium

According to the analysis method described below only Cr(VI) is determined. The content of Cr(III) is calculated via the determination of total chromium after Cr(III) has been oxidized to Cr(VI) with H_2O_2.

Work in the fume hood!

In a glass beaker dilute 5.0 mL bath sample with approx. 50 mL ultrapure water and adjust the pH value to approx. 12 with $w(NaOH) = 30\%$. Slowly add 0.5 mL $w(H_2O_2) = 30\%$. Wait for a possible violent initial reaction to subside, then heat and keep boiling for 3 min. Leave to cool down and filtrate through a paper filter into a 100-mL volumetric flask. Rinse the glass beaker and filter with ultrapure water, then make up to the mark with ultrapure water and mix. (The oxidation of the chromium can also be carried out with the 705 UV Digester.)

3.13.1.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer pH = 10
  Dissolve 13.4 g NH_4Cl and 19 mL $w(NH_3) = 25\%$ in ultrapure water, make up with it to 250 mL and mix.
- Standard: $\rho(Cr^{6+}) = 1$ g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Cr^{6+}) = 50$ mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(Cr^{6+}) = 1$ g/L, make up to the mark with ultrapure water and mix.

3.13.1.3 Analysis

Transfer 0.50 mL bath sample and 10 mL ultrapure water (for Cr(VI)) or 10.0 mL prepared sample solution (for total Cr) into the polarographic vessel and add 5 mL supporting electrolyte. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.2 V
Stirrer speed	2000 rpm	End potential	–0.7 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Cr(VI)	approx. –0.48 V
Pulse time	0.04 s		

The chromium content is determined according to the standard addition method.

3.13.2 Manganese

3.13.2.1 Reagents

- Supporting electrolyte:
  Dissolve 3.81 g sodium tetraborate decahydrate (CAS 1303-96-4) and 3 mL w(NaOH) = 30% in ultrapure water, make up to the mark in the 100-mL volumetric flask and mix.
- Ammonia buffer:
  Dissolve 5.36 g NH_4Cl and 15 mL $w(NH_3)$ = 25% in ultrapure water, make up to the mark in the 100-mL volumetric flask and mix.
- Standard: ρ(Mn) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Mn) = 100 mg/L
  Transfer approx. 50 mL ultrapure water into a 100 mL volumetric flask. Add 10.0 mL ρ(Mn) = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.13.2.2 Analysis

Transfer 5 mL ultrapure water and 2.5 mL each of supporting electrolyte and ammonia buffer into the polarographic vessel. Add 200 µL bath sample, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–1.62 V
Mode	DP	End potential	–1.25 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–1.7 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Mn(II)	approx. –1.44 V
Pulse amplitude	–0.075 V		

The manganese content is determined according to the standard addition method.

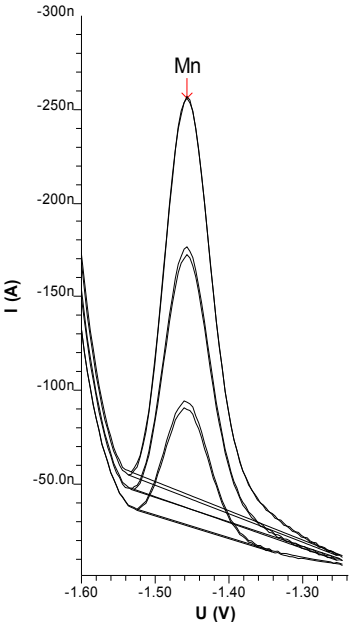

Fig. 23 Determination of 8.5 mg/L manganese in a palladium bath by means of ASV (anodic stripping voltammetry).

3.13.3 Nickel

3.13.3.1 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Under stirring add 53 mL w(HCl) = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime, Na salt (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standard: ρ(Ni) = 1 g/L
  This standard is commercially available ready for use.
- Standard solutions: ρ(Ni) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Ni) = 1 g/L and 1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.13.3.2 Analysis

Transfer 10 mL ultrapure water, 5 mL supporting electrolyte and 200 µL bath sample into the polarographic vessel. Add 100 µL DMG solution, deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.7 V
Stirrer speed	2000 rpm	End potential	–1.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Ni	approx. –0.95 V
Pulse time	0.04 s		

The nickel content is determined according to the standard addition method.

3.13.4 Palladium and selenium

With these baths it is worthwhile to determine also the Pd content voltammetrically.

3.13.4.1 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Dissolve13.4 g NH_4Cl and 19 mL $w(NH_3)$ = 25% in ultrapure water, make up with it to 250 mL and mix.
- Ammonia: $w(NH_3)$ = 25%
- Hydrochloric acid: w(HCl) = 30%
- Standard: ρ(Pd) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Pd) = 200 mg/L
  Transfer 2.0 mL ρ(Pd) = 1 g/L into a 10-mL volumetric flask, add 2 mL supporting electrolyte, make up to the mark with ultrapure water and mix.
- Standard: $\rho(Se^{4+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Se^{4+})$ = 100 mg/L
  Transfer 1.0 mL $\rho(Se^{4+})$ = 1 g/L into a 10-mL volumetric flask, add 2 mL supporting electrolyte, make up to the mark with ultrapure water and mix.

3.13.4.2 Analysis

Transfer 10 mL ultrapure water, 2 mL supporting electrolyte and 50 µL bath sample into the polarographic vessel. Adjust the pH value of the mixture to exactly 8.5 with ammonia or hydrochloric acid, deaerate with nitrogen and record the DP polarogram under the following conditions:

	Se	Pd
Working electrode	DME	DME
Stirrer speed	2000 rpm	2000 rpm
Mode	DP	DP
Purge time	300 s	300 s
Equilibration time	3 s	3 s
Pulse amplitude	0.05 V	0.05 V
Pulse time	0.04 s	0.04 s
Start potential	–1.3 V	–0.2 V
End potential	–1.7 V	–1.0 V
Voltage step	0.006 V	0.006 V
Voltage step time	0.6 s	0.6 s
Sweep rate	0.01 V/s	0.01 V/s
Peak potential Pd		approx. –0.73 V
Peak potential Se(VI)	approx. –1.48 V	

The palladium and selenium contents are determined according to the standard addition method.

Because of the large concentration differences (Pd = main component, Se = secondary component) we recommend to carry out the selenium determination first!

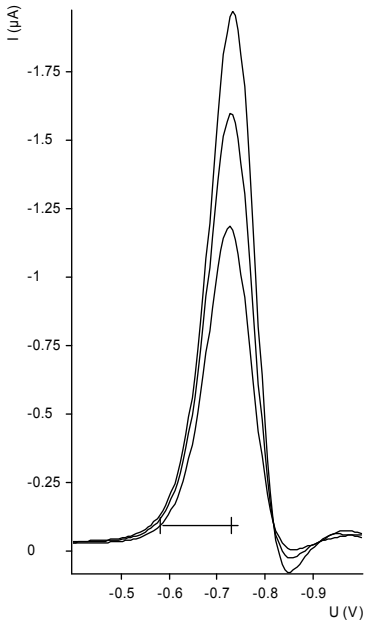

Fig. 24 Polarographic determination of 6.8 g/L palladium in a palladium bath.

3.13.5 Saccharin

3.13.5.1 Reagents

- Ammonia buffer:
  Dissolve13.4 g NH_4Cl and 17 mL $w(NH_3)$ = 25% in ultrapure water, make up with it to 250 mL and mix.
- KCN solution: w(KCN) = 10%
  Dissolve 10 g KCN in ultrapure water, make up with it to 100 mL and mix.
- Acetic acid ethyl ester: p.a. (CAS 141-78-6)
- Tetrachloromethane: p.a. (CAS 56-23-5)
- Standard solution: ρ(saccharin) = 1 g/L
  Dissolve 100 mg saccharin (CAS 81-07-2) in c(NaOH) = 0.1 mol/L in a 100-mL volumetric flask, make up to the mark with c(NaOH) = 0.1 mol/L and mix.

3.13.5.2 Sample preparation

Work in the fume hood, toxic HCN and solvent vapors are released!

As Pd interferes in the determination it has to be separated as a cyanide complex. Transfer 1.0 mL bath sample, 20 mL ultrapure water and 5 mL KCN solution into a separating funnel and mix. After the addition of 5 mL hydrochloric acid and 20 mL each of ethyl acetate and tetrachloromethane, the saccharin is extracted by shaking during 2 min. After the phase separation, the aqueous phase is discarded. Add 20 mL ammonia buffer to the organic phase and reextract the saccharin by shaking out into the aqueous phase during 1 min. After the phase separation, drain the aqueous phase into a glass beaker, add 5 mL hydrochloric acid and heat briefly to eliminate any remaining solvents. Leave to cool down, rinse quantitatively into a 50-mL volumetric flask with ultrapure water, make up with it to the mark and mix.

3.13.5.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 200 µL original bath) and 2.5 mL ammonia buffer into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.8 V
Stirrer speed	2000 rpm	End potential	–1.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.01 V	Peak potential saccharin	approx. –1.07 V
Pulse time	0.04 s		

The saccharin content is determined according to the standard addition method.

3.14 Rhodium baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Acidic Rh baths	Rh, H_2SO_4, H_3PO_4	Cu, Fe, Ni	

3.14.1 Copper

3.14.1.1 Reagents

- Supporting electrolyte: $w(NH_4OOCCH_3)$ = 4 mol/L
  Dissolve 154 g ammonium acetate (CAS 631-61-8) in ultrapure water, make up with it to 500 mL and mix.
- Standard: ρ(Cu) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Cu) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Cu) = 1 g/L and 0.1 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.14.1.2 Sample preparation

Transfer 5.0 mL bath sample into a glass beaker, heat and evaporate to dryness. Add 5 mL supporting electrolyte, heat and keep boiling for 2...3 min, then leave to cool.

3.14.1.3 Analysis

Using ultrapure water, rinse the prepared sample solution quantitatively into the polarographic vessel, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.3 V
Mode	DP	End potential	+0.2 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.3 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Cu	approx. –0.01 V
Pulse amplitude	0.05 V		

The copper content is determined according to the standard addition method.

3.14.2 Iron

3.14.2.1 Reagents

- Supporting electrolyte: *c*(ammonium oxalate) = 1 mol/L
  Dissolve 142 g ammonium oxalate (CAS 6009-70-7) in approx. 700 mL ultrapure water. Adjust the pH value with w(HCl) = 30% to 4.0, make up with ultrapure water to 1 liter and mix.
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use and may be used directly as standard solution.

3.14.2.2 Analysis

Transfer 10 mL supporting electrolyte and 100 µL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	0 V
Stirrer speed	2000 rpm	End potential	–0.4 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Fe	approx. –0.18 V
Pulse time	0.04 s		

The iron content is determined according to the standard addition method.

3.14.3 Nickel

3.14.3.1 Reagents

- Supporting electrolyte:
  Dissolve 10.17 g 5-sulfosalicylic acid dihydrate (CAS 5965-83-3) in ultrapure water, make up with it to 100 mL and mix.
- Ammonia: *w*(NH_3) = 25%
- Dimethylglyoxime, Na salt (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.

- Standard: ρ(Ni) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Ni) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL ρ(Ni) = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.14.3.2 Analysis

Transfer 10 mL ultrapure water and 100 µL bath sample into the polarographic vessel. Add 2 mL supporting electrolyte, 1 mL ammonia and 100 µL DMG solution, deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	–0.8 V
Stirrer speed	2000 rpm	End potential	–1.2 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Ni	approx. –1.02 V
Pulse time	0.04 s		

The nickel content is determined according to the standard addition method.

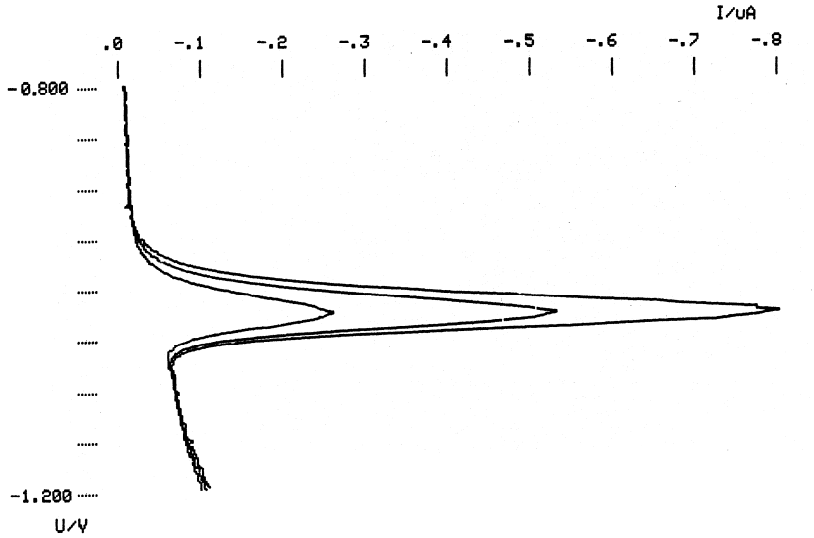

Fig. 25 Polarographic determination of 19.3 mg/L nickel in a rhodium bath.

3.15 Tin baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Fluoroborate baths	Sn, HBF_4, H_3BO_3	Bi, Cd, Cu, In, Ni, Pb, Zn	
Sulfate baths	$SnSO_4$, H_2SO_4	Bi, Cd, Cu, In, Ni, Pb, Zn	Alkylphenols, heterocyclic aldehydes
Phenolsulfonate baths	Sn, phenol-sulfonic acid	Fe, Ni Zn	Ethoxylated ß-naph-tholsulfonic acids
Stannate baths	$K_2Sn(OH)_6$, KOH	Cu, Ni, Zn	

3.16 Acidic tin baths

3.16.1 Bismuth and indium

3.16.1.1 Reagents

- Supporting electrolyte: *c*(HMTA) = 2 mol/L
  Dissolve 56 g hexamethylenetetramine (CAS 100-97-0) in ultrapure water, make up with it to 200 mL and mix.
- Hydrochloric acid: *w*(HCl) = 30%
- Bi standard: ρ(Bi) = 1 g/L
  This standard is commercially available ready for use.
- Bi standard solution: ρ(Bi) = 2 mg/L
  Transfer 10 mL ultrapure water into a 20-mL volumetric flask. Add 2 mL each of supporting electrolyte and hydrochloric acid plus 40 µL ρ(Bi) = 1 g/L, make up to the mark with ultrapure water and mix. This solution has to be freshly prepared every other day and left standing for at least 30 min before use.
- In standard: $\rho(In^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- In standard solution: $\rho(In^{3+})$ = 50 mg/L
  Transfer 10 mL ultrapure water into a 20-mL volumetric flask. Add 2 mL each of supporting electrolyte and hydrochloric acid plus 1.0 mL $\rho(In^{3+})$ = 1 g/L, make up to the mark with ultrapure water and mix. This solution has to be freshly prepared every other day and left standing for at least 30 min before use.

3.16.1.2 Analysis – Bi

Transfer 10 mL ultrapure water, 3 mL each of supporting electrolyte and hydrochloric acid plus 200 µL bath sample into the polarographic vessel. Leave standing for 25 min, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse amplitude	0.01 V
Stirrer speed	2000 rpm	Pulse time	0.04 s
Mode	DP	Start potential	–0.2 V
Purge time	300 s	End potential	–0.03 V
Addition purge time	60 s	Voltage step	0.006 V
Deposition potential	–0.2 V	Voltage step time	0.2 s
Deposition time	75 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Bi	approx. –0.1 V

The bismuth content is determined according to the standard addition method.

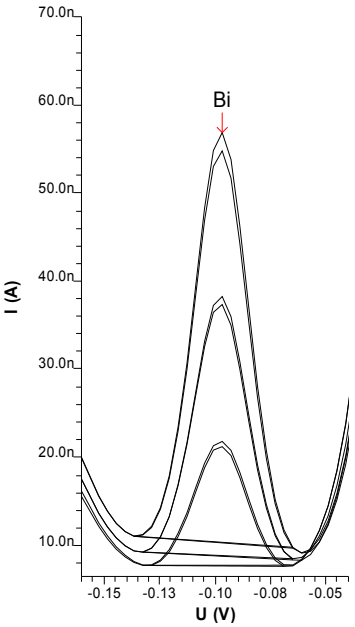

Fig. 26 Determination of 1.7 mg/L bismuth in a tin bath by means of ASV (anodic stripping voltammetry).

3.16.1.3 Analysis – In

Transfer 10 mL ultrapure water, 3 mL each of supporting electrolyte and hydrochloric acid, plus 50 µL bath sample into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse amplitude	0.05 V
Stirrer speed	2000 rpm	Pulse time	0.05 s
Mode	DP	Start potential	–0.68 V
Purge time	300 s	End potential	–0.53 V
Addition purge time	60 s	Voltage step	0.006 V
Deposition potential	–0.68 V	Voltage step time	0.2 s
Deposition time	5 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential In(III)	approx. –0.60 V

The indium content is determined according to the standard addition method.

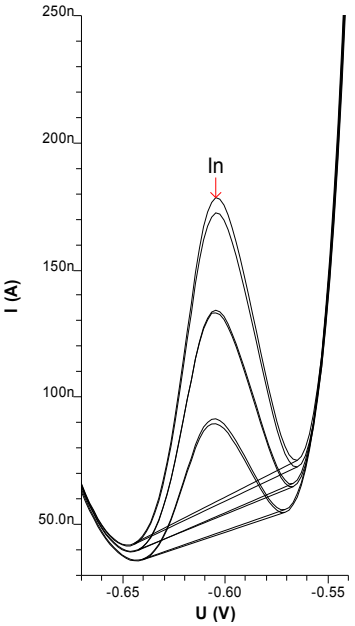

Fig. 27 Determination of 61.4 mg/L indium in a tin bath by means of ASV (anodic stripping voltammetry).

3.16.2 Cadmium, copper and lead

3.16.2.1 Sample preparation

The very large tin content interferes with the determination of Cd and Pb. Tin is therefore separated as $SnBr_4$ by distillation.

Transfer 10.0 mL bath sample, 20 mL ultrapure water, 10 g KBr and 30 mL $w(H_2SO_4)$ = 96% into a three-neck round-bottomed flask, connect it to the distillation apparatus and introduce nitrogen. Then heat to 230 °C and maintain at this temperature for 10 min. Leave to cool down, rinse the cooler with ultrapure water, heat again and add portions of $w(H_2O_2)$ = 30% until the flask contents remain clear even when SO_3 fumes appear. Leave to cool down, rinse the flask contents with ultrapure water quantitatively into a glass beaker. Add 2 g ammonium acetate (CAS 631-61-8) and neutralize the mixture with w(NaOH) = 30% to a pH value of 4...5. Heat again and keep the solution boiling for 1...2 min. Leave to cool down, rinse the solution into a 100-mL volumetric flask with ultrapure water, make up to the mark and mix.

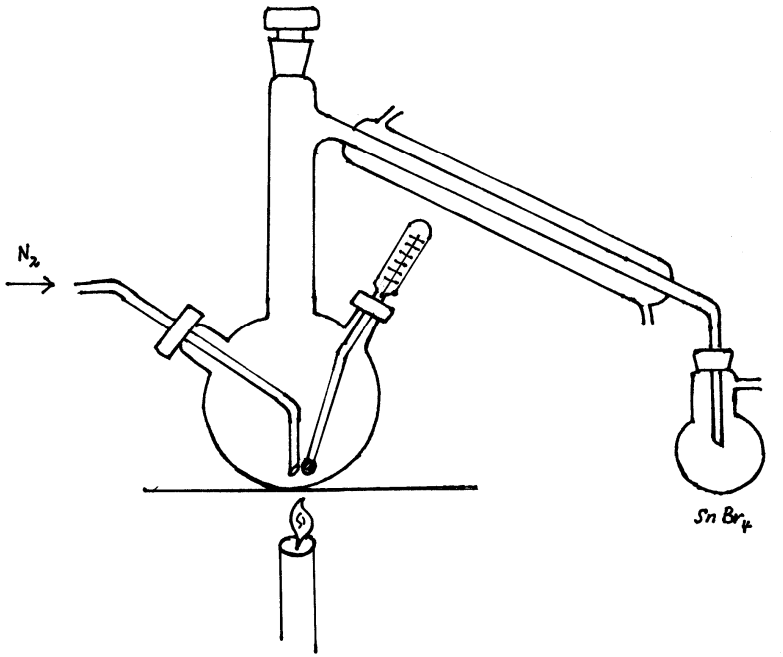

Fig. 28 Distillation apparatus for the elimination of tin.

3.16.2.2 Reagents

- Standards: ρ(Me) = 1 g/L (Me = Cd, Cu, Pb)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Me) = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.16.2.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 1 mL original bath) into the polarographic vessel, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Start potential	–0.8 V
Stirrer speed	2000 rpm	End potential	–0.1 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.2 s
Deposition potential	–0.8 V	Sweep rate	0.03 V/s
Deposition time	60 s	Peak potential Cd	approx. –0.62 V
Equilibration time	5 s	Peak potential Pb	approx. –0.46 V
Pulse amplitude	0.01 V	Peak potential Cu	approx. –0.25 V
Pulse time	0.04 s		

The metal contents are determined according to the standard addition method.

3.16.3 Copper, nickel and zinc

3.16.3.1 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Add under stirring 53 mL *w*(HCl) = 30% and 112.5 mL *w*(NH_3) = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Dimethylglyoxime, Na salt: (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standards: *ρ*(Me) = 1 g/L (Me = Cu, Ni, Zn)
  These are commercially available ready for use.
- Standard solutions: *ρ*(Me) = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL *ρ*(Me) = 1 g/L and 1 mL *w*(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.16.3.2 Analysis

Transfer 10 mL ultrapure water, 5 mL supporting electrolyte and 0.50 mL bath sample into the polarographic vessel. Add 100 µL DMG solution, deaerate with nitrogen and record the DP polarogram under the following conditions:

Working electrode	DME	End potential	–1.45 V
Stirrer speed	2000 rpm	Voltage step	0.006 V
Mode	DP	Voltage step time	0.6 s
Purge time	300 s	Sweep rate	0.01 V/s
Equilibration time	3 s	Peak potential Cu	approx. –0.25 V
Pulse amplitude	0.05 V	Peak potential Ni	approx. –0.95 V
Pulse time	0.04 s	Peak potential Zn	approx. –1.33 V
Start potential	–0.1 V		

The metal contents are determined according to the standard addition method.

3.17 Zinc baths

Bath type	Main constituents	Secondary constituents/ contaminants	Organic additives
Alkaline cyanide bath	$Zn(CN)_2$, NaCN, NaOH, Na_2CO_3, Na_XS_Y	Bi, Cd, Co, Cu, Fe, Ge, Ni, Pb, Sb, Tl	Alkylphenols, heterocyclic aldehydes
Acidic chloride bath	$ZnCl_2$, NH_4Cl	Cu, Fe, Ni	Polyamines, heterocyclic carbonyl compounds

3.17.1 General

Alkaline zinc baths have to be decomposed by acids, as cyanide ions interfere with the voltammetric determination of the metals.

With *acidic zinc baths or zinc electrolytes* a decomposition is usually not required. The corresponding amount of bath sample may be measured directly into the polarographic vessel.

3.17.2 Antimony

3.17.2.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 5.0 mL bath sample into a Kjeldahl flask. Carefully add 5 mL *w*(HCl) = 30%, heat and keep boiling for approx. 3 min. Leave to cool down, transfer the solution with ultrapure water quantitatively into a 50-mL volumetric flask, make up to the mark with ultrapure water and mix.

3.17.2.2 Reagents

- Supporting electrolyte: *w*(HCl) = 10%
  Transfer 83 mL *w*(HCl) = 30% into a 250-mL volumetric flask, make up to the mark with ultrapure water and mix.
- Sb standard: ρ(Sb) = 1 g/L
  This standard is commercially available ready for use.
- Sb standard solution: ρ(Sb) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL each of ρ(Sb) = 1 g/L and *w*(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.17.2.3 Analysis

Transfer 10 mL supporting electrolyte and 5.0 mL prepared sample solution (corresponding to 0.5 mL original bath) into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.3 V
Mode	DP	End potential	0 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.3 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Sb	approx. –0.10 V
Pulse amplitude	0.01 V		

The antimony content is determined according to the standard addition method.

3.17.3 Bismuth

3.17.3.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 5.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Carefully add 3 mL $w(H_2SO_4)$ = 96%, heat and evaporate until SO_3 fumes appear. Leave to cool down, transfer the solution with ultrapure water quantitatively into a 100-mL volumetric flask, make up to the mark with ultrapure water and mix.

3.17.3.2 Reagents

- Supporting electrolyte: w(HCl) = 6%
  Transfer 50 mL w(HCl) = 30% into a 250-mL volumetric flask, make up to the mark with ultrapure water and mix.
- Bi standard: ρ(Bi) = 1 g/L
  This standard is commercially available ready for use.

- Bi standard solution: ρ(Bi) = 2 mg/L
  Transfer approx. 50 mL ultrapure water and 20 mL w(HCl) = 30% into a 100-mL volumetric flask. After the addition of 200 µL ρ(Bi) = 1 g/L make up to the mark with ultrapure water and mix.

3.17.3.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 0.5 mL original bath) and 10 mL supporting electrolyte into the polarographic vessel. Deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.3 V
Mode	DP	End potential	–0.05 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.3 V	Voltage step time	0.2 s
Deposition time	60 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Bi	approx. –0.14 V
Pulse amplitude	0.05 V		

The bismuth content is determined according to the standard addition method.

3.17.4 Cadmium, copper and lead

3.17.4.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 10.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Carefully add 5 mL $w(H_2SO_4)$ = 96%, heat and evaporate until SO_3 fumes appear. Leave to cool down and transfer the flask contents with ultrapure water quantitatively into a glass beaker. Add 3 g ammonium acetate (CAS 631-61-8) and neutralize the mixture with w(NaOH) = 30% to a pH value of 4...5. Heat and keep boiling for 1...2 min. Leave to cool down, rinse the solution into a 100-mL volumetric flask with ultrapure water, make up to the mark and mix.

3.17.4.2 Reagents

- Standards: ρ(Me) = 1 g/L (Me = Cd, Cu, Pb)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask, add 1.0 mL ρ(Me) = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.17.4.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 1 mL original bath) into the polarographic vessel, deaerate with nitrogen and record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Start potential	–0.8 V
Stirrer speed	2000 rpm	End potential	–0.1 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.2 s
Deposition potential	–0.8 V	Sweep rate	0.03 V/s
Deposition time	60 s	Peak potential Cd	approx. –0.62 V
Equilibration time	5 s	Peak potential Pb	approx. –0.46 V
Pulse amplitude	0.01 V	Peak potential Cu	approx. –0.25 V
Pulse time	0.04 s		

The metal contents are determined according to the standard addition method.

3.17.5 Cobalt and nickel

3.17.5.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 1.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Carefully add 1 mL $w(H_2SO_4)$ = 96%, heat and evaporate until SO_3 fumes appear. Leave to cool down, rinse the flask contents into a 100-mL volumetric flask with ultrapure water, make up to the mark and mix.

3.17.5.2 Reagents

- Supporting electrolyte: NH_3-NH_4Cl buffer
  Under stirring add 53 mL $w(HCl)$ = 30% and 112.5 mL $w(NH_3)$ = 25% to approx. 300 mL ultrapure water. Leave to cool down, make up to 500 mL with ultrapure water and mix.
- Ammonia: $w(NH_3)$ = 25%
- Dimethylglyoxime, Na salt (CAS 75006-64-3)
  Dissolve 0.15 g DMG-Na_2 in 5 mL ultrapure water. This solution has to be freshly prepared every other day.
- Standards: ρ(Me) = 1 g/L (Me = Co, Ni)
  These are commercially available ready for use.
- Standard solutions: ρ(Me) = 10 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 1.0 mL ρ(Me) = 1 g/L and 0.5 mL $w(HNO_3)$ = 65%, make up to the mark with ultrapure water and mix.

3.17.5.3 Analysis

Transfer 1.0...10.0 mL prepared sample solution (corresponding to 0.01...0.1 mL original bath; if necessary make up to 10 mL with ultrapure water) and 0.5 mL supporting electrolyte into the polarographic vessel. Adjust the pH of the mixture to 8.5...9 with ammonia, add 100 µL DMG solution and deaerate with nitrogen. Record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.7 V
Mode	DP	End potential	–1.15 V
Purge time	300 s	Voltage step	0.004 V
Deposition potential	–0.7 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.02 V/s
Equilibration time	5 s	Peak potential Ni	approx. –0.95 V
Pulse amplitude	0.05 V	Peak potential Co	approx. –1.07 V

The metal contents are determined according to the standard addition method.

3.17.5.4 Remarks

With this method very low contents of Co or Ni can be determined. There is, however, an upper determination limit. Including the increments, not more than 100 µg/L Co or Ni should be present because at higher concentrations the surface of the HMDE will become overloaded by the accumulated DMG complex.

3.17.6 Iron

3.17.6.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 10.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Carefully add 6 mL $w(H_2SO_4)$ = 96%, heat and evaporate until SO_3 fumes appear. Leave to cool down, rinse the flask contents quantitatively into a 100-mL volumetric flask with ultrapure water, make up to the mark and mix.

3.17.6.2 Reagents

- Supporting electrolyte: citrate/EDTA
  Dissolve 14.7 g trisodium citrate dihydrate (CAS 6132-04-3) and 18.6 g $Na_2EDTA \times 2\ H_2O$ (CAS 6381-92-6) in approx. 200 mL ultrapure water. Adjust the pH value to 6.0 with $w(H_2SO_4)$ = 96%. Leave to cool down, make up to 250 mL with ultrapure water and mix.
- Ammonia: $w(NH_3)$ = 25%
- Standard: $\rho(Fe^{3+})$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Fe^{3+})$ = 50 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 5.0 mL $\rho(Fe^{3+})$ = 1 g/L and 0.2 mL $w(H_2SO_4)$ = 96%, make up to the mark with ultrapure water and mix.

3.17.6.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 1 mL original bath) and 10 mL supporting electrolyte into the polarographic vessel. Adjust the pH of the solution to 6.0 with ammonia, deaerate with nitrogen, then record the DP polarogram under the following conditions:

Working electrode	DME	Start potential	+0.1 V
Stirrer speed	2000 rpm	End potential	–0.3 V
Mode	DP	Voltage step	0.006 V
Purge time	300 s	Voltage step time	0.6 s
Equilibration time	3 s	Sweep rate	0.01 V/s
Pulse amplitude	0.05 V	Peak potential Fe(III)	approx. –0.09 V
Pulse time	0.04 s		

The iron content is determined according to the standard addition method.

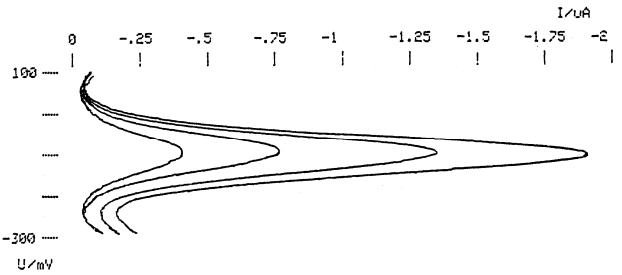

Fig. 29 Polarographic determination of 97 mg/L iron in a zinc bath.

3.17.7 Germanium

3.17.7.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 10.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Carefully add 6 mL $w(H_2SO_4)$ = 96%, heat and evaporate until SO_3 fumes appear. Leave to cool down, rinse the solution into a 100-mL volumetric flask with ultrapure water, make up to the mark and mix.

3.17.7.2 Reagents

- Sulfuric acid: $w(H_2SO_4)$ = 96%
- Pyrocatechol violet: c(PCV) = 0.001 mol/L
  Dissolve 38.6 mg pyrocatechol violet (CAS 115-41-3) in 10 mL ultrapure water. Dilute 1.0 mL of this solution with ultrapure water to 10 mL.

- Standard: ρ(Ge) = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: ρ(Ge) = 1 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 100 µL ρ(Ge) = 1 g/L and 1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.17.7.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 1 mL original bath), 5 mL ultrapure water and 0.25 mL $w(H_2SO_4)$ = 96% into the polarographic vessel. Add 75 µL pyrocatechol violet solution, deaerate with nitrogen, then record the DP stripping voltammogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.2 V
Mode	DP	End potential	–0.45 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.25 V	Voltage step time	0.2 s
Deposition time	5 s	Sweep rate	0.03 V/s
Equilibration time	10 s	Peak potential Ge	approx. –0.34 V
Pulse amplitude	0.05 V		

The germanium content is determined according to the standard addition method.

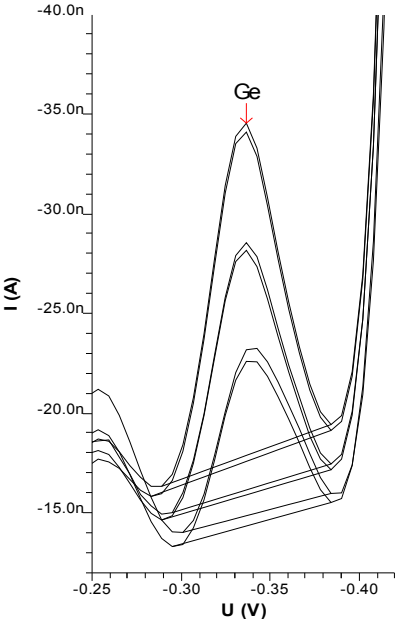

Fig. 30 Determination of 19.5 µg/L germanium in a zinc bath by means of AdSV (adsorptive stripping voltammetry)

3.17.8 Thallium

3.17.8.1 Sample preparation

Work in the fume hood, toxic HCN is formed!

Transfer 10.0 mL bath sample into a Kjeldahl flask and dilute with approx. 10 mL ultrapure water. Carefully add 6 mL $w(H_2SO_4)$ = 96%, heat and evaporate until SO_3 fumes appear. Leave to cool down, rinse the solution into a 100-mL volumetric flask with ultrapure water, make up to the mark and mix.

3.17.8.2 Reagents

- Hydrochloric acid: w(HCl) = 30%
- Permanganate solution: $c(KMnO_4)$ = 0.02 mol/L
  This standard is commercially available ready for use.
- Ascorbic acid solution:
  Dissolve 1 g ascorbic acid (CAS 50-81-7) in 50 mL ultrapure water.

- Standard: $\rho(Tl^+)$ = 1 g/L
  This standard is commercially available ready for use.
- Standard solution: $\rho(Tl^+)$ = 1 mg/L
  Transfer approx. 50 mL ultrapure water into a 100-mL volumetric flask. Add 100 µL $\rho(Tl^+)$ = 1 g/L and 1 mL w(HCl) = 30%, make up to the mark with ultrapure water and mix.

3.17.8.3 Analysis

Transfer 10.0 mL prepared sample solution (corresponding to 1 mL original bath) into the polarographic vessel. Add 0.5 mL w(HCl) = 30% and 100 µL permanganate solution, stir for approx. 1 min and then dropwise add ascorbic acid solution until the pink coloration disappears. Deaerate with nitrogen and record the DP stripping polarogram under the following conditions:

Working electrode	HMDE	Pulse time	0.04 s
Stirrer speed	2000 rpm	Start potential	–0.6 V
Mode	DP	End potential	–0.3 V
Purge time	300 s	Voltage step	0.006 V
Deposition potential	–0.6 V	Voltage step time	0.2 s
Deposition time	30 s	Sweep rate	0.03 V/s
Equilibration time	5 s	Peak potential Tl(I)	approx. –0.44 V
Pulse amplitude	0.05 V		

The thallium content is determined according to the standard addition method.

4 Appendix

4.1 Application Bulletins

No. 036 Polarographic analysis – half-wave potentials of inorganic substances

No. 074 Polarographic and stripping voltammetric analysis methods for thallium, antimony, bismuth and iron (copper, vanadium)

No. 076 Polarographic determination of nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) according to DIN 38413 part 5

No. 110 Polarographic determination of free cyanide

No. 113 Determination of lead, cadmium and copper in foodstuffs, waste water and sewage sludge by anodic stripping voltammetry after digestion

No. 114 Polarographic determination of five metals (copper, cobalt, nickel, zinc and iron) in a single operation

No. 116 Polarographic/voltammetric determination of chromium in small quantities

No. 146 Direct polarographic determination of trace amounts of molybdenum in water

No. 147 Simultaneous trace determination of seven metals in «electronic grade» materials using stripping voltammetry

No. 176 Simultaneous determination of lead and tin by anodic stripping voltammetry

No. 199 Polarographic determination of sulfide and sulfite

No. 220 Voltammetric determination of platinum and rhodium in the ultratrace range

No. 231 Voltammetric determination of zinc, cadmium, lead, copper, thallium, nickel and cobalt in water samples according to DIN 38406 Part 16

No. 266 Voltammetric determination of titanium and uranium

No. 276 Validation of Metrohm VA instruments using Standard Operating Procedures

4.2 Application Notes

V-1 Iron, cadmium, lead and copper in cobalt acetate solution

V-15 Nickel, antimony, cadmium, thallium and copper in neutral, highly concentrated zinc solution

V-16 Nickel, iron and copper in a silver plating bath

V-17 Chromium and selenium in a silver plating bath

V-18 Tin and lead in organo plating bath

V-19 Lead in nickel plating bath

V-20 Zinc, lead and iron in NH_4Cl and $CuSO_4$

V-21 Chromium and nickel in NH_4Cl and $CuSO_4$

V-22 Antimony and bismuth in alkaline ZnO solution in one run

V-23 Aluminum in alkaline ZnO solution

V-24 Copper and chromium in etching bath

V-25 Iron in a nickel sulfamate bath containing surfactants

V-26 Iron and zinc in a nickel sulfate bath containing surfactants

V-27 Copper in nickel sulfate bath containing surfactants

V-30 Zinc, cadmium, lead, nickel and cobalt in $FeCl_3$ solution 40%

V-49 Standard buffers and reagents in voltammetry

V-50 Concentrations and standards in voltammetry

V-61 Speciation of Fe(III) and Fe(II) in standard

V-72 Determination of NTA and EDTA in waste water

V-76 Determination of cobalt in gold plating baths

V-77 Determination of nickel and cobalt in concentrated zinc solutions

V-78 Determination of antimony in zinc solution

V-79 Determination of germanium in electroplating baths

V-80 Determination of germanium in lead

V-83 Zn, Cd, Pb and Cu in waste water after UV digestion

V-84 Total chromium in waste water after UV digestion

V-105 Tl besides excess of Cd in zinc plant electrolyte

V-106 Ni in waste water after UV digestion

V-107 Sn in waste water after UV digestion

V-108 Tl in waste water after UV digestion

V-110 Cr in waste water after UV digestion

V-111 Ge in zinc plant electrolyte

V-112 Thiourea in nickel plating baths

V-128 Fe(total) in a Cr electroplating bath

V-133 Suppressor Copper Gleam 2001 Carrier (Rohm and Haas) in acid copper baths

V-134 Brightener Copper Gleam 2001 Additive (Rohm and Haas) in acid copper baths

V-139 Thiourea in acid copper baths

V-140 Sb(total) in acid copper baths

V-141 Suppressor MACuSpec PPR 100 Wetter (MacDermid) in acid copper baths

V-142 Brightener MACuSpec PPR 100 (MacDermid) in acid copper baths

V-143 Suppressor Multibond 100 Part A20 (MacDermid) in tin baths

V-144 Suppressor ShipleyRonal TP (Rohm and Haas) in acid copper baths

V-145 Suppressor Solderon ST-200 Primary (Rohm and Haas) in tin baths

V-148 Ni in Ni plating bath

V-149 Co in Ni plating bath

V-150 Cu in Ni plating bath

V-151 Sb(III) and Sb(total) in electroless Ni bath

V-152 Tl in Au bath

V-153 Au(I) in Au bath

V-154 NTA in cyanide Au bath

V-155 Suppressor Thrucup EVF-B (Uyemura) in acid copper baths

V-156 Brightener Thrucup EVF-1A in acid Cu bath (Uyemura)

V-157 Leveler Thrucup (Uyemura) in acid copper baths

V-158 In in Sn bath

V-159 Bi in Sn bath

V-160 Pd in activator

V-161 Cu in Cu bath

V-163 Fe in degreasing bath

V-164 Ti in Ti pickle bath

V-165 Zn in phosphatation bath

V-166 Ni in phosphatation bath

V-167 Cd in phosphatation bath

V-168 Pb in phosphatation bath

V-177 Fe in Cr bath (triethanolamine-bromate-method)

V-182 Suppressor «Top Lucina α-M» (Okuno Chemical Industries) in acid copper baths

V-183 Brightener «Top Lucina α-2» (Okuno Chemical Industries) in acid copper baths

V-184 Leveler «Top Lucina α-3» (Okuno Chemical Industries) in acid copper baths