

Application Bulletin 254/2 e

Determination of zinc, cadmium and lead by anodic stripping voltammetry at a mercury film electrode

Summary

This Application Bulletin describes the determination of zinc at a mercury film electrode (MFE). Zinc can also be determined simultaneously with cadmium and lead. The determination of copper at the MFE is not possible. The mercury film is plated *ex-situ* on a glassy carbon electrode and can be used for half a day up to one day.

Zinc can be determined at the mercury film electrode by anodic stripping voltammetry (ASV). The presence of copper, which is naturally present in many samples, affects the determination of zinc due to the formation of an intermetallic compound. As a result the determined concentrations of zinc are too low. The addition of gallium can eliminate the interference to a certain extent since the intermetallic complex of gallium and copper is more stable than the complex of zinc and copper.

With a deposition time of 10 s, the limit of detection is $\beta(Zn^{2+}) = 0.15~\mu g/L$. The linear working range goes up to approx. 300 $\mu g/L$. With the deposition time of 10 s the method is suitable for samples between 10 $\mu g/L$ and 150 $\mu g/L$ Zn content. For samples with lower concentrations the results are more reliable if the deposition time is increased to e.g. 30 s. Samples with higher concentrations have to be diluted.

Samples

Surface water, ground water, sea water, waste water

Instruments

884 Professional VA	2.884.0210
Accessories	
viva 2.0	6.6065.20x
Electrode equipment with GC-RDE	6.5339.040
Containing (besides the three electrodes):	
Measuring vessel 5 mL	6.1415.150
Electrolyte c(KCI) = 3 mol/L	6.2308.020
Polishing set	6.2802.000

Electrodes

WE	Glassy carbon electrode tip	6.1204.600
	Driving axle for RDE	6.1204.510
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L)	6.0728.120
	Electrolyte vessel Filled with c(KCI) = 3 mol/L	6.1245.010
AE	Glassy carbon rod	6.1247.000
	Electrode holder	6.1241.120

Reagents

- Zn standard stock solution, β(Zn²⁺) = 1 g/L
- Hg standard stock solution, β(Hg²⁺) = 1 g/L
- Ga standard stock solution, β(Ga³⁺) = 1 g/L
- Nitric acid, w(HNO₃) = 65%, for trace analysis*, CAS 7697-37-2
- Hydrochloric acid, w(HCl) = 30%, for trace analysis*, CAS 7647-01-0
- Acetic acid, w(CH₃COOH) = 100%, for trace analysis*, CAS 64-19-7
- Sulfuric acid, w(H₂SO₄) = 96%, for analysis, CAS 7664-93-9
- Ammonium hydroxide solution, w(NH₃) = 25%, for trace analysis*, CAS 1336-21-6
- Potassium chloride, KCI, for trace analysis*, CAS 7447-40-7
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

In addition if UV digestion is required:

 Hydrogen peroxide solution, w(H₂O₂) = 30%, for trace analysis*, CAS 7722-84-1

In addition if also Cd and Pb should be determined:

- Cd standard stock solution, β(Cd²⁺) = 1 g/L
- Pb standard stock solution, β(Pb²⁺) = 1 g/L

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



Solutions

Hg plating solution	β(Hg ²⁺) = 20 mg/L c(HCl) = 0.1 mol/L 0.4 mL Hg standard stock solution and 0.2 mL hydrochloric acid are diluted to 20 mL with ultrapure
	water.
Electrolyte	c(CH ₃ COOH) = 2 mol/L c(NH ₃) = 1 mol/L c(KCI) = 1.5 mol/L 55.9 g KCI are dissolved in approx. 300 mL water. 55.5 mL acetic acid and 37 mL ammonium hydroxide solution are added and filled up to 500 mL with ultrapure water.
Ga solution	β(Ga ²⁺) = 100 mg/L Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 5 mL Ga standard stock solution are added. The solution is made up to the mark with ultrapure water.

Standard solutions

Zn standard solution 5 mg/L	β(Zn ²⁺) = 5 mg/L Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL w(HNO ₃) = 65% and 0.25 mL Zn standard stock solution are added. The solution is made up to the mark with ultrapure water.
Zn standard solution 1 mg/L	β(Zn ²⁺) = 1 mg/L Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL w(HNO ₃) = 65% and 0.05 mL Zn standard stock solution are added. The solution is made up to the mark with ultrapure water.
Cd standard solution	$\beta(\text{Cd}^{2+}) = 0.5 \text{ mg/L}$ Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL w(HNO ₃) = 65% and 0.025 mL Cd standard stock solution are added. The solution is made up to the mark with ultrapure water.
Pb standard solution	$\beta(Pb^{2+}) = 1$ mg/L Approx. 40 mL ultrapure water is filled into a 50 mL volumetric flask. 0.05 mL w(HNO ₃) = 65% and

0.05 mL Pb standard stock solution are added. The solution is made up to the mark with ultrapure water.

Check standard solutions

One on one one	4
Check standard	$\beta(Zn^{2+}) = 5 \mu g/L$
5 μg/L	The check standard solution is prepared <i>in-situ</i> with 10 mL ultrapure water, 0.5 mL electrolyte, 0.1 mL Ga solution and 0.05 mL Zn standard solution 1 mg/L.
Check standard	$\beta(Zn^{2+}) = 10 \ \mu g/L$
10 µg/L	The check standard solution is prepared <i>in-situ</i> with 10 mL ultrapure water, 0.5 mL electrolyte, 0.1 mL Ga solution and 0.1 mL Zn standard solution 1 mg/L.
Check standard	$\beta(Zn^{2+}) = 50 \ \mu g/L$
50 µg/L	The check standard solution is prepared <i>in-situ</i> with 10 mL ultrapure water, 0.5 mL electrolyte, 0.1 mL Ga solution and 0.1 mL Zn standard solution 5 mg/L.
Check standard	$\beta(Zn^{2+}) = 100 \ \mu g/L$
100 μg/L	The check standard solution is prepared <i>in-situ</i> with 10 mL ultrapure water, 0.5 mL electrolyte, 0.1 mL Ga solution and 0.2 mL Zn standard solution 5 mg/L.

Sample preparation

- Ground water, drinking water, sea water, and mineral water can usually be analyzed directly.
- Water that contains interfering organic substances is digested using the 909 UV Digester:

10 mL acidified water sample (pH = 2) with 20 μ L w(HCl) = 30% and 100 μ L w(H₂O₂) = 30% are irradiated for 90 min at 90 °C.

Comments

- No platinum auxiliary electrode should be used in combination with a glassy carbon working electrode.
- Measuring vessel and reference electrode have to be free of platinum traces. Therefore it is recommended to have accessories dedicated to this application.





Mercury film plating

Preparation of the glassy carbon electrode

The glassy carbon electrode has to be clean and free of any insulating material before the mercury film can be plated. For cleaning the following procedure is recommended.

- With a soft tissue deposit, e.g. an old mercury film, is wiped off the electrode surface.
- For polishing the glassy carbon electrode a small amount of aluminum oxide (5 ... 10 mg) is mixed with a few drops of water (0.2 ... 0.5 mL) on the polishing cloth (part of the polishing set 6.2802.000) to form a slurry. The electrode is then polished with small 8shaped movements on the polishing cloth.
- The slurry is rinsed off the electrode with ultrapure water.
- The electrode is then rinsed with ethanol and afterwards thoroughly with ultrapure water.

This procedure should be carried out each time before plating the mercury film.

Plating the mercury film

20 mL Hg plating solution are transferred into the measuring vessel. The plating is carried out using the parameters given under «Parameters for mercury film plating» with 2 replications for the plating.

Measuring solution

20 mL Hg plating solution

Parameters for mercury film plating

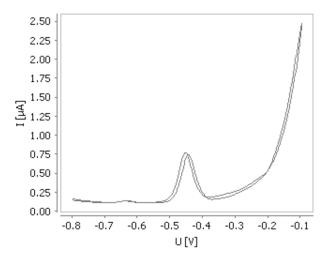
Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min ⁻¹
Cyclovoltammetric	
pretreatment	
Start potential	-1.2 V
Vertex potential	-0.1 V
No. of cycles	50
Potentiostatic pretreatment	
Potential 1	-0.15 V
Waiting time 1	2 s
Potential 2	-1.3 V
Waiting time 2	180 s
Equilibration time	5 s

Sweep	
Start potential	-0.8 V
End potential	-0.1 V
Potential step	0.006 V
Potential step time	0.1 s
Sweep rate	0.06 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s

Comments

- The Hg plating solution can be reused several times (approx. 20 times). The solution itself is stable for at least one month. But with the number of plating processes the concentration of Hg in the solution decreases and the amount of contamination increases. Therefore the solution has to be replaced when no proper mercury film can be plated anymore.
- The waste Hg plating solution contains mercury.
 Therefore, care has to be taken for an appropriate disposal, in accordance with the local legislation.

Example curve for mercury plating







Determination of Zn

Analysis

10 mL (diluted) sample, 0.5 mL electrolyte and 0.1 mL Ga solution are pipetted into the measuring vessel. The measuring solution is purged for 5 min and the determination is carried out using the parameters given under «Parameters for determination of zinc».

The concentration of zinc is quantified by two additions of Zn standard solution.

Measuring solution

10 mL (diluted) sample

0.5 mL electrolyte

0.1 mL Ga solution

Standard addition

0.1 mL Zn standard solution 5 mg/L

Parameters for determination of zinc

Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min ⁻¹
Cyclovoltammetric pretreatment	
Start potential	-1.4 V
Vertex potential	-0.7 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	-0.1 V
Waiting time 1	5 s
Potential 2	-1.4 V
Waiting time 2	10 s
Equilibration time	5 s
Sweep	
Start potential	-1.2 V
End potential	-0.9 V
Potential step	0.004 V
Potential step time	0.1 s
Sweep rate	0.04 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
Potentiostat	
Highest current range	2 mA

Lowest current range	20 μΑ
Substance	
Name	Zn
Characteristic potential	-1.05 V

Results

Average of 3 determinations with relative standard deviation.

Deposition time 30 s

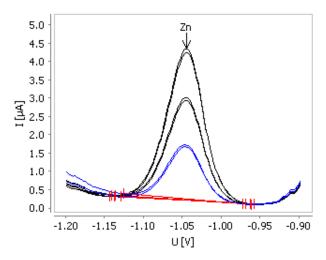
Sample	β(Zn)	Recovery
Check standard 5 μg/L	4.89 μg/L ± 1.7%	95.3%
Check standard 15 µg/L	14.57 μg/L ± 5.5%	97.2%
Certified reference material BCR-505*	10.73 μg/L ± 2.1%	95.4%

^{*} reference value $\beta(Zn) = 11.25 \mu g/L \pm 0.72 \mu g/L$

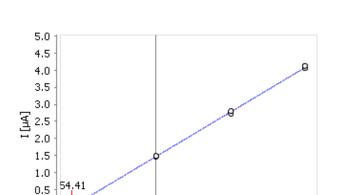
Deposition time 10 s

Sample	β(Zn)	Recovery
Check standard 10 µg/L	10.97 μg/L ± 2.7%	109.7%
Check standard 50 µg/L	51.99 μg/L ± 1.7%	104.0%
Check standard 100 μg/L	104.86 μg/L ± 0.6%	104.9%
Tap water	112.09 μg/L ± 2.7%	

Example determination







75

100

Limit of detection and linear range

-25

0.0

-50

The limit of detection was determined using the «regression approach» [1], where the limit of detection is calculated as $(3\cdot s_y)$, with s_y as the residual standard deviation of a linear regression. The linear working range was estimated from a calibration curve.

n

25

c [µg/L]

50

Deposition time	Limit of detection	Linear range
10 s	0.15 μg/L	300 μg/L
30 s	0.05 μg/L	40 μg/L

The limit of detection and linear range were determined in standard solutions. Depending on the condition of the electrode, quality of the mercury film or the sample matrix, these values can differ.

Assessment of mercury film

To test the quality of the mercury film it is recommended to run a determination in standard solution using the parameters given under «Parameters for determination of zinc». Measuring solution e.g.:

10 mL (diluted) sample

0.5 mL electrolyte

0.1 mL Ga solution

0.05 mL Zn standard solution $\beta(Zn) = 1$ mg/L

Assessment criteria

- The curve of the background current should be smooth.
- The background current should be stable.
- The replications should be reproducible.
- The peak maximum should not shift significantly.

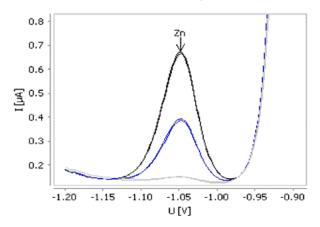
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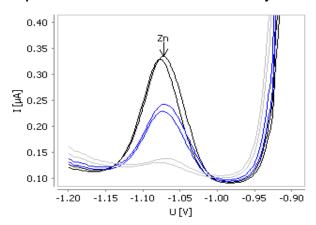
• The sensitivity should not be significantly lower than with a fresh mercury film.

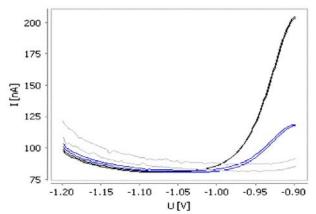
If one of the criteria is not fulfilled it is recommended to remove the mercury film, carry out the cleaning and polishing procedure as described under «Preparation of the glassy carbon electrode» and plate a fresh mercury film.

Example for a determination with a good mercury film



Examples for determinations with a bad mercury film







Comments

- The increase in current at around -0.95 V is due to the presence of gallium.
- Under the given conditions the measuring solution contains 1 mg/L Ga. This concentration is sufficient to eliminate the interference of maximum 100 µg/L Cu. Higher concentrations of Ga should not be used since this can cause interferences, too. If a sample contains more than 100 µg/L Cu, it needs to be diluted for the determination.
- Deposition time and standard addition (volume and/or concentration of the standard solution) have to be adapted to the concentration of analyte in the measuring vessel. In this context it is important to consider the linear working range. For samples with concentrations between 10 and 150 μg/L it is recommended to use a deposition time of 10 s (Zn standard solution 5 mg/L). For samples with lower Zn content (<15 μg/L) it is recommended to increase the deposition time to 30 s (Zn standard solution 1 mg/L). Samples with concentrations between 10 μg/L and 15 μg/L can be analyzed with 10 s as well as with 30 s deposition time. Samples with concentrations
 >150 μg/L have to be diluted since a deposition time of 0 s has not proven useful.
- The mercury film can be used for half a day up to one day. But effects from the sample matrix can reduce the lifetime of the mercury film. Indications for a fading mercury film are:
 - o bad reproducibility of the replications
 - o decreasing sensitivity of the additions (slope)
 - o increasing or noisy background current
 - o peak is displaced

The mentioned indications can also be caused by matrix interferences. Therefore, in case of a suspicious mercury film, it is recommended to run a blank determination as described under «Assessment of mercury film» and to decide based on these curves whether the film needs to be renewed.

- If the mercury film is not used it is recommended to keep either diluted electrolyte or diluted nitric acid (c(HNO₃) ~ 0.05 mol/L) in the measuring vessel. Storing the mercury film with ultrapure water is not recommended since it passivates the film.
- Care has to be taken that the nitrogen bubbles do not gaze the mercury film during purging. The bubbles can mechanically destroy the film. In this case the gas inlet tube has to be bent in a direction that the nitrogen does not bubble over the working electrode.

- To remove fouling from electrodes and measuring vessel it is recommended to clean with sulfuric acid from time to time. For that, fill 1–2 mL concentrated sulfuric acid into the slightly wet measuring vessel. Attention, the solution gets hot! Carefully turn the measuring vessel to wet the entire surface with H₂SO₄. Then add 30–40 mL ultrapure water. Be very careful of splashing of the hot solution. Place the measuring vessel under the measuring head and turn on the stirring until the solution cooled down to room temperature. Empty the measuring vessel and rinse everything thoroughly with ultrapure water. Please note that this procedure is not suitable to remove metal blanks.
- Traces of metals can be removed with diluted nitric acid (c(HNO₃) ~ 0.1 mol/L). For cleaning, place 20–30 mL diluted nitric acid in the measuring vessel and switch on the stirrer for 10–30 min. Empty the measuring vessel and rinse everything thoroughly with ultrapure water.

Determination of Zn, Cd and Pb

Zn can be determined together with Cd and Pb in one run, which is only advisable if the concentrations of the three elements are in the same range.

In many samples the concentration of zinc is significantly higher. In these cases Cd and Pb are favorably be determined with a separate method as described in Application Bulletin 241 [2].

Analysis

10 mL (diluted) sample and 0.5 mL electrolyte are pipetted into the measuring vessel. The measuring solution is purged for 5 min and the determination is carried out using the parameters given under «Parameters for determination of zinc, cadmium and lead».

The concentration of zinc is quantified by two additions of Zn, Cd and Pb standard solution(s).

Measuring solution

10 mL (diluted) sample 0.5 mL electrolyte 0.1 mL Ga solution



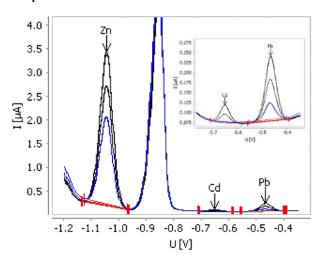
Parameters for determination of zinc, cadmium and lead

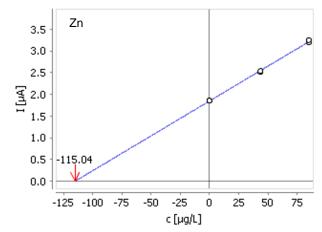
	·
Voltammetric	
Measuring mode	DP – Differential pulse
Stirring rate	2000 min ⁻¹
Cyclovoltammetric	
pretreatment	
Start potential	-1.4 V
Vertex potential	-0.7 V
No. of cycles	10
Potentiostatic pretreatment	
Potential 1	-0.1 V
Waiting time 1	5 s
Potential 2	-1.4 V
Waiting time 2	10 s
Equilibration time	5 s
Sweep	
Start potential	-1.2 V
End potential	-0.35 V
Potential step	0.004 V
Potential step time	0.1 s
Sweep rate	0.04 V/s
Pulse amplitude	0.05 V
Pulse time	0.04 s
Potentiostat	
Highest current range	2 mA
Lowest current range	20 μΑ
Substance	
Name	Zn
Characteristic potential	-1.05 V
Name	Cd
Characteristic potential	-0.65 V
Name	Pb
Characteristic potential	-0.46 V

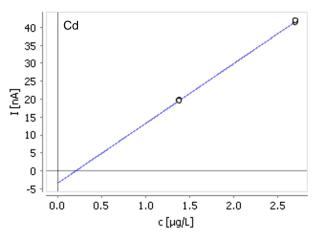
Results

Sample	β(Zn)	β(Cd)	β(Pb)
Tap water	121.94 µg/L	n/a	5.01 µg/L

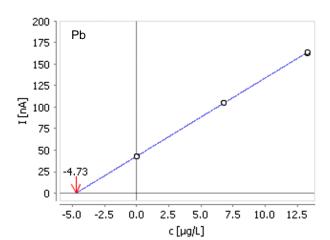
Example











Comments

- The huge signal between -0.95 V and -0.8 V is caused by the added gallium.
- For more information on the determination of cadmium and lead please refer to Application Bulletin 241 [2].
- The determination of copper at the mercury film electrode is generally not possible, since the calibration curve is not linear.

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Determination of zinc, cadmium and lead by anodic stripping voltammetry at a mercury film electrode

References

- [1] J. Mocak, A. Bond, S. Mitchell and G. Scollary, "A statistical overview of standard (IUPAC and ACS) and new procedures for determining the limits of detection and quantification: Application to voltammetric and stripping techniques," *Pure and Applied Chemistry*, vol. 69, no. 2, pp. 297-328, 1997.
- [2] Metrohm AG, «Application Bulletin 241 Determination of cadmium and lead by anodic stripping voltammetry at a mercury film electrode».

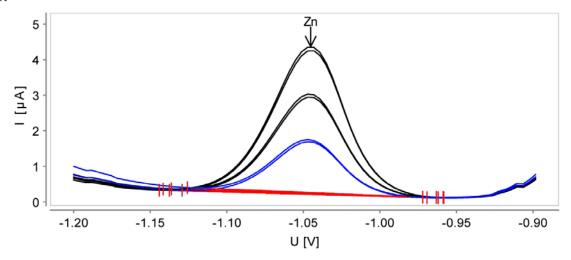


Appendix

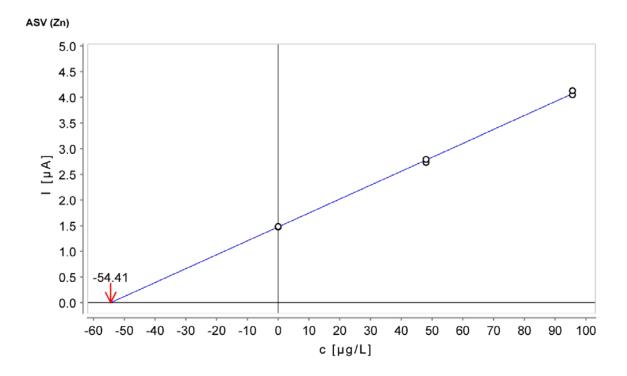
Report of the example determination Zn in tap water

viva	Result report 20 20 20 20 20 20 20 20 20 20 20 20 20	17-10-10	10:00:31
Determination			
Determin	nation start	2	
User nar	me (short)	u	
User nar	me Barbara Zumbräge	:l	
Methode	enname	d	
Sample data			
Sample	type Sampl	9	
ID 1)	
ID 2		.)	
ID 3		4	
Sample	amount	L	
Analytica	al volume		
Dilution	volume		
Results overview			
ASV.Zn.	Concentration	9 µg/L	
ASV.Zn.	Concentration.ASD) µg/L	

ASV







Concentration
Absolute standard deviation
Relative standard deviation
Function
Coefficient of determination R ²
Evaluation quantity
Curve type
Weighting

CALL	Var	Rep	Peak potential [V]	Height [µA]	Used
Measure sample	1	1	-1.047	1.48	used
Measure sample	1	2	-1.046	1.47	used
Measure additions	2	1	-1.046	2.79	used
Measure additions	2	2	-1.046	2.73	used
Measure additions	3	1	-1.045	4.13	used
Measure additions	3	2	-1.045	4.05	used

ASV (Zn)

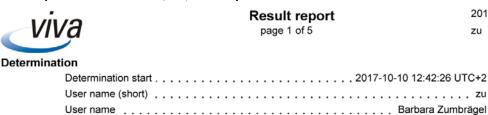
CALL	VAR	REP	POT	HGT	HGT.MNV	HGT.ASD	HGT.RSD	HGT.MNVDELTA
			V	μΑ	μΑ	nA	%	μΑ
Measure sample	1	1	-1.047	1.48	1.48	6.65	0.4	0.00
Measure sample	1	2	-1.046	1.47	1.48	6.65	0.4	0.00
Measure additions	2	1	-1.046	2.79	2.76	42.13	1.5	1.28
Measure additions	2	2	-1.046	2.73	2.76	42.13	1.5	1.28
Measure additions	3	1	-1.045	4.13	4.09	56.79	1.4	1.33
Measure additions	3	2	-1.045	4.05	4.09	56.79	1.4	1.33



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Report of the example determination Zn, Cd, Pb in tap water



Sample data

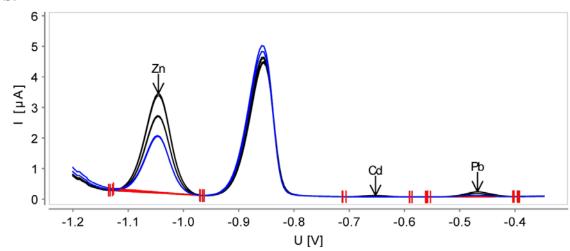
ID 1 Tap water Zn, Cd, Pb ID 2 10 mL sample + 0.5 mL NH4Ac/KCl + 0.1 mL Ga (100 mg/L) Analytical volume ... Dilution volume

Methodenname AB 254 Determination of ZnCdPb_auto add

Results overview

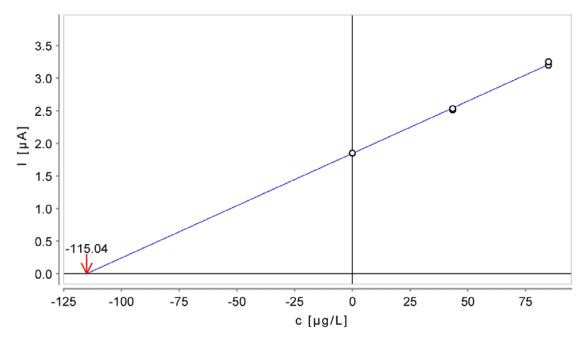
ASV.Cd.Concentration.ASD invalid ASV.Cd.Concentration.RSD invalid

ASV





ASV (Zn)



Concentration
Absolute standard deviation
Relative standard deviation
Function
Coefficient of determination R ²
Evaluation quantity
Curve type
Weighting used

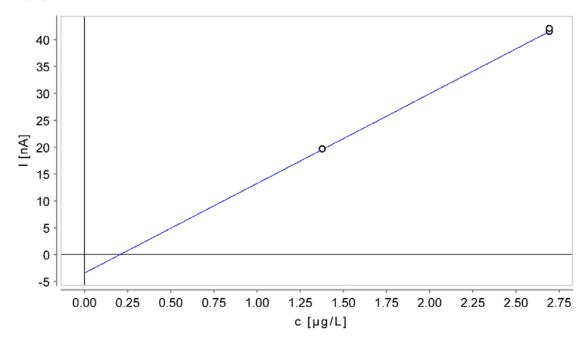
CALL	Var	Rep	Peak potential [V]	Height [µA]	Used
Measure sample	1	1	-1.047	1.85	used
Measure sample	1	2	-1.046	1.85	used
Measure additions	2	1	-1.046	2.53	used
Measure additions	2	2	-1.046	2.51	used
Measure additions	3	1	-1.045	3.25	used
Measure additions	3	2	-1.045	3.20	used

ASV (Zn)

CALL	VAR	REP	POT	HGT	HGT.MNV	HGT.ASD	HGT.RSD	HGT.MNVDELTA
			V	μΑ	μΑ	nA	%	nA
Measure sample	1	1	-1.047	1.85	1.85	1.58	0.1	0.00
Measure sample	1	2	-1.046	1.85	1.85	1.58	0.1	0.00
Measure additions	2	1	-1.046	2.53	2.52	16.07	0.6	672.48
Measure additions	2	2	-1.046	2.51	2.52	16.07	0.6	672.48
Measure additions	3	1	-1.045	3.25	3.22	39.06	1.2	701.10
Measure additions	3	2	-1.045	3.20	3.22	39.06	1.2	701.10



ASV (Cd)



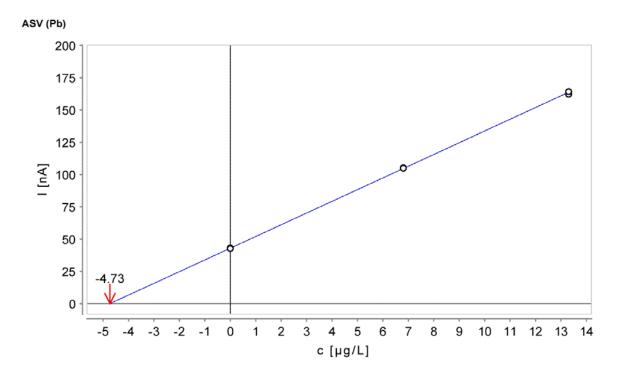
Function	
Coefficient of determination R ²	
Evaluation quantity	
Curve type	
Weighting used	

CALL	Var	Rep	Peak potential [V]	Height [nA]	Used
Measure sample	1	1			used
Measure sample	1	2			used
Measure additions	2	1	-0.653	19.68	used
Measure additions	2	2	-0.653	19.74	used
Measure additions	3	1	-0.652	42.11	used
Measure additions	3	2	-0.652	41.54	used

ASV (Cd)

CALL	VAR	REP	POT	HGT	HGT.MNV	HGT.ASD	HGT.RSD	HGT.MNVDELTA
			V	nA	nA	рА	%	nA
Measure sample	1	1						
Measure sample	1	2						
Measure additions	2	1	-0.653	19.68	19.71	37.20	0.2	0.00
Measure additions	2	2	-0.653	19.74	19.71	37.20	0.2	0.00
Measure additions	3	1	-0.652	42.11	41.82	406.44	1.0	22.11
Measure additions	3	2	-0.652	41.54	41.82	406.44	1.0	22.11





Concentration,	
Absolute standard deviation	
Relative standard deviation	
Function	
Coefficient of determination R ²	
Evaluation quantity	
Curve type	
Weighting used	

CALL	Var	Rep	Peak potential [V]	Height [nA]	Used
Measure sample	1	1	-0.471	42.66	used
Measure sample	1	2	-0.471	43.13	used
Measure additions	2	1	-0.469	104.91	used
Measure additions	2	2	-0.469	105.32	used
Measure additions	3	1	-0.468	164.12	used
Measure additions	3	2	-0.468	162.19	used

ASV (Pb)

CALL	VAR	REP	POT	HGT	HGT.MNV	HGT.ASD	HGT.RSD	HGT.MNVDELTA
			V	nA	nA	nA	%	nA
Measure sample	1	1	-0.471	42.66	42.89	0.33	0.8	0.00
Measure sample	1	2	-0.471	43.13	42.89	0.33	0.8	0.00
Measure additions	2	1	-0.469	104.91	105.12	0.29	0.3	62.22
Measure additions	2	2	-0.469	105.32	105.12	0.29	0.3	62.22
Measure additions	3	1	-0.468	164.12	163.15	1.37	0.8	58.04
Measure additions	3	2	-0.468	162.19	163.15	1.37	0.8	58.04