

Application Bulletin 438/1

Determination of cadmium and lead in water samples by anodic stripping voltammetry with a Bi drop electrode

Summary

Heavy metals, particularly cadmium and lead, are known to be highly toxic to humans. They can cross the blood-brain barrier and cause severe damage to the brain and kidneys. Cases of chronic poisoning caused by these heavy metals are well documented. Therefore, controlling the cadmium and lead content in drinking water is of utmost importance. In many countries (e.g., CH [1], EU [2], USA [3]), the limit in drinking water for cadmium is between 3 and 5 µg/L, and for lead it is between 5 µg/L [4] and 15 µg/L [3]. These trace concentrations can reliably be determined with the method described in this Application Bulletin.

The determination is carried out by anodic stripping voltammetry (ASV) using the non-toxic Bi drop electrode in a slightly acidic electrolyte (pH 4.6). The 884 Professional VA is used here. With a deposition time of only 60 s, the method is suitable for samples with $\beta(\text{Cd}) = 0.1\text{--}15\text{ }\mu\text{g/L}$ and $\beta(\text{Pb}) = 0.5\text{--}15\text{ }\mu\text{g/L}$. The limit of detection is 0.1 µg/L for Cd and 0.5 µg/L for Pb. This method is best suited for tap water and mineral water samples.

Samples

Tap water, mineral water, and sea water

Instruments and accessories

884 Professional VA manual for MME	2.884.0110
Electrode equipment with Bi drop electrode for 884 Professional VA	6.5339.080
Containing:	
Stirrer for 884	6.1204.500
Measuring vessel 10 mL	6.1415.210
Threaded stopper	6.1446.040
Cap	6.2753.210
viva 2.1	6.6065.21X

Electrodes

WE	Bi drop electrode	6.0346.000
RE	Ag/AgCl reference electrode Ag/AgCl/c(KCl) = 3 mol/L	6.0728.120

	Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.1245.010
AE	Glassy carbon electrode rod	6.1248.040
	Electrode holder	6.1241.120

Overview

The Application Bulletin describes the following methods:

Activation/cleaning of Bi drop electrode

A new sensor needs to be activated first. The activation must be carried out prior to the first use, and whenever the sensor has not been used for more than 1 hour. If the electrode needs to be cleaned either before, in between, or after determinations, the procedure described in the subchapter «Activation/cleaning of Bi drop electrode» should be used.

Determination of cadmium and lead

Cadmium and lead are determined by anodic stripping voltammetry. In a slightly acidic electrolyte (pH 4.6), free ions are electrochemically reduced and deposited as metallic cadmium and lead on the bismuth drop surface. In the subsequent stripping step, the elements are re-oxidized giving the analytical signal.

Standard operating procedure

- Activation of the Bi drop electrode
- Determination of cadmium and lead in a blank or a check standard solution to validate electrode performance
- Determination of samples
- Rinsing of the Bi drop electrode with ultrapure water
- Dry storage in the storage vessel 6.2008.040

For more information about the standard operating procedure please refer to the comments in the chapters «Activation/cleaning of Bi drop electrode» and «Comments» at the end of this document.

Reagents

- Cd(II) standard stock solution, $\beta(\text{Cd(II)}) = 1 \text{ g/L}$, commercially available
- Pb(II) standard stock solution, $\beta(\text{Pb(II)}) = 1 \text{ g/L}$, commercially available
- Acetic acid, $w(\text{acetic acid}) = 100\%$, for trace analysis*, CAS 64-19-7
- Ammonium hydroxide solution, $w(\text{NH}_3) \geq 25\%$, for trace analysis*, CAS 1336-21-6
- Nitric acid, $w(\text{HNO}_3) = 65\%$, for trace analysis*, CAS 7697-37-2
- Sodium hydroxide solution, $w(\text{NaOH}) = 30\%$, for trace analysis*, CAS 1310-73-2
- Triethanolamine, $w(\text{triethanolamine}) \geq 99.0\%$, for analysis, CAS 102-71-6
- Potassium bromate, $w(\text{KBrO}_3) \geq 99.8\%$, for analysis, CAS 7758-01-2
- Hydrogen peroxide solution, $w(\text{H}_2\text{O}_2) = 30\%$, for trace analysis*, CAS 7722-84-1
- Ultrapure water, resistivity $>18 \text{ M}\Omega \cdot \text{cm}$ (25 °C), type I grade (ASTM D1193)

*e.g. Honeywell Fluka TraceSELECT® or Merck Suprapur®

Solutions

Supporting electrolyte	Acetate buffer pH 4.6 $c(\text{acetic acid}) = 2 \text{ mol/L}$ $c(\text{NH}_3) = 1 \text{ mol/L}$ 11.1 mL acetic acid and 7.4 mL ammonium hydroxide solution are added to approximately 70 mL of ultrapure water and the solution is made up to 100 mL with ultrapure water.
Cleaning electrolyte	$c(\text{NaOH}) = 1 \text{ mol/L}$ $c(\text{triethanolamine}) = 0.1 \text{ mol/L}$ $c(\text{KBrO}_3) = 0.4 \text{ mol/L}$ 10 mL sodium hydroxide solution, 1.32 mL triethanolamine, and 6.7 g potassium bromate are dissolved and filled up to 100 mL with ultrapure water in a volumetric flask.

Standard solutions

Standard addition solution 1	$\beta(\text{Cd(II)}) = 10 \text{ mg/L}$ $\beta(\text{Pb(II)}) = 10 \text{ mg/L}$
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1 mL Cd(II) standard stock solution, 1 mL Pb(II) standard stock solution, and 0.1 mL nitric acid are added and made up to 100 mL with ultrapure water in a 100 mL volumetric flask.

Standard addition solution 2

$\beta(\text{Cd(II)}) = 0.1 \text{ mg/L}$
 $\beta(\text{Pb(II)}) = 0.1 \text{ mg/L}$
1 mL standard addition solution 1 and 0.1 mL nitric acid are added and made up to 100 mL with ultrapure water in a 100 mL volumetric flask.

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 ($\text{pH} = 2$) with $10 \mu\text{L } w(\text{HNO}_3) = 65\%$ and $100 \mu\text{L } w(\text{H}_2\text{O}_2) = 30\%$ are irradiated for 90 min at 90 °C.

Activation/cleaning of the Bi drop electrode

Analysis

10 mL ultrapure water and 1 mL cleaning electrolyte are pipetted into the measuring vessel. The activation/cleaning is carried out using the parameters given under «Parameters for activation/cleaning». The measuring solution is purged for 5 minutes before the activation/cleaning.

Measuring solution

10 mL ultrapure water
1 mL cleaning electrolyte

Parameters for activation/cleaning

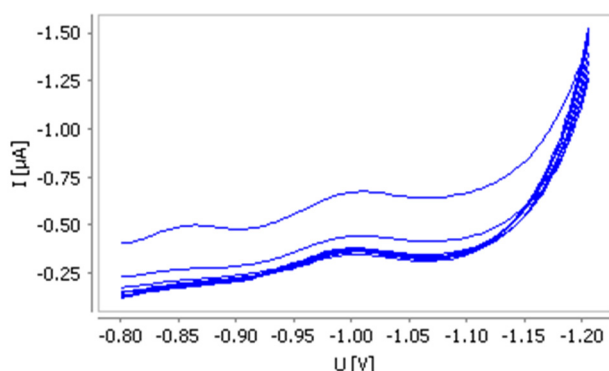
Voltammetric	
Measuring mode	DP – Differential pulse
Cyclovoltammetric pretreatment	
Start potential	0.2 V
Vertex potential	-1 V
No. of cycles	10

Potentiostatic pretreatment

Potential	-2 V
Waiting time	15 s
Sweep	
Start potential	-0.8 V
End potential	-1.2 V
Potential step	0.006 V
Potential step time	0.1 s
Pulse amplitude	0.05 V
Potentiostat	
Highest current range	2 mA
Lowest current range	200 μ A

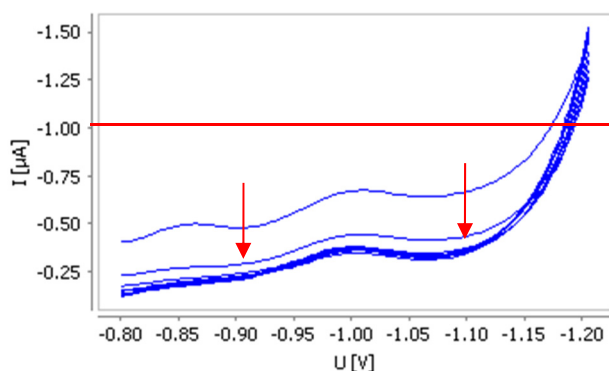
More detailed method parameters can be found in the method printout, which is available as a separate document.

Example



Comments

The current at -0.9 V and -1.1 V should not be more negative than -1 μ A. If the current is more negative than -1 μ A, further cleaning is required.



Determination of Cd and Pb

Analysis

10 mL sample and 1 mL supporting electrolyte are pipetted into the measuring vessel. The determination is carried out using the parameters given under «**Parameters for Cd and Pb determination**». The measuring solution is purged for 5 min before the determination.

Measuring solution

10 mL sample
1 mL supporting electrolyte

Quantification is carried out by two additions of standard addition solution 2.

Parameters for Cd and Pb determination

Voltammetric

Measuring mode DP – Differential pulse

Cyclovoltammetric pretreatment

Start potential 0 V

Vertex potential -1 V

No. of cycles 10

Potentiostatic pretreatment

Potential -1.1 V

Waiting time 60 s

Equilibration time 10 s

Sweep

Start potential -1 V

End potential -0.35 V

Potential step 0.006 V

Potential step time 0.1 s

Pulse amplitude 0.05 V

Potentiostat

Highest current range 2 mA

Lowest current range 200 μ A

Substance

Name Cd

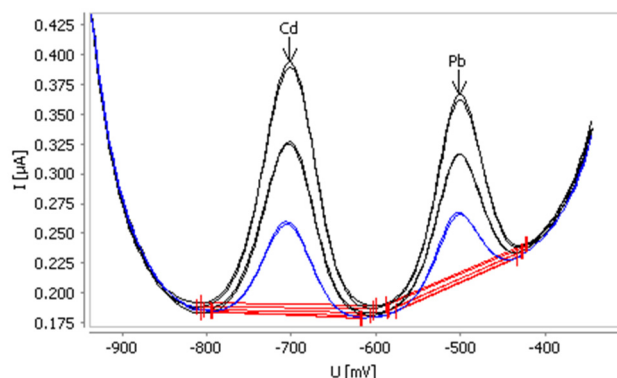
Characteristic potential -0.71 V

Name Pb

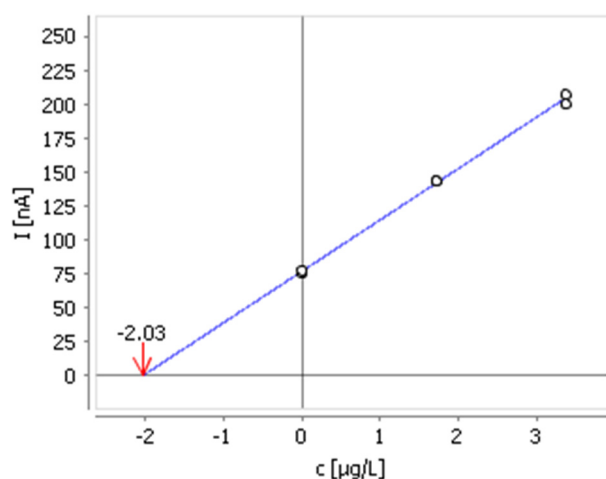
Characteristic potential -0.52

More detailed method parameters can be found in the method printout, which is available as a separate document.

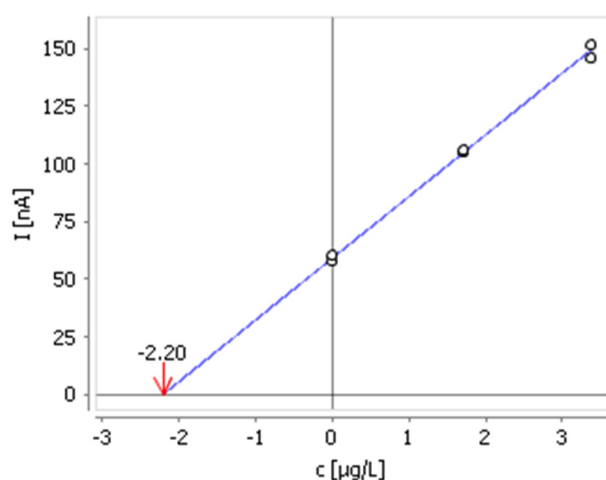
Example determination in tap water spiked with 2 µg/L cadmium and lead (deposition time 60 s)



Cd:



Pb:



Results

Cadmium

Sample	$\beta(\text{Cd}^{2+})^*$ µg/L	RSD	Recovery
Check standard 0.5 µg/L Cd	0.44	2%	88%
Check standard 2 µg/L Cd	2.03	5%	101%
Tap water	< LOD		
Tap water spiked 2 µg/L Cd	2.23	2%	115%
Mineral water	< LOD		
Mineral water spiked 2 µg/L Cd	2.12	2%	106%
Sea water	< LOD		
Sea water spiked 2 µg/L Cd	1.64	2%	82%

* - mean value of 3 determinations (10 determinations for check standard 2 µg/L)

RSD - relative standard deviation

Recovery – Recovery of the spiked amount

Lead

Sample	$\beta(\text{Pb}^{2+})^*$ µg/L	RSD	Recovery
Check standard 0.5 µg/L Pb	0.44	2%	88%
Check standard 2 µg/L Pb	2.02	5%	96%
Tap water	< LOD		
Tap water spiked 2 µg/L Pb	2.3	3%	111%
Mineral water	< LOD		
Mineral water spiked 2 µg/L Pb	1.92	2%	96%
Sea water	< LOD		
Sea water spiked 2 µg/L Pb	-	-	-

* - mean value of 3 determinations (10 determinations for check standard 2 µg/L)

RSD - relative standard deviation

Recovery – Recovery of the spiked amount

Comments

Electrode activation, electrode cleaning

Prior to the first use, the Bi drop electrode has to be activated by using the procedure described under «Activation/cleaning of the Bi drop electrode». This procedure can be used for both the activation and cleaning of the Bi drop electrode, and is repeated until the background current is more positive than $-1 \mu\text{A}$. It is recommended to run the activation/cleaning procedure if the electrode has not been used for more than one hour.

Electrode storage

When the electrode is not used for $<12 \text{ h}$ (e.g., overnight), it can be stored in diluted cleaning electrolyte (10 mL ultrapure water + 1 mL cleaning electrolyte). Keeping the electrode in ultrapure water or a different solution will cause the bismuth drop to turn black, which will require the aggressive regeneration of the surface (see «Regeneration of the Bi drop electrode»).

When the electrode is not used for a longer period of time, it must be stored dry. Before storage, thoroughly rinse the Bi drop with ultrapure water and leave it to dry. When the electrode is completely dry, store it in the storage vessel 6.2008.040 for mechanical protection.

Blackening of the Bi drop electrode

When the electrode has been stored under unsuitable conditions, the bismuth drop surface tends to turn completely black as soon as the first potential in the method is applied. To the best of our knowledge, this behavior does not depend on the measuring solution or the first applied potential. When the bismuth drop has turned black, the electrode has to be regenerated as described under «Regeneration of the Bi drop electrode».

Regeneration of the Bi drop electrode

If the bismuth drop is covered with a black film (not dark gray), proceed as follows:

Dip the black-colored bismuth drop for a short period of time (3–5 s) in concentrated nitric acid ($w(\text{HNO}_3) = 65\%$), rinse thoroughly with ultrapure water and perform the electrochemical cleaning procedure as described under «Activation/cleaning of Bi drop electrode». The electrochemical cleaning procedure may have to be repeated several times, always in a new cleaning solution, until the baseline current is more positive than $-1 \mu\text{A}$.

No other procedures, such as e.g. prolonged cleaning without treatment with nitric acid, results in a satisfactory baseline. It is necessary to remove a portion of the bismuth surface to restore the performance.

The regeneration procedure is aggressive to the electrode and should be carried out only when the surface of the bismuth drop has turned completely black, but not when it is only dark gray. The treatment with nitric acid can only be repeated 2–3 times in the lifetime of the electrode. Then the Bi drop electrode cannot be recovered anymore.

Automation

When the Bi drop electrode is used in an automated system, it is recommended to run one activation/cleaning method at the end of the determination series, and to keep the measuring vessel filled with the measuring solution (diluted cleaning electrolyte). It is important that the Bi drop electrode is stored in the cleaning electrolyte to prevent the Bi drop from turning black. However, the electrode should not be in solution for more than 12 hours (see «Electrode storage»). If the electrode is kept in the cleaning electrolyte for more than 12 hours, repeated cleaning/activation is required.

Interference of heavy metals

The influence of different anions (Cl^-) and cations (Cu^{2+} , Zn^{2+}) on the determination of a check standard solution of $\beta(\text{Cd}) = 1 \mu\text{g/L}$ and $\beta(\text{Pb}) = 1 \mu\text{g/L}$ was tested with a deposition time of 60 s. The shape of the background current, height, and shape of Cd and Pb peaks were evaluated.

Cu	The recovery does not change up to $\beta(\text{Cu}) = 50 \mu\text{g/L}$. In the presence of $\beta(\text{Cu}) = 100 \mu\text{g/L}$, the recovery rate decreases to 75% for both elements.
Zn	No effect on Cd and Pb determination can be observed for $\beta(\text{Zn}) < 1000 \mu\text{g/L}$. For $\beta(\text{Zn}) = 5 \text{ mg/L}$, a doubled sensitivity of Cd can be observed. However, the recovery of $\beta(\text{Cd}) = 1 \mu\text{g/L}$ decreases to 60%. Pb is unaffected up to $\beta(\text{Zn}) = 10 \text{ mg/L}$ in the measuring solution.
Cl^-	Chloride concentrations within the legal limits for drinking water ($c(\text{Cl}^-) = 250 \text{ mg/L}$) do not interfere. Higher chloride concentrations shift the Bi oxidation to more cathodic potentials, resulting in an overlap with the Pb peak. Furthermore, the background current increases, which

results in a higher limit of detection. Samples with high chloride concentration, e.g. sea water ($\beta(\text{Cl}^-) \approx 15 \text{ g/L}$), could only be analyzed after appropriate dilution with the corresponding consequences on the limit of detection.

Limit of detection

The limit of detection was determined using the «regression approach» [4], where the limit of detection is calculated as « $3 \cdot s_y$ », with s_y as the residual standard deviation of a linear regression.

Deposition	Cd	Pb
30 s*	0.5 µg/L	2.1 µg/L
60 s	0.1 µg/L	0.5 µg/L
90 s	0.1 µg/L	0.4 µg/L

* With 30 s deposition time, the calibration curve is not linear at concentrations below $\beta(\text{Cd}) = 1 \text{ µg/L}$ and $\beta(\text{Pb}) = 5 \text{ µg/L}$. It is therefore recommended to use this deposition time only for samples with concentrations higher than $\beta(\text{Cd}) = 5 \text{ µg/L}$ and $\beta(\text{Pb}) = 25 \text{ µg/L}$.

Maximum concentration of the linear range

The maximum concentration of the linear range was read out from a calibration curve recorded with the respective deposition time.

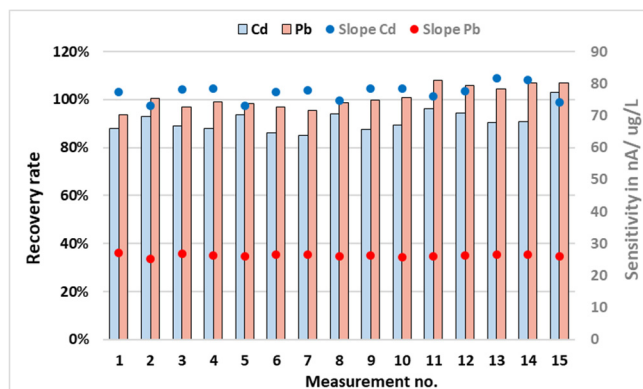
Deposition	Cd	Pb
30 s	50 µg/L	100 µg/L
60 s	25 µg/L	25 µg/L
90 s	15 µg/L	15 µg/L

Working range of the method

With a deposition time of 60 s and two standard additions ($\beta(\text{Cd}) = 5 \text{ µg/L}$ and $\beta(\text{Pb}) = 5 \text{ µg/L}$), the method is suitable for samples with $\beta(\text{Cd}) = 0.1\text{--}15 \text{ µg/L}$ and $\beta(\text{Pb}) = 0.5\text{--}15 \text{ µg/L}$. This allows to monitor the regulatory limits for Cd and Pb in drinking water.

Reproducibility and recovery rate

The overview for reproducibility and recovery rate is shown in the following illustration.



References

- [1] EDI - Das Eidgenössische Departement des Innern, "817.022.11 - Verordnung des EDI über Trinkwasser sowie Wasser in öffentlich zugänglichen Bädern und Duschanlagen," 1 May 2018. <https://www.admin.ch/opc/de/classified-compilation/20143396/index.html>.
- [2] The Council of the European Union, "Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Annex I Part B," 6 October 2015. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:01998L0083-20151027>.
- [3] United States Environmental Protection Agency, "National Primary Drinking Water Regulations," May 2009. [Online]. Available: <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations>.
- [4] Council of the European Union, „Proposal for a Directive of the European Parliament and of the Council on the quality of water intended for human consumption,“ Brussels, 2020.
- [5] 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.