

## Application Bulletin 113/3 e

# Determination of cadmium, lead and copper in foodstuffs, waste water and sewage sludge by anodic stripping voltammetry after digestion

### Summary

Cadmium, lead and copper can be determined simultaneously in oxalate buffer by anodic stripping voltammetry (ASV) after digestion with sulfuric acid and hydrogen peroxide. Tin present in the sample does not interfere with the determination of lead.

For the voltammetric determination of tin, refer to Application Bulletin 176.

### Instruments

VA instrument

capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode

«Hach Digesdahl» digestion apparatus with special quartz vessels for open wet digestion

### Electrodes

WE	Multi-Mode Electrode pro	6.1246.120
	Mercury drop capillary	6.1226.030
	or	6.1226.050
RE	Ag/AgCl reference electrode	6.0728.x20
	Ag/AgCl/KCl (3 mol/L)	
	Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.1245.010
AE	Pt rod electrode	6.0343.x00

## Sample preparation

### Digestion

Approx. 250 mg sample is weighed exactly into the flask of the digestion apparatus. 4 mL  $w(\text{H}_2\text{SO}_4) = 96\%$  is added and the mixture heated to 200 °C. When any water present has evaporated and the mixture taken on a brown color, 1 mL  $w(\text{H}_2\text{O}_2) = 30\%$  is added through the dropping funnel. After the reaction has finished and the digestion solution turned brown again, another 1 mL  $w(\text{H}_2\text{O}_2) = 30\%$  is added. The

mixture is now heated up to 350 ... 400 °C. The addition of  $\text{H}_2\text{O}_2$  has to be repeated at this temperature until the digestion solution stays clear and colorless at the boiling point of sulfuric acid. Typically, a total of up to 5 mL hydrogen peroxide solution is needed to achieve complete digestion.

After cooling down, the digestion flask is made up to 100 mL with ultrapure water. An aliquot of this digestion solution is then used for the voltammetric determination.

### Removing the excess of sulfuric acid

The described digestion procedure can also be used for other applications. If the voltammetric determination is to be carried out in a supporting electrolyte with higher pH value, then the high content of sulfuric acid in the digestion solution has to be neutralized first. A large quantity of sodium hydroxide solution would be necessary for this, resulting in high blanks.

To avoid this, the sulfuric acid is evaporated almost to dryness in the digestion flask over the flame of a Bunsen burner. After cooling down, make up to 100 mL with ultrapure water.

## Determination of Cd, Pb and Cu

### Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis\*).

- Sulfuric acid,  $w(\text{H}_2\text{SO}_4) = 96\%$ , for trace analysis\*, CAS 7664-93-9
- Hydrogen peroxide solution,  $w(\text{H}_2\text{O}_2) = 30\%$ , for trace analysis\*, CAS 7722-84-1
- Hydrochloric acid,  $w(\text{HCl}) = 30\%$ , for trace analysis\*, CAS 7647-01-0
- Ammonium oxalate  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 1 \text{ H}_2\text{O}$ , for analysis, CAS 6009-70-7
- Ammonium chloride  $\text{NH}_4\text{Cl}$ , for trace analysis\*, CAS 12125-02-9

- Cadmium standard stock solution,  $\beta(\text{Cd}^{2+}) = 1 \text{ g/L}$  (commercially available)
- Lead standard stock solution,  $\beta(\text{Pb}^{2+}) = 1 \text{ g/L}$  (commercially available)
- Copper standard stock solution,  $\beta(\text{Cu}^{2+}) = 1 \text{ g/L}$  (commercially available)
- Ultrapure water, resistivity  $>18 \text{ M}\Omega\cdot\text{cm}$  (25 °C), type I grade (ASTM D1193)

\* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

### Solutions

Oxalate buffer (pH = 1)	$c((\text{NH}_4)_2\text{C}_2\text{O}_4) = 0.25 \text{ mol/L}$ $c(\text{NH}_4\text{Cl}) = 0.35 \text{ mol/L}$ $c(\text{HCl}) = 0.3 \text{ mol/L}$ 35.5 g $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 1 \text{ H}_2\text{O}$ , 18.7 g $\text{NH}_4\text{Cl}$ and 31.6 mL $w(\text{HCl}) = 30\%$ are dissolved in warm water. After cooling down to room temperature, the solution is made up to 1 L with ultrapure water.
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### Standard solutions

Standard solutions with lower concentrations (e.g. 1 mg/L) are prepared from the corresponding stock solutions (1 g/L) by dilution with  $c(\text{HCl}) = 0.01 \text{ mol/L}$  or  $c(\text{HNO}_3) = 0.015 \text{ mol/L}$ .

### Analysis

#### Measuring solution:

- 5 mL oxalate buffer
- + 10 mL (diluted) digestion solution

If the metals to be determined are present in concentrations above the linear working range, the digestion solution has to be diluted accordingly with ultrapure water.

The concentrations are determined by standard addition.

### Parameters

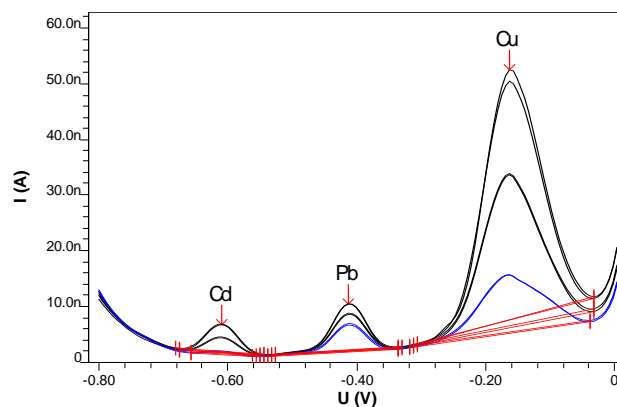
Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 $\text{min}^{-1}$
Potentiostatic pretreatment	
Potential 1	-0.8 V

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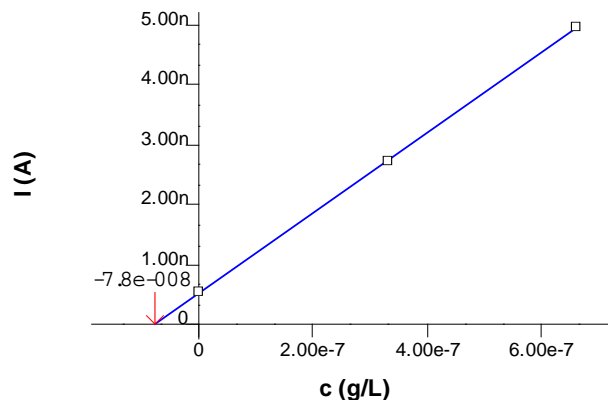
Waiting time 1	60 s
Equilibration time	10 s
Sweep	
Start potential	-0.8 V
End potential	0 V
Potential step	0.006 V
Potential step time	0.15 s
Sweep rate	0.04 V/s
Pulse amplitude	0.05 V
Substance	
Name	Cadmium
Characteristic potential	-0.6 V
Name	Lead
Characteristic potential	-0.41 V
Name	Copper
Characteristic potential	-0.17 V

### Example

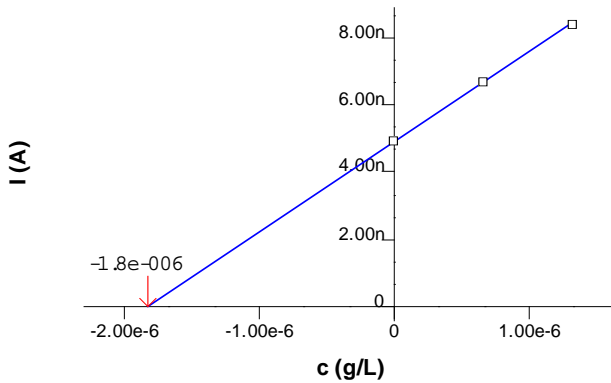


#### Cd

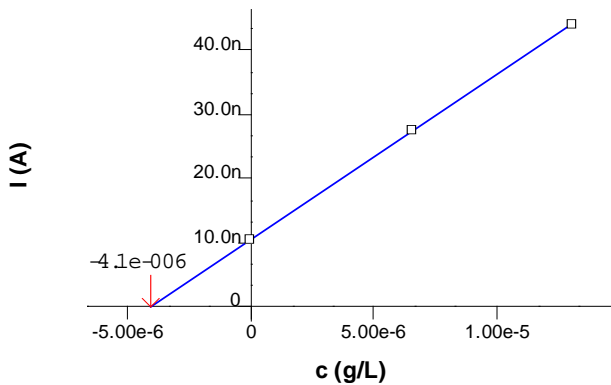
$c = 23.257 \text{ ug/l}$   
 $+/- 1.479 \text{ ug/l (6.36\%)}$



**Pb**  
**c = 549.507  $\mu\text{g}/\text{l}$**   
**+/- 12.186  $\mu\text{g}/\text{l}$  (2.22%)**



**Cu**  
**c = 1.216 mg/l**  
**+/- 0.037 mg/l (3.08%)**



electrode during deposition. To avoid this, the time for deposition (Waiting time 1) can be reduced.

- Limits of quantitation in the digestion solution (deposition time 60 s):
  - Cd 0.1  $\mu\text{g}/\text{L}$
  - Pb 0.1  $\mu\text{g}/\text{L}$
  - Cu 0.5  $\mu\text{g}/\text{L}$

Lower limits of quantitation can be obtained by increasing the time for deposition (Waiting time 1).

## Result

Sample	Artichoke juice
Sample size	1 mL
$\beta(\text{Cd})$	0.023 mg/L
$\beta(\text{Pb})$	0.549 mg/L
$\beta(\text{Cu})$	1.216 mg/L

## Comments

- The digestion procedure can also be applied for the determination of other non-volatile metals.
- For volatile analytes (e.g. As or Hg) a closed digestion apparatus is necessary, e.g. a microwave digestion system or a «High Pressure Asher HPA».
- In order to remain within the linear range of the method, the concentrations of Cd, Pb and Cu in the measuring vessel should not exceed 50 ... 80  $\mu\text{g}/\text{L}$  each. The total concentration of the three metals should not exceed 200  $\mu\text{g}/\text{L}$ . Higher concentrations overload the working

## Appendix

### Full report for the determination of Cd, Pb and Cu in artichoke juice using the 757 VA Computrace

===== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) =====

Determination : 04280943\_digested artichoke.dth  
 Sample ID : digested plant e  
 Creator method : Date : Time:  
 Creator determ.: Date : 1999-04-28 Time: 09:43:13  
 Modified by : --- Date : Time:

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 Method : AB113CdPbCu.mth  
 Title : Cd , Pb and Cu determination according to AB113  
 Remark1 : Digested Artichoke Juice: 1 mL digested, filled up to 100 mL)  
 Remark2 : 5mL Oxalate buffer + 10mL sample (5mL digested sample + 5mL water)  
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Sample amount : 5.000 mL  
 Cell volume : 15.000 mL  
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Substance : Cd  
 Conc. : 77.522 ng/L  
 Conc.dev. : 4.931 ng/L ( 6.36%)  
 Amount : 1.163 ng  
 Add.amount : 5.000 ng

VR	V	nA	I.mean	Std.Dev.	I.delta	Comments
1 - 1	-0.609	0.524	0.531	0.010	0.000	
1 - 2	-0.609	0.539				
2 - 1	-0.609	2.722	2.715	0.010	2.184	
2 - 2	-0.609	2.708				
3 - 1	-0.609	4.910	4.955	0.064	2.240	
3 - 2	-0.609	5.000				

Substance : Pb  
 Conc. : 1.832 ug/L  
 Conc.dev. : 0.041 ug/L ( 2.22%)  
 Amount : 27.475 ng  
 Add.amount : 10.000 ng

VR	V	nA	I.mean	Std.Dev.	I.delta	Comments
1 - 1	-0.413	4.911	4.888	0.032	0.000	
1 - 2	-0.413	4.865				
2 - 1	-0.413	6.653	6.644	0.012	1.756	
2 - 2	-0.413	6.636				
3 - 1	-0.413	8.285	8.346	0.088	1.702	
3 - 2	-0.413	8.408				

Substance : Cu  
 Conc. : 4.052 ug/L  
 Conc.dev. : 0.125 ug/L ( 3.08%)  
 Amount : 60.782 ng  
 Add.amount : 100.000 ng

VR	V	nA	I.mean	Std.Dev.	I.delta	Comments
1 - 1	-0.163	10.34	10.41	0.108	0.00	
1 - 2	-0.169	10.49				
2 - 1	-0.163	27.38	27.46	0.115	17.04	
2 - 2	-0.163	27.54				
3 - 1	-0.163	42.94	43.95	1.424	16.49	
3 - 2	-0.163	44.96				

Substance	Calibr.	Y.reg/offset	Slope	Mean	deviat.	Corr.Coeff.
Cd	std.add.	5.192e-010	6.697e-003	5.552e-011	0.99985	
Pb	std.add.	4.897e-009	2.674e-003	7.119e-011	0.99962	
Cu	std.add.	1.043e-008	2.574e-003	5.283e-010	0.99909	

Final results		+/-	Res. dev.	%	Comments
Cd:					
default	=	23.257	ug/l	1.479	6.361
Pb:					
default	=	549.507	ug/l	12.186	2.218
Cu:					
default	=	1.216	mg/l	0.037	3.082

**Method print for the determination of Cd, Pb and Cu with the 757 VA Computrace**-----  
Method parameters  
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Method : AB113CdPbCu.mth  
Title : Cd , Pb and Cu determination according to AB113  
Remark1 : Digested Artichoke Juice: 1 mL digested, filled up to 100 mL)  
Remark2 : 5mL Oxalate buffer + 10mL sample (5mL digested sample + 5mL water)

Calibration : Standard addition  
Technique : Batch

Cell volume (mL) : 15.000  
Sample amount (mL) : 5.000  
Sample ID : digested plant e

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Voltammetric parameters  
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Mode : DP - Differential Pulse

Highest current range : 1 mA  
Lowest current range : 100 nA

Electrode : HMDE  
Drop size (1..9) : 4  
Stirrer speed (rpm) : 2000

No. of additions : 2  
No. of replications : 2

Measure blank : No  
Addition purge time (s) : 30

Initial purge time (s) : 300

Conditioning cycles  
Start potential (V) : 0.000  
End potential (V) : 0.000  
No. of cycles : 0

Cleaning potential (V) : 0.000  
Cleaning time (s) : 0  
Deposition potential (V) : -0.800  
Deposition time (s) : 60

Sweep  
Equilibration time (s) : 15  
Start potential (V) : -0.800  
End potential (V) : 0.000  
Voltage step (V) : 0.006  
Voltage step time (s) : 0.150  
Sweep rate (V/s) : 0.040  
Pulse amplitude (V) : 0.050  
Pulse time (s) : 0.040

Cell off after measurement : Yes

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Peak evaluation  
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Peak evaluation : Height  
Minimum peak width (V.steps) : 5  
Minimum peak height (A) : 1.000e-010  
Smooth factor : 4  
Reverse peaks : No  
Reverse sweep : No

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Substances  
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Cd : -0.600 V +/- 0.050 V  
Standard solution : 1 0.100 mg/L  
Addition volume (mL) : 0.050  
default : Final result (Cd) = (1e+006 / 0.01) \* Mass.conc + 0 - 0

Pb : -0.400 V +/- 0.050 V  
Standard solution : 2 1.000 mg/L  
Addition volume (mL) : 0.010  
default : Final result (Pb) = (1e+006 / 0.01) \* Mass.conc + 0 - 0

Cu : -0.150 V +/- 0.050 V  
Standard solution : 3 1.000 mg/L  
Addition volume (mL) : 0.100  
default : Final result (Cu) = (1000 / 0.01) \* Mass.conc + 0 - 0