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# Application Bulletin

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Of interest to:      General analytical laboratories; Environmental protection;      B 1, 2, 4, 7, 8  
Pharmaceutical industry; Biology; Food

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

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### 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 No. 176.

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### Instruments and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
- 757 VA Computrace
- «Hach Digesdahl» digestion apparatus with special quartz vessels for open wet digestion

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### Reagents

All reagents used should be of the highest purity (p.a. or «suprapur»). Only ultrapure water should be used.

- Sulfuric acid,  $w(\text{H}_2\text{SO}_4) = 96\%$ , suprapur
- Hydrogen peroxide solution,  $w(\text{H}_2\text{O}_2) = 30\%$ , suprapur
- Hydrochloric acid,  $w(\text{HCl}) = 30\%$ , suprapur
- Ammonium oxalate  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 1 \text{ H}_2\text{O}$ , p.a., CAS 6009-70-7
- Ammonium chloride  $\text{NH}_4\text{Cl}$ , suprapur, CAS 12125-02-9
- Cadmium stock solution,  $\rho(\text{Cd}^{2+}) = 1 \text{ g/L}$  (commercially available)
- Lead stock solution,  $\rho(\text{Pb}^{2+}) = 1 \text{ g/L}$  (commercially available)
- Copper stock solution,  $\rho(\text{Cu}^{2+}) = 1 \text{ g/L}$  (commercially available)

**Ready-to-use solutions**

- 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  $c(\text{HNO}_3) = 0.015 \text{ mol/L}$ .
- 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.

**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.

**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 voltammogram is recorded using the following parameters:

working electrode	HMDE
stirrer speed	2000 rpm
mode	DP
purge time	300 s
pulse amplitude	50 mV
deposition potential	-800 mV
deposition time	60 s
equilibration time	10 s
start potential	-800 mV
end potential	0 V
voltage step	6 mV
voltage step time	0.15 s
sweep rate	40 mV/s
peak potential (Cd)	-600 mV
peak potential (Pb)	-410 mV
peak potential (Cu)	-170 mV

The concentrations are determined by standard addition.

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### Remarks

- 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 µg/L each. The total concentration of the three metals should not exceed 200 µg/L. Higher concentrations overload the working electrode during deposition. To avoid this, the deposition time can be reduced.
- Limits of quantitation (deposition time 60 s):
  - Cd 0.1 µg/L
  - Pb 0.1 µg/L
  - Cu 0.5 µg/L

Lower limits of quantitation can be obtained by increasing the deposition time.

**Figures**

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Method: AB113      .mth          OPERATION SEQUENCE
Title : Determination of Cd, Pb and Cu after digestion
    
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	Instructions	t/s	Main parameters	Auxiliary parameters	
1	DOS>M		Soln.name H2O	V.add	5.000 mL
2	DOS>M		Soln.name OxalBuff	V.add	5.000 mL
3	SMPL>M		V.fraction 5.000 mL	V.total	0.1 L
4	PURGE				
5	STIR	300.0	Rot.speed 2000 /min		
6	(ADD				
7	PURGE				
8	STIR	30.0	Rot.speed 2000 /min		
9	OPURGE				
10	SEGMENT		Segm.name ASV		
11	ADD>M		Soln.name Cd-std	V.add	0.010 mL
12	ADD>M		Soln.name Pb-std	V.add	0.020 mL
13	ADD>M		Soln.name Cu-std	V.add	0.050 mL
14	ADD) 2				
15	END				

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Method: AB113          SEGMENT
                        ASV
    
```

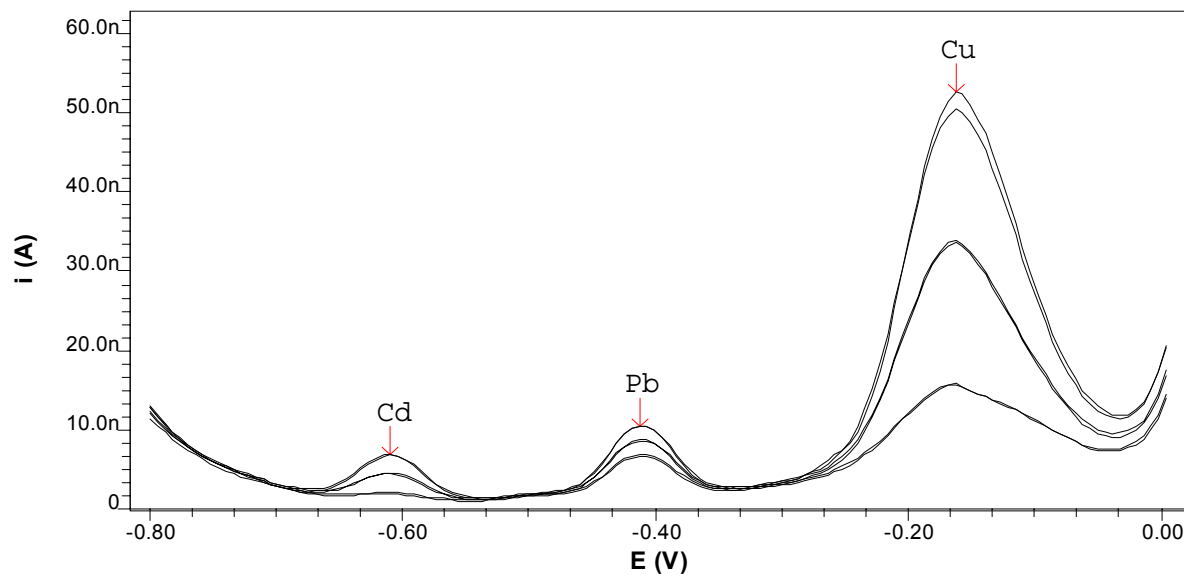
	Instructions	t/s	Main parameters	Auxiliary parameters	
1	(REP				
2	STIR	2.0	Rot.speed 2000 /min		
3	HMDE		Drop size 4	Meas.cell	normal
4	DPMODE		U.ampl 50 mV	t.meas	20.0 ms
			t.step 0.15 s	t.pulse	40.0 ms
5	MEAS	60.0	U.meas -800 mV		
6	OSTIR	10.0			
7	SWEEP	20.4	U.start -800 mV	U.step	6 mV
			U.end 0 mV	Sweep rate	40 mV/s
8	OMEAS		U.standby mV		
9	REP) 1				
10	END				

**Fig. 1:** Method for the determination of Cd, Pb and Cu with the 746 VA Trace Analyzer.

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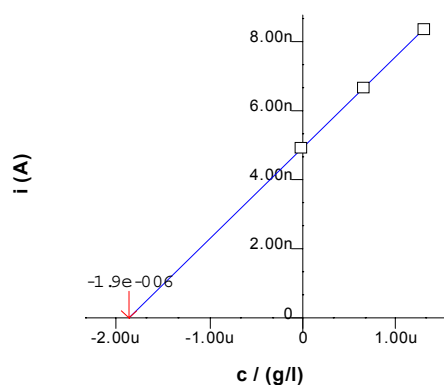
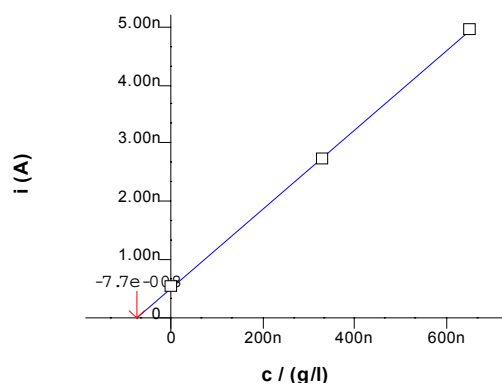
===== METROHM 757 VA COMPUTRACE (5.757.0010) =====
Determ.      : 04280943_digested_artichoke.dth
Date         : 1999-04-28           Time: 08:43:13
Modified    : 2000-08-29 08:34:35   User:
Cell volume  : 15.000 ml
-----
Ident        : digested plant e           Sample volume
                                           5.000 ml
-----
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)
-----
Substance   : Cd                               Comments
Mass conc.  : 76.590 ng/l
MC.dev.     : 8.263 ng/l           ( 10.79%)
Mass        : 1.149 ng
Add.mass    : 5.000 ng
-----
          VR      V      nA      i.mean  Std.Dev.  i.delta  Comments
          -----
          1-1     -0.609  0.524  0.532   0.050
          1-2     -0.609  0.541
          2-1     -0.609  2.722  2.715   0.050   2.183
          2-2     -0.609  2.708
          3-1     -0.609  4.910  4.958   0.067   2.243
          3-2     -0.609  5.005
-----
Substance   : Pb                               Comments
Mass conc.  : 1.852 ug/l
MC.dev.     : 0.069 ug/l           ( 3.70%)
Mass        : 27.784 ng
Add.mass    : 10.000 ng
-----
          VR      V      nA      i.mean  Std.Dev.  i.delta  Comments
          -----
          1-1     -0.413  4.911  4.888   0.050
          1-2     -0.413  4.865
          2-1     -0.413  6.626  6.635   0.050   1.747
          2-2     -0.413  6.644
          3-1     -0.413  8.272  8.335   0.089   1.700
          3-2     -0.413  8.398
-----
Substance   : Cu                               Comments
Mass conc.  : 4.033 ug/l
MC.dev.     : 0.078 ug/l           ( 1.94%)
Mass        : 60.488 ng
Add.mass    : 100.000 ng
-----
          VR      V      nA      i.mean  Std.Dev.  i.delta  Comments
          -----
          1-1     -0.163  10.34  10.41   0.108
          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      Nonlin.      Mean deviat.
-----
Cd          std.add.      5.167e-010      6.760e-003
Pb          std.add.      4.890e-009      2.642e-003
Cu          std.add.      1.042e-008      2.583e-003
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Final results      +/- Res. dev.      %      Comments
-----
Cd = 22.977 ug/l      2.479      10.789
Pb = 555.678 ug/l    20.560      3.700
Cu = 1.210 mg/l      0.024      1.943
    
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**Fig. 2:** Full Report for the determination of Cd, Pb and Cu in artichoke juice using the 757 VA Computrace.

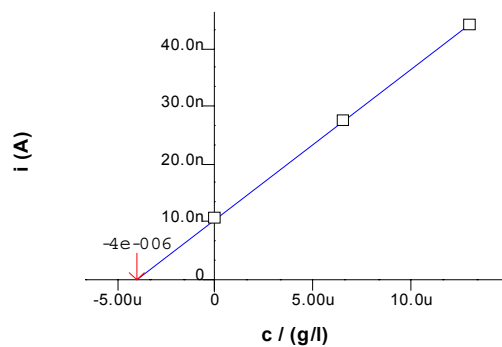


Cd  
 $c = 22.977 \mu\text{g/l}$   
 $\pm 2.479 \mu\text{g/l} (10.79\%)$

Pb  
 $c = 555.678 \mu\text{g/l}$   
 $\pm 20.560 \mu\text{g/l} (3.70\%)$



Cu  
 $c = 1.210 \text{ mg/l}$   
 $\pm 0.024 \text{ mg/l} (1.94\%)$



**Fig. 3:** Voltammograms and standard addition curves for the determination of Cd, Pb and Cu in artichoke juice using the 757 VA Computrace.