



# SIMULTANEOUS DETERMINATION of Pb, Cd, Cr, Ni, and Cu in PLANTS using microwave digestion and graphite furnace AAS

## Introduction

The determination of lead, cadmium, chromium, nickel, and copper in plants is part of several biological monitoring programs. Monitoring these elements is important in order to observe and document the damage on plants caused by environmental pollution. The samples consist of leaves and needles collected from different types of trees. These trees are selected species monitored over a long period of time. The method described shows how Pb, Cd, Cr, Ni, and Cu can be measured simultaneously using electrothermal atomic absorption spectrometry (ETAAS).

The following standard reference materials were used to verify the method:

NBS reference material:

NIST 1571 (Orchard Leaves)

NIST 1572 (Citrus Leaves)

NIST 1575 (Pine Needles)

BCR reference material:

CRM 60 (Igarosiphon major)

CRM 62 (olive leaves)

## Experimental

A standard PerkinElmer SIMAA™ 6100 simultaneous atomic absorption spectrometer with transversely heated graphite furnace and Zeeman-effect background correction was employed. An electrodeless discharge lamp (EDL) was used for Cd, whereas hollow cathode lamps (HCL) were used for Pb, Ni, Cr, and Cu. The concentration of the palladium-magnesium nitrate matrix modifier was 5 µg Pd and 3 µg Mg(NO<sub>3</sub>)<sub>2</sub> per analysis.

The PerkinElmer multielement standard (Part Number N930-0244) was used to prepare the reference solutions. All reference solutions and samples were acidified using 0.2% (v/v) ultrapure HNO<sub>3</sub>.

The samples were collected from reference trees using the seventh verticil from the top. The needle samples from conifers were collected during the winter pause of vegetation growth and the leaves from deciduous trees were collected during foliage.

## Microwave Sample Digestion

The decompositions were performed in a PerkinElmer Multiwave Microwave Digestion System:

- The plant samples were first dried at 105°C for 6 to 8 hours.

- The standard reference materials (NIST and CRM) were dried at 80°C for 2 hours.
- 0.5 gram of the dry material was decomposed in a quartz vessel using 1 mL HCl and 4 mL HNO<sub>3</sub>.
- The digested samples were made up to 25-mL volume using deionized water.

## Multiwave Program

Step	Power from	Power to	Time
1	100 W	500 W	5 min
2	800 W	800 W	15 min
3	cool	cool	15 min

## Instrument Parameter

Element	Pb	Cd	Cr	Ni	Cu
Wavelength (nm)	283.3	228.8	357.9	232.0	324.8
Lamp	HCL	EDL	HCL	HCL	HCL
Lamp current (mA)	10	200	25	25	25
Integration time (s)	3.5	2.5	5.0	5.0	4.0
Std 1 (µg/L)	60	3	12	30	30
Std 2 (µg/L)	120	6	24	60	60
Std 3 (µg/L)	200	10	40	100	100
Technique	----- AA-BG -----				
Signal processing	----- Peak Area -----				
Modifier (10 µL)	5 µg Pd + 3 µg Mg (NO <sub>3</sub> ) <sub>2</sub>				
Replicates	3				
Modifier (10 µL)	5 % Pd (NO <sub>3</sub> ) <sub>2</sub> + 0.5% Mg (NO <sub>3</sub> ) <sub>2</sub>				

## THGA Program

Step	Temp (°C)	Ramp time (s)	Hold time (s)	Internal flow (mL/min)	Gas type	Read
1	110	1	30	250	Ar	
2	130	25	30	250	Ar	
3	400	10	20	250	Ar	
4	2300	0	5	0	Ar	X
5	2450	1	5	250	Ar	

## Precision and Recoveries

The results of the analyses of the microwave-digested plant reference materials are shown in the following tables.

### Orchard Leaves (NIST 1571)

Analyte	Certified value (mg/kg)	Average results (mg/kg)	SD	RSD (%)	Recovery (%)
Pb	45 ± 3	40.75	0.408	1.0	83.8
Cd	0.1 ± 0.01	0.10	0.002	1.7	92.1
Cr	2.6 ± 0.3	2.32	0.005	0.2	98.9
Ni	1.3 ± 0.2	1.37	0.025	1.8	99.0
Cu	12 ± 1	11.90	0.037	0.3	91.2

### Citrus Leaves (NIST 1572)

Analyte	Certified value (mg/kg)	Average results (mg/kg)	SD	RSD (%)	Recovery (%)
Pb	13.3 ± 2.4	12.41	0.273	2.2	101.4
Cd	0.03 ± 0.01	0.04	0.002	4.6	99.0
Cr	0.8 ± 0.2	0.74	0.009	1.2	98.9
Ni	0.6 ± 0.6	0.61	0.029	4.9	102.9
Cu	16.5 ± 1.0	16.57	0.116	0.7	101.7

### Pine Needles (NIST 1575)

Analyte	Certified value (mg/kg)	Average results (mg/kg)	SD	RSD (%)	Recovery (%)
Pb	10.8 ± 0.5	9.34	0.037	0.4	87.9
Cd	< 0.50	0.2	0.004	2.1	107.4
Cr	2.60 ± 0.2	2.58	0.021	0.8	92.2
Ni	(3.50)	2.36	0.054	2.3	96.4
Cu	3.00 ± 0.3	2.91	0.020	0.7	112.7

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## Lagarosiphon Major (CRM 60)

Analyte	Certified value (mg/kg)	Average results (mg/kg)	SD	RSD (%)	Recovery (%)
Pb	63.8 ± 3.2	65.50	0.196	0.3	91.0
Cd	2.20 ± 0.10	2.27	0.029	1.3	101.4
Cr	nn	25.15	0.151	0.6	98.9
Ni	(40)	40.77	0.367	0.9	102.2
Cu	51.2 ± 1.9	57.72	0.404	0.7	93.9

## Olive Leaves (CRM 62)

Analyte	Certified value (mg/kg)	Average results (mg/kg)	SD	RSD (%)	Recovery (%)
Pb	25.0 ± 1.5	25.96	0.649	2.5	87.9
Cd	0.10 ± 0.02	0.08	0.006	6.1	87.2
Cr	nn	1.63	0.030	1.8	98.0
Ni	(8)	3.16	0.231	7.3	101.1

## Pine Needles (Real Sample)

Analyte	Results (mg/kg)	SD	RSD (%)	Recovery (%)	
Cu	46.6 ± 1.8	145.95	0.229	0.5	101.2
Pb	29.07	0.486	1.7	101.5	
Cd	0.42	0.009	2.1	100.5	
Cr	6.70	0.070	1.0	100.2	
Ni	5.79	0.218	3.7	96.1	

Cu 52.10 0.374 0.7 94.3

## Summary

The method described is applicable for the determination of low (ppb) levels of metals in digests of plant samples. Standard THGA graphite tubes were used.

The methodology and results presented demonstrate the potential of simultaneous graphite furnace AAS for the accurate determination of trace metals in plants.

In addition, there is significant time savings using fast microwave sample digestion, followed by the simultaneous atomic absorption determination of five elements.

