

## Determination of Cd, Pb, Cu and Zn in Wood by Differential Pulse Anodic Stripping Voltammetry

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This paper presents a new method for the determination of cadmium, lead, copper and zinc in the wood of oaks *Quercus robur L.*, using differential pulse anodic stripping voltammetry at the hanging mercury drop electrode. Wood samples were mineralized by a mixture of 30 % hydrogen peroxide with a small addition of concentrated nitric acid. The base electrolyte was 0.2 mol l<sup>-1</sup> acetic acid in the case of Cd, Pb and Cu and 0.2 mol l<sup>-1</sup> acetate buffer at pH 4.5 in the case of Zn. The accuracy and precision of the described method were satisfactory (the relative standard deviation was 11.8 % for Cd, 1.4 % for Pb, 9.0 % for Cu and 15.9 % for Zn).

W pracy przedstawiono metodę oznaczania kadmu, ołowiu, miedzi i cynku w drewnie dębów *Quercus robur L.*, metodą woltamperometrii różnicowej pulsowej, z użyciem wiszącej rtęciowej elektrody kropłowej. Próbki drewna mineralizowano mieszaniną 30 % wody utlenionej z niewielkim dodatkiem stężonego kwasu azotowego. Elektrolitem podstawowym był 0,2 mol l<sup>-1</sup> roztwór kwasu octowego w przypadku oznaczania Cd, Pb i Cu oraz 0,2 mol l<sup>-1</sup> bufor octanowy (pH 4.5) w przypadku oznaczania Zn. Dokładność i precyzja opracowanej metody są zadowalające (względne odchylenie standardowe opracowanej metody wynosi 11.8 % dla Cd, 1.4 % dla Pb, 9.0 % dla Cu i 15.9 % dla Zn).

An increasing pollution of natural environment with heavy metals emitted by industry presents more and more problems. In this connection it has become necessary to determine concentrations of heavy metals in many components of the environment. Very important in the control over heavy metal concentrations are reliable analytical methods.

Electrochemical methods, particularly voltammetric methods, are exceptionally useful in this respect. They have high detectability, exceeding that of atomic absorption spectrophotometry (AAS), and sufficient precision and accuracy. A proper choice of the supporting electrolyte makes possible to determine several ions simultaneously, whereas the apparatus is simple and easily available. Voltammetric methods have been used many times for determinations of metals in natural environment, for instance, in soil [1–3], industrial wastes [4], biological materials [5], pine and poplar wood [6, 7] as well as in oak wood, after mineralization by a mixture of  $\text{HNO}_3 + \text{HClO}_4$  and application of  $\text{HClO}_4$  as a supporting electrolyte [8, 9].

This paper presents the application of the differential pulse anodic stripping voltammetry method (DPASV) at the hanging mercury drop electrode for determination of Cd, Pb, Cu and Zn in the wood of oaks *Quercus robur L.* Heavy metals accumulated in the xylem of trees constitute a long-lasting indicator of contamination by heavy metals. Studies of heavy metals absorption by oak wood are also very significant since the oak stand decline has been observed in Europe in recent years and the reason of that has not been elucidated unambiguously [10]. The supporting electrolyte was  $0.2 \text{ mol l}^{-1}$  acetic acid in the case of Cd, Pb and Cu and  $0.2 \text{ mol l}^{-1}$  acetate buffer at pH 4.5 in the case of Zn. The obtained results were compared with the data obtained by the AAS method.

## EXPERIMENTAL

### Apparatus

Anodic stripping voltammograms were obtained with a PA-4 Polarographic analyzer, Laboratorni Pristroje (Czecho-Slovakia).

The electrochemical measurements were performed in a 3-electrode system: hanging mercury drop electrode (HMDE), produced by Laboratorni Pristroje (Czecho-Slovakia), saturated calomel electrode (SCE) and Pt wire electrode. The differential pulse amplitude was 50 mV and the scan rate was  $10 \text{ mV s}^{-1}$ .

Measurements with AAS were conducted by the AAS 1N flame spectrophotometer (Zeiss, Jena).

### Reagents

The reagents: acetic acid, nitric acid and sodium hydroxide were Suprapur (Merck). Hydrogen peroxide, analytical grade, was produced by POCh (Poland). Standard solutions of Cd, Pb, Cu and Zn were prepared by dissolving the metals in  $\text{HNO}_3$ . Solutions with concentrations below  $10^{-3} \text{ mol l}^{-1}$  were prepared just before use. Water was doubly distilled in a quartz still.

### Materials

Wood samples were taken from the oak trees *Quercus robur L.* originating from areas with a varied pollution of the soil with heavy metals (Table 1). The samples were taken from several oak trees on each investigated forest area with the aid of Pressler's bore at an altitude of 1.30 m from the ground.

Table 1. The state of oak stands under study

Location of stand	Research area	Age of trees	Soil pollution [2, 6, 7]
Copper Basin	Biechów – 2 km from Głogów Smelter	about 80	Cu, Pb
Zawiercie	3 km from Zawiercie Steel Mill	about 130	Zn, Pb, Cd, Cu
Kórnik	Experimental Forest Zwierzyniec	about 100	non polluted

### Procedure

The cores were polished with a piece of glass in order to avoid surface contamination of the sample. Then wood samples were dried (105°C, 24 h) and homogenized by powdering in a ball mill. About 0.5 g wood samples were put into a conical quartz 100 ml cup and 1 ml of concentrated nitric acid and 1 ml of 30 % hydrogen peroxide were added. This mixture was covered with a quartz watch glass and heated. Then, 15 ml H<sub>2</sub>O<sub>2</sub> were added in 1ml portions to keep the mixture boiling gently. After wood mineralization the solution was evaporated to wet salts. The salt residue was 5 times dissolved in 1 ml of water and evaporated each time to dryness. The mineralized sample was dissolved in acetic acid (in a quantity giving the final concentration in the analysed solution 0.2 mol l<sup>-1</sup>), and transferred into a 50 ml flask, filled up with water to the mark.

40 ml of solution was transferred into a voltammetric cell and deaerated with pure nitrogen for 15 min. The electrolytic deposition in stirred solution at -0.90 V vs. SCE was performed for 2 to 6 min, depending on the expected metals content. The voltammogram of Cd, Pb and Cu was recorded from -0.90 to +0.10 V. The concentrations of metals were estimated by the standard-addition method.

The procedure for zinc determination depends on its content in a sample. When the concentration of zinc is below 7 ppm, it can be determined from the same solution. For that purpose pH should be adjusted to 4.5 by sodium hydroxide and Zn is determined at  $E_{dep} = -1.40$  V. For determination of higher concentrations of Zn in the wood the analysed solution should be diluted.

### RESULTS AND DISCUSSION

In the applied supporting electrolytes the determined ions give well defined peaks. The potential of Zn peak in 0.2 mol l<sup>-1</sup> acetate buffer at pH 4.5 is -1.02 V. The potentials of Cd, Pb and Cu in 0.2 mol l<sup>-1</sup> acetic acid are -0.60, -0.42 and -0.05 V, respectively.

The developed method was statistically evaluated by estimating the precision and recovery of the metals determined in the wood samples from Kórnik (Table 2). The recovery of added metals was very good and the precision of their determination was satisfactory (the relative standard deviation ranged within 1.4 to 15.9 %).

**Table 2.** Recovery and precision of metal determination in wood by DPASV

Metal	Found ( <i>n</i> = 8) $\mu\text{g g}^{-1}$	S.D. $\mu\text{g g}^{-1}$	R. S. D. %	Added $\mu\text{g g}^{-1}$	Total found $\mu\text{g g}^{-1}$
Cd	0.22	0.026	11.8	0.22	0.45
				0.67	0.85
Pb	0.45	0.065	1.4	0.83	1.28
				1.66	2.12
Cu	0.63	0.057	9.0	0.51	1.16
				1.52	2.12
Zn	7.50	1.19	15.9	10.4	17.7
				31.4	39.0

Following the described procedure the concentrations of Zn, Cd, Pb and Cu were determined in the wood of oaks growing in two other research areas. The performed studies showed a significant increase in Cu content in the oak wood from the copper basin as compared with that from the referred area in Kórnik, and an increase in Zn content in the oak wood from Zawiercie.

The results were compared with data obtained with the use of the atomic absorption spectrophotometric method. In the case of Cd and Pb determination by AAS additional concentration of the extract was required (Table 3). The results indicate that the determined concentrations of Zn, Cd, Pb and Cu in the wood were similar using both methods. The use of DPASV, however, increases the sensitivity of the method.

The developed method was used in estimation of the effect of industrial pollutions on oak stand decline on the Krotoszyn Plateau (West-Central part of Poland) [11].

**Table 3.** Determination of Cd, Pb, Cu and Zn in oak trees ( $\mu\text{g g}^{-1}$ ) by two independent methods

Sampling regions	Cd		Pb		Cu		Zn	
	DPASV	AAS	DPASV	AAS	DPASV	AAS	DPASV	AAS
Głogów	0.15	0.17	0.93	0.95	15.8	15.2	12.9	12.8
Zawiercie	0.12	0.13	0.38	0.40	1.10	1.01	25.3	26.0

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