DISTRIBUTION OF TRACE METALS IN THE ICE STALAGMITE

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Abstract. Concentration of trace metals (Cd, Pb, Cu and Zn) in melted fractions of ice stalagmite from the "Ledena Pecina" (Ice cave) on Durmitor mountain was determined. Differential pulse anodic stripping voltammetry was applied as one of the predominant methods in trace metal analysis. Obtained results indicate gradually decreasing contents of metals from central to surface layers of ice stalagmite. Logarithm of concentration is a decreasing linear function of ice stalagmite volume. This linearity indicates that the reactions between trace metals in a solution and solid surface of ice stalagmite can be described as a quasi-first order reaction. It might be the result of kinetic processes between the growth of stalactite and its corresponding ice stalagmite followed by present interactions between trace metals and increasing of sample surface.

Keywords: ice stalactite, ice stalagmite, trace metals, distribution, sorption.

AIMS AND BACKGROUND

"Ledena Pecina" (Ice cave) is situated on Durmitor mountain at 2150 m a.s.l. Freezing of water, that penetrates through the soil, has formed the existing ice stalactites and ice stalagmites. In our previous works, trace metals analysis of water, snow and ice samples from the different locations on Durmitor mountain[1-3] have been done. In this study the aim of our investigation was to determine Cd, Pb, Cu and Zn concentrations in successively melted fractions (layers) of ice stalagmite.

EXPERIMENTAL

Apparatus: anodic stripping voltammetry, model ECP 140, connected with electrochemical stand ECP 102, both manufactured by EDT analytical Ltd.; pH/ionmeter, model ECM221 Micron 2, manufactured by EDT analytical Ltd.; UV mercury lamp (300W) manufactured by OSRAM.

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Laboratory: Environmental Physics Laboratory at the Institute of Physics, Belgrade. This laboratory was designed to be "Clean room" class 100.

Reagents and solutions: 0.1 M HNO_3 solution was prepared using concentrated HNO_3 (Merck, s.p.); ammonia/ammonium chloride buffer solution; solutions of 0.1, 1 and 10 μg ml⁻¹ Cd, Pb, Cu and Zn were prepared by dissolving corresponding metals (99.99%).

All chemicals were of spectroscopic grade and ultrapure water was prepared by demineralization and double distillation in a quartz apparatus.

The sample of ice stalagmite was taken on August 20th 1999 and transported to the laboratory in the polyethylene bag using insulated field carrier. Ice stalagmite was mounted at a modified holder and positioned opposite to its natural position (the base facing upward). Melting the stalagmite layer by layer six different fractions (0.75 l each) were separated. Water drops were collected in clean polyethylene bottles.

Samples were irradiated by UV light to destroy dissolved organic substances that may interfere determination. Differential pulse anodic stripping voltammetry was applied to determine Cd, Pb, Cu and Zn concentration. Analytical procedure was described in our previous paper[4].

RESULTS AND DISCUSSION

The obtained results are presented in Table 1.

Table 1. Concentration of trace metalas in different melting fractions

No of fraction*	Concentration of trace metals (μg l⁻¹)			
	Cd	Pb	Cu	Zn
1	0.41	2.67	3.86	37.3
2	0.36	1.62	2.45	26.3
3	0.29	1.07	1.78	17.6
4	0.23	0.61	1.06	11.7
5	0.18	0.52	0.70	7.50
6	–	0.46	0.47	5.32

*Number of the separated fraction is related to the melting layer starting from central to the surface of the ice stalagmite.

These experimental results imply on analysed trace metals contents distribution through the layers of ice stalagmite. For explanation of this phenomenon, some valid conditions in the Ice cave must be established:

- Inflow of the water is constant in the case for a longer period.
- Concentration of analyzed trace metals in inflowing water is constant.

The amount of analyzed metals in penetrating water depends on the soil contents. Since the observed area of Durmitor mountain is relatively isolated (far

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away from possible sources of contamination), the contents of substances in the soil are constant, including analyzed metals.

- Temperature in the cave is practically constant and around $-9°C$.

The dynamics of processes in the Ice cave related to the growth of ice stalactite and ice stalagmite was used to explain the obtained distribution in stalagmite layers. Water is penetrating the cave through the soil from above. Since the temperature in the cave is less than $0°C$, some of inflowing water remain frozen on the cave ceiling forming ice stalactite. Unfrozen water is dripping from ice stalactite to the ground below, forming ice stalagmite. Therefore, formation of ice stalagmite is closely related to the formation of ice stalactite. During the growth of ice stalactite, analysed metals in the inflowing water are held on the solid phase surfaces. As the consequence of the constant water inflow and increasing surface, bounding of trace metals takes place on newly formed active centers. This conclusion implies the increase of analysed metals contents on the ice stalactite surface. Therefore, ice stalagmites were formed from unfrozen water containing lower concentration of trace metals. Consequently, concentration and distribution of trace metals in ice stalagmite correspond to the concentration and distribution of trace metals in the liquid phase that pours all over ice stalactite surface.

Increasing of water volume with time is given by:

$$V = \omega t \tag{1}$$

where ω is the volume rate of water inflow and, according to the first condition, is constant.

The following relation can display forming of ice stalactite surface by freezing of the part of the liquid volume in contact with surface per unit of time:

$$P + V_p \rightarrow P' \tag{2}$$

where P is the starting surface, P' – the newly formed surface and V_p – the volume of water per unit time poured all over P.

Since water inflow is constant (first condition) and losses of V_p due to freezing are minor, we assume that V_p is constant. Relation (2) could be observed as quasi-first order reaction. The rate of formation of P' is defined by:

$$\frac{dP'}{dt} = kP \tag{3}$$

where k is the first order rate constant.

After integration of equation (3), with boundary conditions that for $t = 0, P' = P_0,$ we obtain:

$$\ln \frac{P'}{P_0} = \frac{k}{\omega} t \tag{4}$$

By replacing t from equation (1) into equation (4), it becomes:

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$$\ln\frac{P'}{P_0} = \frac{k}{\omega}V \tag{5}$$

From the equation for the coefficient of distrubution K_d, the surface of solid phase can be expressed as:

$$P' = \frac{m_s V_p}{K_d C_1} = \frac{m_s V_p}{K_d (C_0 - C_s)} \tag{6}$$

where m_s is the amount of metals that has been sorbed on P', C_1 – the equilibrium concentration in liquid phase, C_0 – the concentration of metals in inflow water and C_s – the concentration of metals that has been sorbed on P'.

From equation (6) it follows that surface P' is proportional to m_s and C_1^{-1}. By substituting P' with C_1 from equation $P = aC_1^{-1}$, where a is a constant, equation (5) can be written as:

$$\ln C_1 = -\frac{k}{\omega}V + \ln P_0 \tag{7}$$

The last equation (7) is a modified equation for first order reactions in which the time is substituted with volume. It has been already explained that the concentration of trace metals in ice stalagmite layer (C) is the same as the concentration of these metals in liquid phase on the surface of ice stalactite (C_1).
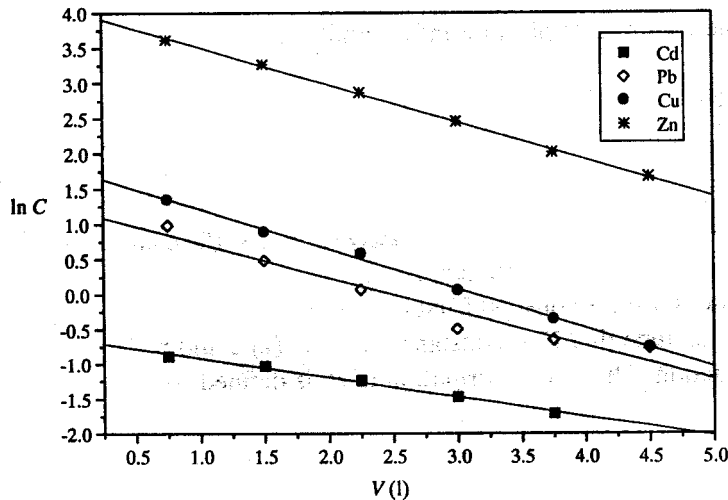

Fig. 1. The variation of ln$C$ versus volume increase of ice stalagmite

CONCLUSIONS

Since the dependence ln$C$ = $f(V)$ in our experiment is linear (Fig. 1), it can be concluded that one of the dominant processes between trace metals in liquid and solid surface of ice stalactite is sorption.

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It has to be mentioned that the explanation of this phenomenon is probably valid in the case of low metal concentration, as it was the case in our experiment. Also, the additional condition was that influence of other interactions was constant.

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