

SHORT COMMUNICATION

**Accumulation of cadmium and zinc in bottom sediments of different waters of Lithuania**

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*Abstract:* Distribution of cadmium and zinc in the bottom sediments of different waters of Lithuania was investigated using flame atomic absorption spectrometry (FAAS). Two methodologies (liquid and heating mineralization) for the mineralization of the bottom sediments were employed and compared. The accuracy of the FAAS method was evaluated in comparison with a photometric method. The obtained results demonstrate that the suggested procedure could be successfully applied for the analysis of bottom sediments of different water complexes with satisfactory accuracy.

*Keywords:* cadmium, zinc, bottom sediments, FAAS, mineralization.

INTRODUCTION

Heavy metals concentration in bottom sediments is an unbiased and reliable index of the contamination of a water body and thereby the total anthropogenic load. Accumulation of heavy metals in bottom sediments in concentrations exceeding standard and background levels endangers water quality owing to the risk of secondary pollution (export of microelements from the bottom sediments to the water column). High concentrations of heavy metals in bottom sediments have a negative effect on biological components. Thus, environmental protection requires a constant analytical control not only of waters but also of bottom sediments.

Zinc in trace levels is essential for living organism<sup>1–4</sup> but toxic doses of zinc can lead to serious problems. On the contrary, cadmium is a carcinogen and does not have any known positive biological role.<sup>5,6</sup> For the determination of zinc and cadmium in bottom sediments different analytical methods are used: inductively coupled plasma atomic emission spectrometry,<sup>7–9</sup> inductively coupled plasma-mass spectrometry,<sup>10</sup> neutron activation analysis,<sup>11</sup> X-ray fluorescence.<sup>12,13</sup> However, atomic absorption spectrometry (AAS) is one of the most extensively used tech-

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niques for the determination of cadmium and zinc in bottom sediments. This analytical technique is remarkable for its selectivity, speed and fairly low operational cost.<sup>14,15</sup> Zinc and cadmium have been determined in sediments of stream, pond, lake, river, marine and in sewage sludge.<sup>16–20</sup>

Determination of heavy metals in bottom sediments is a more fraught procedure in comparison to water analysis. For water samples, direct analysis with the atomic absorption spectrometer can be employed, while samples of bottom sediments must be mineralized prior to their analysis. Before the analysis by AAS, the samples of bottom sediments can be dissolved in mineral acids or their mixtures.<sup>7,16–18,20–22</sup> The samples of bottom sediments can also be decomposed by heating in an ordinary furnace at a particular temperatures.<sup>19</sup>

The aim of this work was to investigate the accumulation of two heavy metals (zinc and cadmium) in bottom sediments from different waters of Lithuania using the FAAS technique. For the successful FAAS determination of Zn and Cd both the liquid and heating mineralization procedures were also compared in this work.

#### EXPERIMENTAL

A Hitachi 170–50 (Japan) flame atomic absorption spectrometer equipped with hollow cathode lamps was used for the determination of Zn and Cd in bottom sediments. The optimum conditions for the determination of the metals by the flame AAS method are summarized in Table I. For comparison, the amounts of cadmium and zinc in the samples were also determined by photometric analysis<sup>23</sup> with a KFK-3 photometer. Cd was determined in aqueous medium with dithizon and Zn with rhodamine C. The photometric measurements were carried out at wavelengths of  $\lambda = 508$  nm (Cd) and 630 nm (Zn).

TABLE I. The optimum conditions for the determination cadmium and zinc by the flame AAS method

Metal	Radiation nm	Gas	Electric current mA	Gas pressure/Pa	Air pressure/Pa
Cd	228.8	Propane–butane–air	10	$0.74 \cdot 10^4$	$1.47 \cdot 10^5$
Zn	213.8	Acetylene–air	10	$0.98 \cdot 10^4$	$0.98 \cdot 10^5$

Double–distilled water and analytical–grade reagents were used in all the experiments. Standard solutions of cadmium and zinc ( $1 \text{ mg ml}^{-1}$ ) were prepared by dissolving an appropriate amount of metallic cadmium (99.99 % purity) in nitric acid (1:1) and ZnO in hydrochloric acid (1:1), respectively. The standard solutions of Zn and Cd were diluted daily to obtain working standard solutions ( $10 \text{ } \mu\text{g ml}^{-1}$ ).

The samples of bottom sediments (0.5 g) were dissolved in 10 ml of a mixture of HCl and HNO<sub>3</sub> (3:1). The cooled remnants were digested by addition of 10 ml of concentrated HCl, evaporated to a minimum size, filtered and diluted to 100 ml with water. Also, identical amounts of bottom sediments samples were placed in a sand beaker and heated at  $825 \pm 25$  °C for 2 h in the furnace. The cooled remnants were digested by addition of 10 ml of a mixture of HCl and HNO<sub>3</sub> (3:1) and diluted to 100 ml with water.

#### RESULTS AND DISCUSSION

The amount of zinc and cadmium was determined in several bottom sediments samples from different waters of Lithuania. The results obtained for the determination of zinc by the FAAS method using the two mineralization procedures are com-

pared and summarized in Tables II and III. As can be seen from the results presented in both Tables, the mineralization procedure does not have any influence on the determined amount of zinc in different samples. Consequently, it can be concluded that both mineralized methods could be successfully used for the determination of zinc in bottom sediments. For the determination of cadmium in bottom sediments, the method of liquid mineralization was chosen in this work. The results obtained for the determination of cadmium by the FAAS method were compared with those achieved by a conventional photometric method and are summarized in Table IV.

TABLE II. Results obtained for the determination of zinc in bottom sediment samples after liquid mineralization ( $n = 5$ ,  $P = 0.95$ ), with standard deviations, %, in parentheses

Sample	Zn found by FAAS method, mg kg <sup>-1</sup>	Zn found by photometric method/mg kg <sup>-1</sup>
Sea Kuršių	221 (1.4)	225 (3.4)
Lake Drūkšiai	67 (3.0)	64 (4.8)
Lake Žaliejį	105 (2.5)	99 (5.2)
Standard sludge from Lithuania	261 (2.0)	265 (4.2)
Standard sludge from the Environment Institute of the Europe Committee	540 (1.8)	548 (3.7)

TABLE III. Results obtained for the determination of zinc in bottom sediment samples after heating mineralization ( $n = 5$ ,  $P = 0.95$ ), with standard deviations, %, in parentheses

Sample	Zn found by FAAS method/mg kg <sup>-1</sup>	Zn found by photometric method/mg kg <sup>-1</sup>
Sea Kuršių	229 (1.3)	228 (3.6)
Lake Drūkšiai	69 (3.0)	67 (4.8)
Lake Žaliejį	106 (2.3)	103 (5.4)
Standard of sludge from Lithuania	264 (2.2)	263 (4.0)
Standard of sludge from Environment Institute of Europe Committee	542 (1.7)	545 (4.2)

As seen from Table II and III, the highest level of zinc was found in standard sludge from the Environment Institute of the Europe Committee (540 mg kg<sup>-1</sup>) and the lowest – in Lake Drūkšiai (67 mg kg<sup>-1</sup>). The highest level of cadmium (Table IV) was also found in standard sludge from the Environment Institute of the Europe Committee (14.6 mg kg<sup>-1</sup>) and the lowest – in standard sludge from Lithuania (1.64 mg kg<sup>-1</sup>). The levels of zinc determined in the Sea Kuršių are approximately 2 times higher than that found in Lake Žaliejį and about 3 times higher than that in Lake Drūkšiai. The levels of cadmium determined in the same Sea are also higher than that found in the Lakes. The concentrations of heavy metals in bottom sediments depend on different factors: lithological composition of soils, content of organic carbon in sediments. However, pollution remains one of the most important.

TABLE IV. Results obtained for the determination of cadmium in bottom sediment samples after liquid mineralization ( $n = 5$ ,  $P = 0.95$ ), with standard deviations, %, in parentheses

Sample	Cd found by FAAS method/mg kg <sup>-1</sup>	Cd found by photometric method/mg kg <sup>-1</sup>
Sea Kuršių	4.75 (2.5)	4.92 (3.5)
Lake Drūkšiai	3.52 (3.0)	3.28 (3.8)
Lake Žalieji	2.14 (2.0)	2.34 (4.5)
Standard sludge from Lithuania	1.64 (3.0)	1.86 (5.2)
Standard sludge from the Environment Institute of the Europe Committee	14.6 (2.2)	14.0 (3.5)

The largest part of Kuršių Sea water ( $\approx 98\%$ ) is from the River Nemunas, the watershed of which spreads over the whole area of Lithuania. Moreover, a large part of the pollutions in the Kuršių Sea could be generated by the River Nemunas from Belarus. On the contrary, the Lakes Žalieji and Drūkšiai are evidently not polluted by heavy metals. The results presented in Table II–IV clearly indicate that the amount of zinc in bottom sediments from different waters is much higher than the amount of cadmium. This is fair enough because zinc is essential for living organism while cadmium is very toxic.

#### CONCLUSIONS

The accumulation of cadmium and zinc in bottom sediments of different waters of Lithuania was investigated using flame atomic absorption spectrometry (FAAS). Two methodologies (liquid and heating mineralization) for bottom sediments mineralization were employed and compared. It was demonstrated that the mineralization procedure has no influence on the results of the determinations of the metals by FAAS in different samples. The results obtained showed that the Kuršių Sea is much more contaminated with zinc and cadmium than the Lakes Žalieji and Drūkšiai, which are located in the neighborhood of the capital of Lithuania and the Ignalina nuclear power station, respectively.

#### ИЗВОД

#### АКУМУЛАЦИЈА КАДМИЈУМА И ЦИНКА У ТАЛОЗИМА РАЗЛИЧИТИХ ВОДА У ЛИТВАНИЈИ

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Испитивана је расподела кадмијума и цинка у талозима разних вода у Литванији коришћењем пламене атомске апсорпционе спектрометрије (FAAS). Примењене и упоређене су две методологије (течна минерализација и минерализација загревањем) за минерализацију талога. Оцењена је тачност FAAS методе у поређењу са фотометријском методом. Добијени резултати показују да би сугерисани поступак могао са

задовољавајућом тачношћу успешно да се примењује за анализу талога у различитим узорцима воде.

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#### REFERENCES

1. H. L. Frost, L. H. Ketchum, Jr., *Adv. Env. Res.* **4** (2000) 347
2. R. Chantiwas, R. Beckett, J. Kamunee, I. D. McKelvie, K. Grudpan, *Talanta* **58** (2002) 1357
3. P. Gundersen, E. Steinnes, *Water Res.*, **37** (2003) 307
4. C. Terres, M. Navaro, F. Martin-Lagos, R. Gimenez, H. Lopez, M. C. Lopez, *Food Add. Contam.* **18** (2001) 687
5. R. Prego, A. Cobelo-Garcia, *Env. Poll.* **121** (2003) 425
6. K. Narbutas, S. Ryselis, M. Pileckytė, O. Abdrachmanovas, *Medicina* **32** (1996) 134
7. M. Bettinelli, G. M. Beone, S. Spezia, C. Baffi, *Anal. Chim. Acta* **424** (2000) 289
8. V. Sandroni, C. M. M. Smith, *Anal. Chim. Acta* **468** (2002) 335
9. Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, I. Liu, *Talanta* **62** (2004) 207
10. J. M. Jouanneau, O. Weber, F. E. Grousset, B. Thomas, *Ocean. Acta* **21** (1998) 233
11. J. Al-Jundi, *Nucl. Instr. Meth. Phys. Res. Sec. B* **170** (2000) 180
12. V. Van Alsenoy, P. Bernard, R. Van Grieken, *Science Total Environ.* **133** (1993) 153
13. A. W. Muohi, J. M. Onyari, J. G. Omondi, K. M. Mavuti, *Environ. Int.* **28** (2003) 639
14. S. Cerutti, M. F. Silva, J. A. Gasquez, R. A. Olsiva, L. D. Martinez, *Spectrochim. Acta B* **58** (2003) 43
15. V. Kmetov, V. Stefanova, d. Hristozov, D. Georgieva, A. Canals, *Talanta* **59** (2003) 123
16. I. Narin. M. Soylak, *Talanta* **60** (2003) 215
17. E. C. Lima, F. Barbosa, F. J. Krug, *Anal. Chim. Acta* **409** (2000) 267
18. A. Taher, *Talanta* **52** (2000) 181
19. A. Galkus, R. Stakėnienė, K. Jokšas, *Geografijos metraštis* **30** (1997) 52 (in Lithmanian)
20. D. Baralkiewicz, J. Siepak, *Anal. Chim. Acta* **437** (2001) 11
21. J. L. Mogollon, A. J. Ramirez, C. Bifano, *Chem. Geology* **121** (1995) 263
22. D. Mendil, O. D. Uluoxlu, *Food Chem.* **101** (2007) 739
23. In. Yu. Luv'e, *Analiticheskaya khimiya promychlennykh stochnykh vod*, Khimiya, Moskva, 1984 (in Russian)