DETERMINATION OF LEAD AND CADMIUM IN DANUBE WATER : RESULTS OF INTERLABORATORY STUDY

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Abstract

Several interlaboratory studies of water were organized at the Faculty of Chemistry of Belgrade University in order to improve the quality of the chemical analyses. In one of them the content of lead and cadmium in water was determined. The water of river Danube near Belgrade was used as a sample matrix. Twenty-four laboratories from Serbia and Republika Srpska participated in this interlaboratory study. Four samples were distributed to all participants in both rounds. Determination of lead and cadmium by standard methods (ASTM and Yugoslav standards) was suggested. However, determination by other methods (FAAS, ETAAS, ASV and ICP) was also used. All obtained results were analyzed using the usual statistic methods and Youden graphic method. These results are important for the development of reference materials based on Danube water. Participation in this interlaboratory study was also useful as preparation for similar international interlaboratory studies.

Introduction

The environmental analysis and the globalization of trade require high quality of analyses. The introduction of the quality assurance and quality system based on the ISO 9000 standards in chemical laboratories is the most important way for the improvement of the quality of analyses (1). Laboratory accreditation is one of the activities within this general framework. The criteria for accreditation cover all aspects of laboratory's operations. It includes also the obligation for applying laboratory to participate in interlaboratory studies. As the consequence, the number of interlaboratory studies increased considerably, mostly in developed countries (1).

ISO standards were adopted in Yugoslavia in 1991. During the last few years there were intensive activities regarding the introduction of the quality system based on ISO 9000 standards. At the Faculty of Chemistry of the University of Belgrade, two long-term projects were initiated. One of them included periodical organization of interlaboratory studies in water analysis. Within this project five interlaboratory studies were organized in the period 1995-2000. The interlaboratory study organized in 1998 included determination of lead and cadmium by standard methods. The water of river Danube water near Belgrade was used as sample matrix.

Methods

The interlaboratory studies organized at the Faculty of Chemistry in Belgrade were based on domestic and international experiences such as EURACHEM (2,3), IUPAC (4,5) and ISO

9000. Methodology and evaluation of results of interlaboratory studies within IMEP (International Measurement Evaluation Programme) organized by the Institute for Reference Materials and Measurements (IRMM-European Commission Joint Research Centre) were also very useful (6,7).

Interlaboratory study included two rounds and three meetings of participants. In every round all participants received four samples: A, B, C and D. The task for participants was to determine the content of lead and cadmium in each sample. Standard methods were suggested (ASTM and Yugoslav standards) but participants were also encouraged to use other available methods. Twenty-four laboratories from industry, scientific research institutes, faculties and public health institutes participated in this interlaboratory study.

Results and discussion

Results obtained for the determination of lead by various methods in samples A and B were presented in Figure 1. Results of all laboratories were arranged in ascending order. Different methods were used (FAAS, ETAAS, ASV and ICP). Results for lead determination by AAS in samples C and D in the first round were presented in Figure 2. There was a good agreement between results of most laboratories.

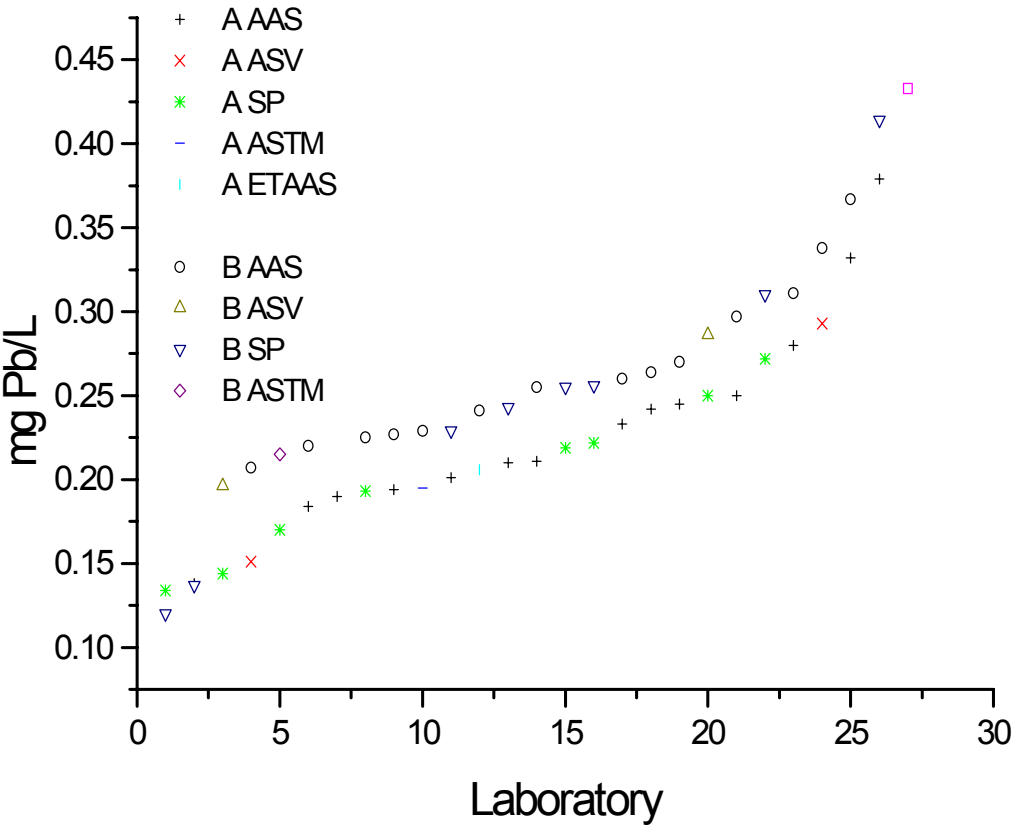

Figure 1. Results of lead determination in the first round (samples A and B)

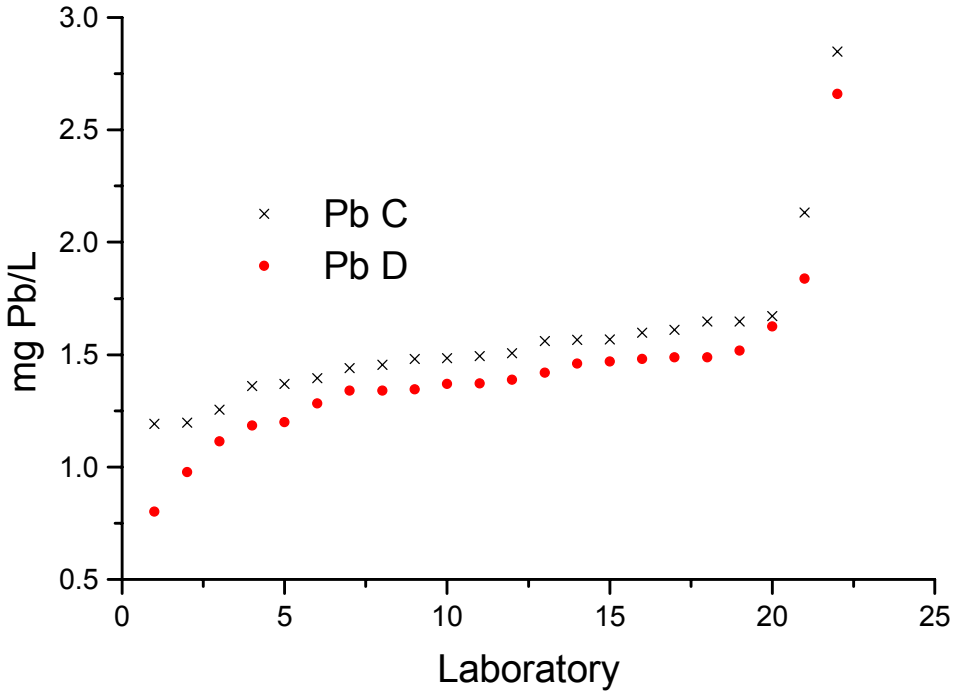

Figure 2. Results of lead determination by AAS in the first round (samples C and D)

Our and international experiences were that the results for the same determination were usually better in the second round. However, that was not the case with the determination of lead and cadmium in the second round (Table 1 and Table 2).

Table 1. Results of lead determination by AAS in rounds I and II
(mg/L, samples C and D)

Sample →	I C	I D	II C	II D
Mean	1.46	1.34	1.70	1.71
Repeatability (r)	0.082	0.091	1.145	1.143
Reproducibility (R)	0.749	0.736	1.087	1.136

Table 2. Results of cadmium determination by AAS in rounds I and II
(mg/L, samples C and D)

Sample →	I C	I D	II C	II D
Mean	0.49	0.48	1.51	1.62
Repeatability (r)	0.029	0.030	0.044	0.046
Reproducibility (R)	0.383	0.382	1.057	0.931

Every participant had to perform three analyses for each sample so that the repeatability value (r) could be calculated as well as the reproducibility value (R). These values were calculated and interpreted in accordance with IUPAC protocol (4,5) and the British standard BS 5497: Part 1: 1987 (8). Repeatability referred to the agreement of results from the same operator/laboratory while the reproducibility corresponded to the agreement among different operators/laboratories. Both values were related to standard deviations of corresponding

results – if values of r and R were smaller the agreement was better. For the determination of lead in cadmium the corresponding r and R values in the second round were higher indicating worse agreement of results. One of the possible explanation that was mentioned during the discussion of results with participants was the following: The content of both elements was higher in the second round and there was probably the deviation from the linearity which was not the case in the first round (the concentrations in the first round were adjusted to the middle of linearity range for most of the instruments used in our laboratories).

Better information on the quality of the results could be obtained by the use of Youden graphical method (9). The same method was used for evaluation of international interlaboratory studies of water (IMEP-3, IMEP-6 and IMEP-9) organized by experts of the European Commission – Institute for Reference Materials and Measurements (6,7). For example, diagonal grouping of the results for lead determination in the second round indicated systematic error for some laboratories (Figure 3).

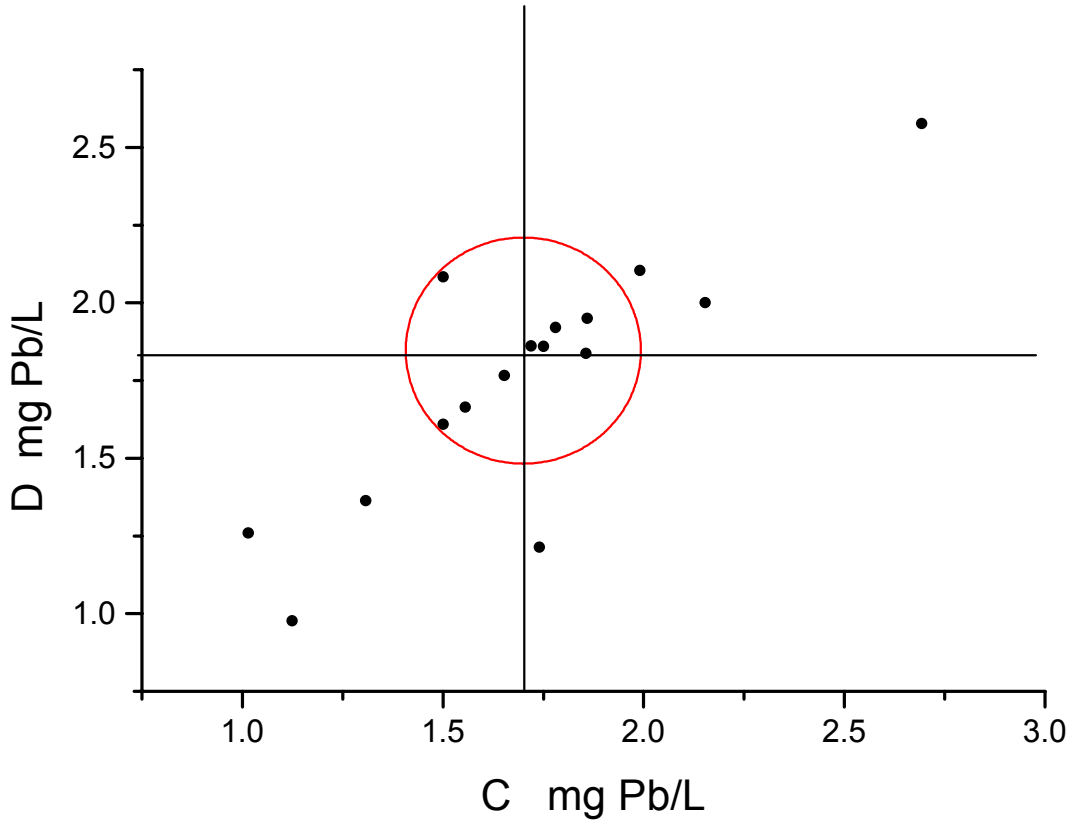

Figure 3. Youden diagram for lead determination in the second round (samples C and D)

Conclusions

Interlaboratory study, which included determination of lead and cadmium in Danube water as the sample matrix, was generally successful and useful for all participants. The participation in this interlaboratory study was a good preparation for participation in international interlaboratory studies such as those organized within the International Measurement Evaluation Programme (7). Some regional interlaboratory studies are also planed in this year (Water Analysis – 2003: The First South-Eastern European Interlaboratory Study).

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