SECTION 9. Chemistry and chemical technology.

ATOMIC ABSORPTION AND ATOMIC EMISSION WITH INDUCTIVELY COUPLED PLASMA DETERMINATION OF LEAD AND CADMIUM IN CHILDREN'S HAIR

Abstract: A systematic study of the effect of microwave, ultrasound and acid decomposition of hair samples on the results of atomic absorption and atomic emission with inductively coupled plasma determination of Lead and Cadmium was held. The data were systematized, comparative tables were compiled, the optimal method for sample preparation of hair samples was chosen - an ultrasonic treatment method. To increase the sensitivity of modern methods for the determination of analytes in the analyzed samples, it was proposed to use Triton X-100 (w = 4%). The results obtained by two independent methods were compared using the F- and t-criteria. It was shown that the difference in the deviations of the results is insignificant and can be explained by random variation. The accuracy of the atomic absorption determination of analytes in the samples was verified using the “injected-found” method.

Key words: Lead, Cadmium, Atomic Absorption Spectroscopy, Atomic Emission with Inductively Coupled Plasma Spectroscopy, Children’s Hair, Sample Preparation, Triton X-100, Analysis, Metrological Characteristics.

Language: English

Citation: Yurchenko, O. I., Chernozhuk, T. V., & Kravchenko, O. A. (2018). Atomic Absorption and Atomic Emission with Inductively Coupled Plasma Determination of Lead and Cadmium in Children’s Hair. ISJ Theoretical & Applied Science, 11 (67), 11-16.

Soi: http://s-o-i.org/1.1/TAS-11-67-2  Doi: https://dx.doi.org/10.15863/TAS.2018.11.67.2

Introduction

The negative ecological situation of the modern industrial city significantly affects the internal microenvironment of the child, changing the microelement composition of the body. Of particular importance is the accumulation in the children’s body of Cadmium and Lead. In such conditions, metabolic processes are hampered, which leads to the formation of chronic pathologies. Maximum permissible concentrations of toxic metals in human hair: Lead - 0.06-0.5 mg / kg, Cadmium - 0.07-0.3 mg / kg.

In recent years, the biological objects analysis has become one of the main areas of instrumental analysis methods application, since such studies are relevant for occupational diseases associated with the specifics of industrial production, environmentally-related diseases, etc.
The development of an accelerated universal method for the quantitative determination of Cadmium and Lead in human hair using atomic absorption and atomic emission with inductively coupled plasma spectrometry makes it possible to quickly and accurately analyze biological materials. Preparation of biological samples plays an important role. Necessary stages are cleaning and drying. To clean the surface of samples from all types of contaminants while preserving the integrity of the surface layers of samples, the effect of ultrasound of low intensity is used. The expediency of intensifying the stage of drying biomedical samples due to the influence of microwave (MW) and ultrasound (US) radiation is shown. It was established that the use of MW and US allows not only to reduce the drying time of samples, but also reduces the time of their mineralization. The combined action of oxidizers by different nature and physical fields significantly accelerates the complete destruction of the organic matrix of samples.

To determine the analytes in the analyzed samples, various methods of sample preparation and methods of analysis were proposed [1,p.23;2,p.24;3,p.122;4,p.134;5,p.14;6,p.5;7,p.14;8,p.1370;9,p.170;10,p.2246;11,p.67;12,p.3;13,p.455;14,p.4;15,p.1880; 16,p.5;17,p.35;18,p.77; 19,p.170;20,p.90;21,p.1153;22,p.507;23,p.140;24,p.3 9;25,p.97;26,p.137].

The main purpose of the work was to develop a modern, express method of atomic absorption and atomic emission with inductively coupled plasma determination of Lead and Cadmium in children's hair.

Experimental part

When analyzing biological samples, the following equipment and reagents were used: atomic absorption spectrometer C-115-M1; lamps with hollow cadmium and lead cathodes; air compressor; measuring laboratory glassware (flasks, pipettes, beaters); nitric acid "chemically pure"; electronic balance TU 292-32126739-032005; system for microwave decomposition MDS-2000 (Innovators in Microwave Technology), CEM Corporation production, USA; atomic emission spectrometer with inductively coupled plasma TRACE SCAN Advantage, Thermo Jarrel production, USA; ultrasonic disperser PS-20 (optimum operation parameters: working power 120 W, frequency 40 kHz); Cadmium and Lead acetylacetonates; non-ionic surfactant Triton X-100 (oxyethylene derivative of alkylphenol); distilled water. The mass fraction of Triton X-100 in aqueous solutions is 4%.

Results and discussion

The use of Triton X-100 (w = 4%) increases the sensitivity of atomic absorption and atomic emission with inductively coupled plasma determination of Cadmium and Lead by 1.8 times. This allows the lower limit of detectable analytes’ amounts to be lowered.

Acid decomposition of hair samples

Sample preparation was carried out according to the following scheme: a sample with a mass 0.300 g was taken on electronic scales, cleaned of contamination with the help of 96% ethanol for 30 minutes, then washed with distilled water, dried in a drying cabinet, mineralized by boiling in 4 ml of concentrated nitric acid for 30 minutes. The solution was filtered and distilled water was added to 10 ml, then 2 ml of Triton X-100 (w = 4%) was added, followed by analysis by atomic absorption spectroscopy (Table 1).

Microwave decomposition of hair samples

Sample preparation was carried out according to the following scheme: a sample with a mass 0.300 g was taken on electronic scales, cleaned of contamination with the help of 96% ethanol for 30 minutes, then washed with distilled water, dried in a drying cabinet, mineralized by mixing with 4 ml of concentrated nitric acid in vials, which were placed in a SEM microwave oven with a power of 650 W at the pressure of 90 psi max for 1 hour. Next, the analyzed sample was washed from the vial walls with distilled water, then distilled water was added to 10 ml, then 2 ml of Triton X-100 (w = 4%) was added, followed by analysis by atomic absorption spectroscopy (Table 2).

Ultrasonic decomposition of hair samples

Sample preparation was carried out according to the following scheme: a sample with a mass 0.300 g was taken on electronic scales, cleaned of contamination with the help of 96% ethanol for 30 minutes, then washed with distilled water, dried in a drying cabinet, mineralized by boiling in 4 ml of concentrated nitric acid for 30 minutes. The obtained solution was sonicated using the UVM-5 ultrasonic disperser at the constant intensity of ultrasound 1.8 W/cm², at the frequency 40 kHz, for 5-7 minutes. Then 2 ml of Triton X-100 (w = 4%) was added, followed by analysis by atomic absorption spectroscopy (Table 3).

The use of ultrasonic treatment significantly increases the homogeneity of the samples due to the mixing effect of ultrasound. When sample preparation of hair samples with ultrasonic treatment, the most complete extraction of Lead and Cadmium is achieved.

Validation of the atomic absorption spectroscopy method

The correctness of the results obtained and the completeness of the extraction of Lead and Cadmium were validated using the “injected-found” method, the results are shown in Tables 4 and 5.
Comparison of the results of Lead and Cadmium determination by atomic absorption spectroscopy and by atomic emission with inductively coupled plasma spectroscopy.

To determine the Cadmium and the Lead in children's hair with ultrasonic decomposition of samples, two methods were used: atomic absorption spectroscopy and atomic emission with inductively coupled plasma spectroscopy. Concentrations of the Cadmium and the Lead in the calibration metals' acetylacetonate solutions were 0.1, 0.3, 0.5, 0.7, 1.0 mg/L.

The results of the Lead and Cadmium determination by atomic absorption spectroscopy and by atomic emission with inductively coupled plasma spectroscopy are shown in Table 6.

To compare the results of these two methods, the F- and t-criteria were used (Table 7, 8).

Practical values of the F- and t-criteria are less than table values. The results obtained by two independent methods are reliable, and the difference in deviations is due to the random variation.

Conclusions

The use of Triton X-100 water solutions and ultrasonic treatment eliminates the use of toxic and expensive reagents, increases the stability and homogeneity of the solutions obtained, reduces sample preparation time, increases the sensitivity of analytes’ determination. New standard samples based on metal acetylacetonates approximate the composition of the analyzed samples to the calibration solutions, which significantly increases the precision of measurements.

Table 1. The results of atomic absorption determination of Cadmium and Lead (mg / kg) in hair samples with acid decomposition (n = 3, P = 0.95).

| № | Sample       | Age, years | Cd    | Sr    | Pb    | Sr   |
|---|--------------|------------|-------|-------|-------|------|
| 1 | Godovanyk K. | 9          | 1,20 ±0,07 | 0.02  | 3,03 ±0,62 | 0.04 |
| 2 | Patsai D.    | 11         | 1,12 ±0,22 | 0.04  | 3,88 ±0,32 | 0.03 |
| 3 | Ponikarchuk O.| 10         | 1,20 ±0,05 | 0.02  | 4,83 ±0,40 | 0.03 |
| 4 | Sorotchan L. | 8          | 0,91 ±0,07 | 0.03  | 3,88 ±0,32 | 0.03 |

Table 2. The results of atomic absorption determination of Cadmium and Lead (mg / kg) in hair samples with microwave decomposition (n = 3, P = 0.95).

| № | Sample       | Age, years | Cd    | Sr    | Pb    | Sr   |
|---|--------------|------------|-------|-------|-------|------|
| 1 | Godovanyk K. | 9          | 0,86 ±0,12 | 0.03  | 2,32 ±0,50 | 0.04 |
| 2 | Patsai D.    | 11         | 0,92 ±0,04 | 0.02  | 3,35 ±0,22 | 0.03 |
| 3 | Ponikarchuk O.| 10         | 0,65 ±0,01 | 0.01  | 2,68 ±0,05 | 0.01 |
| 4 | Sorotchan L. | 8          | 0,32 ±0,01 | 0.01  | 2,97 ±0,37 | 0.04 |

Table 3. The results of atomic absorption determination of Cadmium and Lead (mg / kg) in hair samples with ultrasonic decomposition (n = 3, P = 0.95).

| № | Sample       | Age, years | Cd    | Sr    | Pb    | Sr   |
|---|--------------|------------|-------|-------|-------|------|
| 1 | Godovanyk K. | 9          | 1,04 ±0,01 | 0.01  | 3,60 ±0,22 | 0.02 |
### Impact Factor:

| Impact Factor | Value |
|---------------|-------|
| ISRA (India)  | 3.117 |
| SIS (USA)     | 0.912 |
| ICV (Poland)  | 6.630 |
| ISI (Dubai, UAE) | 0.829 |
| PHHII (Russia) | 0.156 |
| PIF (India)    | 1.940 |
| GIF (Australia)| 0.564 |
| ESJII (KZ)    | 4.102 |
| IBII (India)   | 4.260 |
| JIF           | 1.500 |
| SJIF (Morocco)| 5.667 |

| Sample | Name           | Concentration, mg/kg | Injected, mg/kg | Found out $\overline{C_{\pm \sqrt{n}}} \pm S_r$ mg/kg | $S_r$ |
|--------|----------------|-----------------------|-----------------|-----------------------------------------------------|------|
| 2      | Patsai D.      | 1.09 ±0.06            | 0.03            | 3.93 ±0.40                                           | 0.04 |
| 3      | Ponikarchuk O. | 1.17 ±0.10            | 0.03            | 5.74 ±0.17                                           | 0.01 |
| 4      | Sorotchan L.   | 0.90 ±0.05            | 0.02            | 3.92 ±0.07                                           | 0.01 |

#### Table 4. Verification of the atomic absorption determination of Cadmium in children's hair with ultrasonic decomposition of hair samples ($n = 3, P = 0.95$).

| Sample | Concentration, mg/kg | Injected, mg/kg | Found out $\overline{C_{\pm \sqrt{n}}} \pm S_r$ mg/kg | $S_r$ |
|--------|----------------------|-----------------|-----------------------------------------------------|------|
| 1      | 1.04±0.01            | 1.0             | 2.06±0.01                                           | 0.01 |
| 2      | 1.09±0.06            | 1.0             | 2.11±0.04                                           | 0.03 |
| 3      | 1.17±0.10            | 1.0             | 2.18±0.06                                           | 0.03 |
| 4      | 0.90±0.05            | 1.0             | 1.92±0.05                                           | 0.02 |

#### Table 5. Verification of the atomic absorption determination of Lead in children's hair with ultrasonic decomposition of hair samples ($n = 3, P = 0.95$).

| Sample | Concentration, mg/kg | Injected, mg/kg | Found out $\overline{C_{\pm \sqrt{n}}} \pm S_r$ mg/kg | $S_r$ |
|--------|----------------------|-----------------|-----------------------------------------------------|------|
| 1      | 3.60±0.22            | 3.0             | 6.62±0.17                                           | 0.02 |
| 2      | 3.93±0.40            | 4.0             | 7.95±0.32                                           | 0.04 |
| 3      | 5.74±0.17            | 6.0             | 11.72±0.40                                          | 0.02 |
| 4      | 3.92±0.07            | 4.0             | 7.95±0.10                                           | 0.04 |

#### Table 6. The results of Lead and Cadmium determination in children's hair by AAS and AES-ICP with ultrasonic sample preparation ($n = 3, P = 0.95$).

| Sample | Content of Zn, mg/kg | Content of Mn, mg/kg |
|--------|----------------------|----------------------|
|        | AAS                  | AES-ICP              | AAS                  | AES-ICP              |
|        | $\overline{C_{\pm \sqrt{n}}} \pm S_r$ | $\overline{C_{\pm \sqrt{n}}} \pm S_r$ | $\overline{C_{\pm \sqrt{n}}} \pm S_r$ | $\overline{C_{\pm \sqrt{n}}} \pm S_r$ |
| 1      | 3.60 ± 0.22          | 0.02                 | 3.65 ± 0.15          | 0.02                 |
| 2      | 3.93 ± 0.40          | 0.04                 | 4.05 ± 0.30          | 0.04                 |
| 3      | 5.74 ± 0.17          | 0.01                 | 5.60 ± 0.20          | 0.04                 |
| 4      | 3.92 ± 0.07          | 0.01                 | 3.85 ± 0.11          | 0.02                 |
ISRA (India) = 3.117  SIS (USA) = 0.912  ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829  PIIH (Russia) = 0.156  PIF (India) = 1.940
GIF (Australia) = 0.564  ESJF (KZ) = 4.102  IBI (India) = 4.260
JIF = 1.500  SJF (Morocco) = 5.667

Table 7. Comparison of the results of Lead determination by AAS and AES-ICP.

| Sample | F criteria, practical value | S₁,₂ | t criteria, practical value | F criteria, table value | t criteria, table value |
|--------|-----------------------------|------|----------------------------|-------------------------|-------------------------|
| 1      | 2.13                        | 0.07 | 0.82                       | 19.00                   | 3.20                    |
| 2      | 1.77                        | 0.14 | 1.03                       | 19.00                   | 3.20                    |
| 3      | 1.38                        | 0.07 | 2.29                       | 19.00                   | 3.20                    |
| 4      | 2.46                        | 0.04 | 2.31                       | 19.00                   | 3.20                    |

Table 8. Comparison of the results of Cadmium determination by AAS and AES-ICP.

| Sample | F criteria, practical value | S₁,₂ | t criteria, practical value | F criteria, table value | t criteria, table value |
|--------|-----------------------------|------|----------------------------|-------------------------|-------------------------|
| 1      | 1.00                        | 0.004| 3.06                       | 19.00                   | 3.20                    |
| 2      | 1.44                        | 0.02 | 1.11                       | 19.00                   | 3.20                    |
| 3      | 1.24                        | 0.04 | 0.97                       | 19.00                   | 3.20                    |
| 4      | 1.00                        | 0.02 | 2.45                       | 19.00                   | 3.20                    |

Table 9. The results of the determination of various metals (mg / kg) by atomic absorption spectroscopy in children's hair (age 7-8 years) in Kharkiv (n = 8, P = 0.95).

| Element | c ± ε                      | Sᵣ  |
|---------|----------------------------|-----|
| Cd      | 0.30±0.01                  | 0.03|
| Mn      | 2.70±0.07                  | 0.02|
| Cu      | 8.88±0.21                  | 0.01|
| Ni      | 1.73±0.05                  | 0.02|
| Pb      | 8.77±0.18                  | 0.02|
| Zn      | 180±3                      | 0.02|
| Hg      | 0.66±0.02                  | 0.03|
Impact Factor:

| Country       | Impact Factor |
|---------------|---------------|
| ISRA (India)  | 3.117         |
| ISI (Dubai, UAE) | 0.829        |
| GIF (Australia) | 0.564         |
| JIF           | 1.500         |
| IS (USA)      | 0.912         |
| PIIH (Russia) | 0.156         |
| ESJI (KZ)     | 4.102         |
| SJIF (Morocco)| 5.667         |
| ICV (Poland)  | 6.630         |
| PIF (India)   | 1.940         |
| IBI (India)   | 4.260         |

References:

1. Elsas, L. (2007). *Approach to metabolism*, Philadelphia. Cecil Medicine, pp.1-216.
2. Saevych, O. V. (2008). *Visnyk Dnipropetrovskogo universitety*, V. 3, 23-25.
3. Thcmilenko, T. S. (2003). *Visnyk Dnipropetrovskogo universitety*, V. 4, pp. 120-123.
4. Pogorelov, M. V. (2010). *Micro and macro elements*, Symy, pp.1-147.
5. Vargui, L. (2007). *Joun. Of Antr. Science*, V.85, 173-181.
6. Kordas, K. (2010). *Analytical Science*, V. 27, p.5.
7. Casey, J. (2016). *Spectroscopy*, V. 31, 11-22.
8. Yakubenko, E. (2015). *Inorganic Materials*, V. 51, 1368-1372.
9. Puchur, R. F. (2008). *Doctors data Inc.*, V.62, 167-182.
10. Wang, T. (2009). *Envirom. Pollution*, V.157, 2445-2451.
11. Harishcharishvili, I. (2006). *Experimental and clinical medicine*, V.7, 65-67.
12. Halchenko, S.M. (2009). *Ukr. Phys. Journal*, V.48, 1-5.
13. Stigter, J. (2008). *Environmental Pollution*, V.107. 451-464.
14. Thcmilenko, F. (2002). *Visnyk Dnipropetrovskogo universitety*, V. 8, 3-6.
15. Yang, L. (2013). *J. Chil. Chem. Soc.*, V. 58, 1876-1879.
16. Bass, D. A. (2001). *Alt. Med. Review*, V. 5, p. 5.
17. Samanta, G. (2004). *Science of Enviroment*, V.326, 33-47.
18. Andrushishina, I. (2009). *Actual problems of medicine*, V.4, 75-83.
19. Nekrasov, V. (2005). *Visnyk OGU*, V.12, 168-171.
20. Elenge, M. (2011). *Enviroment Analytic*, V.12, 87-93.
21. Sznkowska, M. (2009). *Polish Journ. of Enviroment*, V.18, 1151-1161.
22. Semenova, I. (2009). *Visnyk OGU*, V.6, 506-508.
23. Sanna, E. (2007). *Giovanni Floris Journal*, V.85, 173-181.
24. Kabanova, O. (2007). *Man and Enviroment*, V.9, 37-40.
25. Gudkov, A. (2001). *Infection pathology in Primorsk area*, V.67, 96-97.
26. Agadjanian, N. A. (2001). *Ecological portrait of man and microelements role*. Moscow, Visha Scola, p.1-236.