METHODICAL PECULIARITIES AND PRACTICE OF DETERMINING ALUMINUM IN BLOOD AND URINE VIA MASS SPECTROMETRY WITH INDUCTIVELY COUPLED PLASMA

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Toxicants produce adverse effects on population health thus causing health risks; assessment of such risks is a relevant trend in contemporary hygienic research. A list of toxic elements that are to be controlled in biological media includes, for example, mercury, lead, cadmium, arsenic, and aluminum (this element belongs to the 2nd hazard category). Aluminum is one of those elements which are the most widely spread in nature and it most frequently occurs in emissions from aluminum, mining, varnish and paint, and other productions.

We developed a procedure for determining mass concentrations of aluminum in blood and urine via mass spectrometry with inductively coupled plasma (ICP-MS) (FR.1.31.2017.27357); the procedure allows determining aluminum contents in blood within a range from 20 to 200 µg/l with 31% precision; within 200–700 µg/l, with 23% precision; in urine, within a range from 0.1 to 10 µg/l, with 30% precision; within 10–1,000 µg/l, with 23% precision.

We analyzed 192 blood and urine samples taken from children (n = 96) and adults (n = 54) who lived in the Eastern Siberia in a zone influenced by a large metallurgic aluminum-producing enterprise. Simple mean (SM) of aluminum contents in children’s and adults’ blood amounted to 21 µg/l; 32 µg/l and 21 µg/l in urine respectively. The article also contains comparative assessment of aluminum contents in blood and urine of people living in Russia against reference concentrations applied in Europe and the USA when national programs for human biological monitoring (HBM) were implemented.

Key words: aluminum, blood, urine, children, adults, mass spectrometry with inductively coupled plasma (ICP-MS), reference concentrations, octopole reaction system (ORS), internal standard.

A priority task for the Russian economy is to intensify industrial production and implement new production technologies; it can often result in environmental contamination and produce negative effects on population health. Determination of chemicals in human biological media is an objective, reliable and evidential way to reveal these negative impacts.

Aluminum is a toxic element and one of the most widely spread metals in nature; it accounts for 8.8 % of the earth crust [1–6]. Aluminum is one of primary metals contained in emissions from metallurgical enterprises, including those located in cities which are in the priority list issued within “Pure air” Federal project. Aluminum toxicity is due to this metal being antagonistic to calcium and magnesium as well as its ability to easily form compounds with proteins and accumulate in the kidneys, bone, and nerve tissue [1–3]. Aluminum is among elements that are subject to control in blood and urine, together with such toxicants as mercury, lead, cadmium, and arsenic [1]. Aluminum compounds belong to the 2nd hazard category.

Element analysis of biological media involves applying practically all spectral techniques with different sample preparation; as a rule, they are sensitive and selective [4, 5, 7, 8–25]. The most widely used techniques are

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¹ G 2.1.10.1920-04. Guide on assessing health risks caused by exposure to chemicals that pollute the environment. – M: The Federal Center for State Sanitary and Epidemiologic Surveillance of the RF Public Healthcare Ministry, 2004. – 143 p.
electrothermal atomic-absorption spectrometry (ET-AAS, GFAAS), atomic-emission spectroscopy with inductively coupled plasma (ICP-AES)\(^2\), and mass spectrometry with inductively coupled plasma (ICP-MS)\(^3\). At present high resolution mass spectrometry or mass spectrometry with dynamic reaction cells (DRS) is considered the most efficient technique. ICP-MS technique has certain advantages such as focus on many elements, low limits of detection, short period of analysis, and small volumes of analyzed samples. GFAAS technique is just as sensitive as ICP-MS when it is applied to analyze biological media; but the technique focuses on only one element and is usually applied as an alternative one to determine certain elements, including aluminum, beryllium, chromium, and thallium [8, 9].

Aluminum is determined in biological media with ICP-MS with preliminary decomposition of a sample or without it. Obviously, when a sample is decomposed improperly, it can make any high precision technique meaningless [7]. Besides, recommended microwave mineralization can’t prevent samples from being contaminated when accompanying reagents are added; however, it makes decomposition faster. Analysis without samples mineralization is more preferable as it helps avoid contamination, minimizes losses, and analysis itself requires less time. As a rule, blood is diluted 10–50 times with water solutions of Triton X-100, 1-butanol, EDTA, \(\text{NH}_3\), or nitric acid; blood serum and urine are diluted 2–10 times with nitric acid solution thus making additional contamination of a sample quite possible [7]. Despite a great number of publications, practically all authors indicate it is difficult to determine aluminum but they often don’t give any comments on obtained results [9, 21, 23].

We developed MG 4.1.3230-14\(^4\) for quantitative determination of 12 chemical elements in biological media (blood and urine) with mass spectrometry with inductively coupled plasma. The procedure for determining 12 elements in blood was patented\(^5\). But still, as determination of aluminum has its peculiarities related to sampling, samples being contaminated during storage, and high aluminum contents in water and reagents, we didn’t include aluminum into the list.

**Our research goal** was to develop an up-to-date and highly sensitive procedure for quantitative determination of aluminum in blood and urine with mass spectrometry with inductively coupled argon plasma; this procedure could be applied in clinical laboratories for diagnostics, treatment, and prevention of health disorders caused by negative impacts exerted by hazardous chemicals and for health risk assessment.

**Data and methods.** When applying ICP-MS for quantitative determination, biomaterials should be preliminary prepared so that matrix effects and polyatomic interferences are eliminated; these effects and interferences are due to not only ions of determined elements occurring in plasma but also ions of argon, hydrogen, oxygen, etc. that are present in plasma in big quantities [26, 27]. A basic aluminum isotope \(^{27}\text{Al}\) has the following spectral folding: \(^{12}\text{C}^{15}\text{N}^+,^{13}\text{C}^{14}\text{N}^+,^{12}\text{C}^2\text{H}_3^+\) \([28, 29]\). We applied our procedure for determining 12 elements which we had previously developed and it didn’t yield us expected results. Aluminum occurred in water in high concentrations even if that water was intensely purified; introduced reagents (nitrogen acid and hydrogen peroxide) and solutions of elements for internal comparison, and laboratory dishes

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\(^2\) MG 4.1.1482-03. Determination of chemicals contents in diagnosed biological substrates, poly-vitamin preparations with microelements, biologically active additives to food and raw materials they are made of via atomic emissions spectroscopy with inductively coupled argon plasma. – М., 2003. – 28 p.

\(^3\) MG 4.1.1483-03. Determination of chemicals contents in diagnosed biological substrates, preparations, and biologically active additives via mass-spectrometry with inductively coupled argon plasma. – М., 2003. – 36 p.

\(^4\) MG 4.1.3230-14. Measuring mass concentrations of chemicals in biological media (blood and urine) with mass spectrometry with inductively coupled plasma. – М., 2014. – 32 p.

\(^5\) N.V. Zaitseva, T.S. Ulanova, A.G. Veikhman, E.V. Steno, O.V. Gilyova, A.V. Nedoshitova, M.A. Bakanina. The procedure for determining concentrations of cadmium, lead, arsenic, chromium, nickel, copper, zinc, manganese, vanadium, strontium, selenium, and thallium in blood with mass spectrometry with inductively coupled plasma. Patent No. 2585369 RU; 2015.
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also made their contributions into aluminum concentrations being too high in a blank sample; those concentrations were often even higher than in an analyzed sample. Obviously, to determine aluminum in blood and urine, we require specific conditions which will allow eliminating spectral and non-spectral (matrix) interferences. It involves specific conditions for samples taking and storage; particularly pure reagents and water; specific degree to which a sample is diluted; a specific procedure for samples preparation before they are analyzed; different ways to prepare calibration solutions; a choice on elements for internal comparison (internal standard) etc.

We quantitatively determined aluminum in blood and urine with Agilent 7500cx (Agilent Technologies, USA) quadrupole mass-spectrometer with inductively coupled plasma and octopole reaction/collision cell (ORS). Plasma generator had power equal to 1,400 W. Samples were introduced via a two-channel spray chamber under 2.0 °C. The mass-spectrometer was equipped with a plasma torch with its injector tube diameter being equal to 2.5 mm. Samples were fed into the spray chamber at a speed equal to 0.4 ml/min. To get plasma burn, we applied extremely high liquid argon with its purity being equal to 99.998 % (TC-2114-005-00204760-99) and it was fed at a speed up to 20 l/min. Pressure in the gas-feeding channel was equal to 700±20 kPa. To calibrate the device, we applied $^7$Li, $^{59}$Co, $^{89}$Y and $^{205}$Tl solution in 2 % HNO$_3$ with concentration of its elements being equal to 1 µg/l. After sufficient sensitivity was reached in the standard mode, we switched the mass-spectrometer into the operation mode with reaction/collision cell functioning. We applied extremely pure helium as a gas-reagent (TC-0271-135-31323949). Maximum suppression of the background signal with optimal sensitivity being reached occurred when helium flow speed was equal to 4.3 ml/min. The distance between the plasma torch and the sampling cone was equal to 7.0 mm.

It is not advisable to use quartz dishes when aluminum is determined [23]. We took plastic dishes and washed them in Elmasonic S 100H ultrasound cleaner (Germany) at 45–50 °C, first with distilled water, and then with diluted HNO$_3$ solution.

We applied extremely pure polypropylene test tubes (Labcon, the USA, LOT 609CE-609C) to analyze blood and urine.

Water was purified with Milli-Q Integral (Millipore SAS, France) system. However, background elements still persisted in concentrations equal to 3.0 µg/l and even higher; therefore, we additionally purified water with Vodoley system (Khimelectronica, Moscow), and background concentrations decreased to 0.55 µg/l. Water should be purified directly before samples are diluted with it and then analyzed.

To prepare solutions of standard samples, we applied a solution of aluminum ions with mass concentration being 1.0 g/dm$^3$ (GSO - 7927-2001) and 1 % solution of high purity HNO$_3$ (Sigma-Aldrich, the USA). To prepare Internal Standard (IS) solutions, we applied a complex standard solution of $^{209}$Bi, $^{73}$Ge, $^{115}$In, $^6$Li, $^{45}$Sc, $^{159}$Tb, $^{89}$Y with its concentration being 10 mg/l in 5 % HNO$_3$ water solution (Internal Standard Mix, the USA).

Impure dishes and an increase in aluminum contents that occurs when samples are stored make a primary contribution into blank sample value [30]. We prepared blank samples simultaneously with preparing samples for analysis.

We prepared calibration samples for determining aluminum in blood and urine out of aluminum solution with its mass concentration being 1.0 g/dm$^3$ (GSO - 7927-2001), IS solution, 1 % HNO$_3$ water solution, and blank sample solution. Concentration of aluminum in calibration solutions was equal to 0.0; 0.1; 0.5; 1.0; 5.0; 10.0; 50.0 µg/l. To prepare calibration solutions, we applied high purity Nitric acid 69 % (Sigma-Aldrich, the USA) or Nitric acid 65 % (PanReac, Espana).

Impacts exerted by non-spectral (matrix) interferences can usually be removed via applying calibration with a selection of calibration solutions matrix, internal standard, or both [10]. When selecting IS, it is necessary to adhere to the following rule: IS should have atomic mass that is as close to atomic mass of
determined elements as it’s only possible, and the lower atomic mass of a determined element is, the stricter this rule should be followed [26, 27].

To prepare internal standard (IS) solutions, we applied a complex standard solution of $^{209}\text{Bi}$, $^{73}\text{Ge}$, $^{115}\text{In}$, $^{6}\text{Li}$, $^{45}\text{Sc}$, $^{159}\text{Tb}$, $^{89}\text{Y}$ with its concentration being 10 mg/dm$^3$ in 5% water solution of nitric acid (Internal Standard Mix, the USA). Table 1 contains the results of determining aluminum in standard blood samples SERONORM L2 and L3 (Sero AS, Billingstad, Norway) and urine samples Seronorm$^\text{TM}$ urine (LOT 0511545, Sero AS, Billingstad, Norway) with use of various elements for internal comparison (IS). Prior to analysis, certified control materials were prepared in the same way as samples for analysis (working samples).

Data in the Table 1 indicate there is quite satisfying coincidence between certified and detected concentrations without IS and with $^{73}\text{Ge}$ at blood level L2. $^{115}\text{In}$ application led to a considerable increase in detection error. Therefore, we didn’t obtain any convincing evidence that it was necessary to apply IS when determining aluminum in blood and urine as well as this or that element for internal comparison having apparent advantages.

We introduced 0.5 ml of urine into tubes of an automated sampler with a dosing device, added 4.45 ml of HNO$_3$ water solution and 0.05 ml of IS solution [31, 32]. Any urine samples with sediment were centrifuged before dilution. Diluted samples were not to be stored. Besides, when aluminum is determined in urine, water should be purified directly before analysis and samples should be diluted on a day they are analyzed.

We took a blood sample with its volume 0.1 ml and added 0.1 ml of complex IS solution and 0.2 ml of concentrated HNO$_3$ to it. We then stirred a test tube with this mixture, kept it for 6–7 hours, added deionized water until mixture volume reached 10 ml and then centrifuged it for 10 minutes at a speed equal to 2,700–3,000 turns per minute on CLMN–P10–01–“Elekon” centrifuge (Russia).

Simultaneously we prepared a blank test for each series of samples; this blank test went through all the stages in sample preparation which involved applying all the reagents as it was the case with analyzed samples.

We should note that when a sample was dissolved with an acid, a structure of an examined sample matrix wasn’t destroyed completely; however, it helps to reduce an amount of time required for samples preparation and to save reagents. Another significant aspect is that a volume of sample necessary for analyzing goes down to 0.1 ml and a blank test becomes almost insignificant when a sample is decomposed in such a way. It is another advantage of acid dissolution.

The procedure for determining aluminum in biological media was metrologically certified; to do that, we applied calculations with a known concentration for an average boundary of a measured range and the standard addition technique in accordance with RM$^6$ and GOST R ISO 5725–1÷GOST R ISO 5725–6–2002 (certificate No. 88-16207-11-RA.RU.310657-2017). The developed procedure for measuring mass

| Table 1 | Certified and determined average values of aluminum concentrations in standard blood and urine samples Seronorm$^\text{TM}$ (Norway), µg/l |
|---------|----------------------------------------------------------------------------------|
| Level   | Certified average value, µg/l | Detected average value / error of the average, $\Delta$, % |
|         | Without IS | $^{73}\text{Ge}$ | $^{115}\text{In}$ |
| Seronorm$^\text{TM}$ blood L2 ($n = 18$) | 70.9 | 82.3/16.1 | 83.6/17.9 | 119.6/68.6 |
| Seronorm$^\text{TM}$ blood L3 ($n = 18$) | 105 | 106.1/1.0 | 117.9/12.3 | – |
| Seronorm$^\text{TM}$ urine L2 ($n = 14$) | 103 | 105.2/2.1 | 115.4/12.0 | 110/6.8 |

$^6$RMG 61-2003 GSI. Parameters that show precision, and correctness of procedures for quantitative chemical analysis. Assessment techniques [Web-source] // Kodeks: and electronic fund of legal and reference documentation. – URL: http://docs.cntd.ru/document/1200037651 (date of visit September 22, 2019).
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Table 2

| Group (medium) | Test group, SM | Reference group, SM | \( P_1 \) | Analysis of frequencies against the reference group |
|---------------|----------------|---------------------|----------|-------------------------------------------------|
|               |                |                     |          | % higher | % The same | % lower |
| Children (blood) | 21              | <20                 | 0.24     | 25       | 0         | 75      |
| Adults (blood)   | 21              | <20                 | 0.01     | 26       | 74        | 0       |
| Children (urine) | 32              | 7                   | 0.005    | 90.1     | 6.6       | 3.3     |
| Adults (urine)   | 21              | 2.4                 | 0.001    | 100      | 0         | 0       |

Note: \( P_1 \) is validity of discrepancies as per SM between urban population and the reference territory.

Aluminum contents (SM) in biological media of children and adults and validity of discrepancies form the reference territory, \( \mu g/l \)

| Group (medium) | Test group, SM | Reference group, SM | \( P_1 \) | Analysis of frequencies against the reference group |
|---------------|----------------|---------------------|----------|-------------------------------------------------|
|               |                |                     |          | % higher | % The same | % lower |
| Children (blood) | 21              | <20                 | 0.24     | 25       | 0         | 75      |
| Adults (blood)   | 21              | <20                 | 0.01     | 26       | 74        | 0       |
| Children (urine) | 32              | 7                   | 0.005    | 90.1     | 6.6       | 3.3     |
| Adults (urine)   | 21              | 2.4                 | 0.001    | 100      | 0         | 0       |

Concentrations of aluminum with ICP-MS allows determining its contents in blood within a range from 20 to 200 \( \mu g/l \) with 31% precision; within a 200–700 \( \mu g/l \) range, with 23% precision. The procedure allows determining aluminum contents in urine within a range from 0.1 to 10 \( \mu g/l \) with 30% precision; within a 10–1,000 \( \mu g/l \) range, with 23% precision.

We established limits of detection and limits of quantification for our procedure. LOD for determining aluminum in blood amounts to 7 \( \mu g/l \); in urine, 0.033 \( \mu g/l \); LOQ for determining aluminum in blood amounts to 21 \( \mu g/l \); urine, 0.1 \( \mu g/l \).

Results and discussion. The developed procedure for determining aluminum in biological media (blood and urine) was tested in the East Siberia on population (adults and children) who lived in a zone exposed to a large metallurgical aluminum-producing enterprise; the research involved analyzing biological media. Overall, we analyzed 192 blood and urine samples taken from children \((n = 96)\) and 106 samples taken from adults \((n = 54)\). We also had two reference groups, children \((n = 53)\) and adults \((n = 30)\) who lived in a zone beyond exposure to the said enterprise; Table 2 contains the results of our analysis.

Simple mean (SM) of aluminum contents in blood of children and adults form the test groups amounts to 21 \( \mu g/l \); children and adults from the reference groups, < 20 \( \mu g/l \). Simple mean of aluminum contents in urine of children and adults amounts to 32 \( \mu g/l \) and 21 \( \mu g/l \) accordingly; ion the reference group, 7 and 2.4 \( \mu g/l \). Aluminum contents in urine taken from children from the test group had authentic discrepancies from that in the reference group (90% samples were higher than in the reference group, by 4.6 times). Aluminum contents in urine taken from adults form the test group also had authentic discrepancies from that in the reference group, 100% having concentrations by 8.8 times higher.

The exposed territory where the examined population lives takes the 3rd rank place as per ambient air contamination both in the Siberian Federal District and among the RF regions as well. Ambient air contamination is caused by an aluminum-producing enterprise and a pulp and paper mill. Analysis of morbidity among population living on this territory over the last five years has revealed increased morbidity with respiratory diseases (chronic bronchitis and bronchial asthma) and musculoskeletal system diseases both among children and adults; the revealed morbidity has negative dynamics as it tends to grow. Our research results can be used to assess sufficiency of activities performed within “Pure air” Federal program in a zone influenced by metallurgical enterprises in the East Siberia as their emissions contain aluminum and it causes ambient air contamination with this metal.

Values obtained for the examined groups were statistically distributed; the results are shown in Table 3. Results were given as simple mean (SM); 25th, 50th, and 75th percentile; we also gave minimum and maximum values for a sampling. Median was close to a simple mean for aluminum contents in urine taken from urban population and it meant that distribution of values was normal. In all other cases values were in a range of smaller concentrations at

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Table 3

Aluminum contents in blood and urine of children and adults, µg/l

| Group             | Test group | Reference group | Reference levels (range) |
|-------------------|------------|-----------------|-------------------------|
|                   | N  AM q25 q50 q75 | Min-Max | N  AM q25 q50 q75 | Min-Max | ALS Scandinavia | Titz | HELIX | ARUP | Kaletina |
| Children blood    | 96 21 10 10 16 | 10–166 | 49 17 10 10 10 | 10–58.3 | 5–192 | 0–100 | 0–15 | – | 200 |
| Adults blood      | 54 21 10 10 21 | 10–100 | 31 12 10 10 10 | 10–29.5 | 0.6–5.1 | ≤20 | 0–31 | 0–7 | 5 |
| Children urine    | 91 32 18.9 31 44.6 | 3.3–61.1 | 41 7 0.1 3.6 10 | 0.1–38.3 | 0.6–5.1 | ≤20 | 0–31 | 0–7 | 5 |
| Adults urine      | 52 28 13.8 22 37.3 | 6.2–104 | 26 2.4 0.1 0.1 1.5 | 0.1–24.0 | 0.6–5.1 | ≤20 | 0–31 | 0–7 | 5 |

LOQ/2. To give reference values, we took data from well-known scientific works by N.I. Kaletina, N. Titz, and data presented by such diagnostic laboratories as ALS Scandinavia (Sweden), ARUP (the USA), and HELIX (Saint Petersburg) [1, 33–35]. There have been numerous works focusing on difficulties involved in comparing analysis results and on standards for contents of many elements in biological media being only conventional [7, 36]. Reference values which we give in our works are no exception. Average aluminum contents in blood and urine vary within quite a wide range of concentrations. And if N.I. kaletina states that maximum permissible aluminum concentration in blood amounts to 200 µg/l, then N. Titz gives another figure, namely 100 µg/l. Maximum aluminum contents which we detected in blood of exposed population do not exceed reference values given by the said authors whereas a reference concentration given by HELIX is practically 10 times lower than the concentration which we detected in blood of the exposed children. Simple mean of aluminum contents in urine in the reference group doesn’t exceed reference values whereas aluminum contents in urine taken from urban population are 5–6 times higher than these values.

Table 4 contains data on aluminum contents in whole blood, blood serum, plasma, and urine of patients from different countries and RF regions obtained via variable analysis techniques [10, 11, 19, 20, 37–40]. These data are also shown in Figures 1 and 2 for adult population.

Aluminum contents detected in blood of exposed adults from the test group were 5 times lower than the reference level given by Titz but quite comparable with contents detected in population in Sweden. Non-exposed adults living in Croatia [37] had aluminum in their blood in concentration that was 2 times higher; exposed adults, 4 times higher. At the same time, those concentrations didn’t exceed reference ones. Workers employed by aluminum-producing enterprises in Germany [39] had 2 times lower aluminum contents in their blood than people from the East Siberia. Aluminum concentrations in non-exposed people from France were comparable with data which we obtained for the reference group in our research.

Aluminum contents detected in urine of adults from the reference group were lower than reference levels given by ALS Scandinavia and ARUP diagnostic laboratories and N. Titz. Aluminum contents in urine of exposed adults from the test group was higher than any reference level and quite comparable with aluminum concentrations detected in urine of workers employed by aluminum-producing enterprises in Germany [39] and Croatia [37]. Aluminum contents detected in urine of non-exposed population in France were comparable with aluminum contents which we detected in the reference group.
### Table 4

Aluminum contents in biological media of exposed and non-exposed population living on different territories, µg/l

| Group (medium) | Territory, procedure, presentation of results |
|---------------|------------------------------------------------|
|               | Croatia, 2010 ICP-MS, NE/E, Me (range) [37] | Sweden, 2013, ICP-MS, NE, SM (Me) [21] | France, 2005, ICP-MS, NE Me (range) [12] | Germany, 1996, AAS ETA, NE/E, SM; Me (range) [39] | Central Russia, 2003, ICP-AES ETA, ICP-MS, 2010 [11]**, NE; 2013, E [40]**SM (range) | Norway, 2013, ICP-MS, [38]**; UK, 2014, [25]**SM (range) | East Siberia, 2016 ICP-MS, NE/E SM (Me) |
| Children (urine) | Not available | – | Not available | – | 14±2** | – | – |
| Adults (urine) | 15.7 (0–100.2) / 46.4 (6.3–110.2) | – | 1.9 (0.16–11.2) | (2.4–30.8) / 29.3; 19.4 (1.4–159.4) | 54.7 (10.5–223)*** | 3.8 (1.3–25.73)** | 2.4 (0.1) / 28 (22) |
| Children (blood) | Not available | – | Not available | – | 3.3 ± 0.3** | – | – |
| Adults (blood) | 42.75 (8.15–108) / 87.6 (17.8–185.6; serum) | 19.2 (17.25. blood) 11.48 (4.52. serum) | 1.3 (1.3–6.4. blood); 3.1 (1.2–17.3. plasma) | (1.5–11) / 8.9; 7.3 (2.3–30.0. plasma) | 56 (40–73)* | 15.5 (10.8–21.7; plasma)* | 12 (10) / 21 (10) |

**Table 4**

Children (urine)
- Not available – Not available – 14±2** – 7 (3.6) / 32 (31)

Adults (urine)
- 15.7 (0–100.2) / 46.4 (6.3–110.2)

Children (blood)
- Not available – Not available – 3.3 ± 0.3** – 17 (10) / 21 (10)

Adults (blood)
- 42.75 (8.15–108) / 87.6 (17.8–185.6; serum)

Figure 1. Aluminum contents in adults’ blood, µg/l
- E means exposed adults; NE non-exposed ones

Figure 2. Aluminum contents in adults’ urine, µg/l

Aluminum contents in blood, µg/l

| Croatia NE | Croatia E | France NE | Germany E | Germany E (workers) | UK NE | East Siberia NE | East Siberia E | Reference level, Tiz | ALS Scandinavia | APUP |
|------------|-----------|-----------|-----------|---------------------|-------|----------------|---------------|-------------------|----------------|-------|
| 4.5        | 3.6       | 1.5       | 1.2       | 1.3                 | 1.2   | 1.5            | 1.5           | 1.5               | 0.8            |

Aluminum contents in urine, µg/l

| Croatia NE | Croatia E | France NE | Germany E | East Siberia NE | East Siberia E | Reference level, Tiz | ALS Scandinavia | APUP |
|------------|-----------|-----------|-----------|----------------|---------------|-------------------|----------------|-------|
| 4.5        | 3.6       | 1.5       | 1.2       | 1.5            | 1.5           | 1.5               | 1.5            | 0.8   |
Conclusions. We have developed a procedure for measuring mass concentrations of aluminum in biological media (blood and urine) with mass spectroscopy with inductively coupled plasma and reaction/collision cell with helium applied to correct polyatomic interferences (FR.1.31.2017.27357). The procedure for measuring aluminum concentrations in blood was metrologically certified for the following ranges: 20–200 µg/l and 200–700 µg/l with its precision being 31 and 23 % accordingly; in urine, for the ranges 0.1–10 µg/l and 10–1,000 µg/l with its precision being 30 and 23 % accordingly. We established limits of detection (LOD) and limits of quantification (LOQ) for the procedure. LOD for determining aluminum in blood is equal to 7 µg/l; in urine, 0.033 µg/l; LOQ for blood amounts to 21 µg/l; urine, 0.1 µg/l. The procedure was applied to analyze biological media of children and adults living in the East Siberia who lived in a zone influenced by an aluminum-producing enterprise (the examined territory). We analyzed 192 blood and urine samples taken from children \((n = 96)\) and 106 samples taken from adults \((n = 54)\). Our reference group included 53 children (100 samples) and 30 adults (60 samples) who lived in a zone which was not influenced by the said enterprise (the reference territory).

Simple average (SM) of aluminum contents in blood of children and adults living on the examined territory amounts to 21 µg/l; the reference territory, < 20 µg/l. Simple mean (SM) of aluminum contents in urine of children and adults living on the examined territory, amounts to 32 µg/l and 21 µg/l accordingly; the reference territory, 7 and 2.4 µg/l accordingly. We detected and authentic discrepancy regarding aluminum contents in urine between children from the test group and those from the reference one (concentration in 90 % samples was 4.6 times higher in the test group). There also was an authentic discrepancy regarding aluminum contents in urine between adults from the test group and those from the reference one (concentration in 100 % samples was 8.8 times higher in the test group). The procedure for measuring mass concentrations of aluminum on blood and urine with mass spectrometry with inductively coupled plasma can be applied by sanitary-hygienic, ecological, medical, and scientific organizations that deal with human occupational pathology and ecology; in can be used in evidence medicine; to organize biological monitoring; to assess anthropogenic loads; to assess efficiency of medical and innovative technologies; to assess population health risks.

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