**Biomonitoring of Boron: Development and characterization of a simple, reliable and quality controlled biomonitoring method**

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**Abstract:**

Boron exposure is of interest and concern from an occupational point of view. Usual daily boron intake is related to boron blood plasma concentration < 1 mg/l and to < 3 mg/l in urine, but after exposure urine concentrations are quickly elevated. Reliable boron biomonitoring, typically in urine, thus is mandatory for occupational health control institutions. This paper reports on the development of a simple, fast and reliable boron determination procedure based on inductively coupled plasma - optical emission spectrometry (ICP-OES). Major aims for this method were simplicity in sample preparation, low risk for artifacts and interferences, high precision and accuracy, possibly low costs, including lower costs for element selective detection, short total analysis time and suitability for occupational health laboratories. Precision data (serial or day-to-day) from urine and doped urine were very good: < 1.5 or < 2%. Accuracy was calculated from analysis of a certified reference material (ERM-CD 281), as 99 % or according to recoveries of doped concentrations ranging from 102 – 109 % recovery. For cross-checking ICP-OES determinations, samples were analyzed also by quadrupole ICP-qMS and by sectorfield ICP-sf-MS at low and medium resolution. Both systems confirmed ICP-OES measurements when using 11B for quantification. Determinations based on 10B however showed some bias, except with ICP-sf-MS at medium resolution. The observed elevated signals are discussed with respect to the known Ne++ interference (as an impurity in Ar), which is not separated in low resolving quadrupole ICP-MS systems or ICP-sf-MS at low resolution.

**Introduction:**

Boron is widely distributed in nature in the form of inorganic borates in low concentrations.
The use of boron compounds in manufacturing glass and glass products such as glass fibers, ceramic glazes, and enamels is commercially most significant. Because of its relatively indolent reaction boron improves the thermal insulation of mineral fibrous insulating material and it is an essential part of refractory borosilicate glasses. It is also used in the production of detergents or in fertilizers and biocides.

Usually boron is taken up with food or tap water. In Germany, a limit value of 1 mg/L for drinking water is set, but rarely more than 0.3 mg of boron per L of drinking water are typically measured. Mineral waters, however, can contain significantly more boron. Also tap water from different regions show elevated B concentration. Cortes et al. reported up to 17.4 mg/L in tap water from a boron – rich region in Chile [1] and Concha et al. up to 5.95 mg/L in Andean villages in Argentina [2]. In food specifically nuts, dried fruits, fruits, vegetables, wine and beer are rich in boron. According to the Scientific Panel on Dietetic Products, Nutrition and Allergies of EFSA the average daily intake of boron is approximately 1.5 mg/d (97.5 percentile: 2.6 mg/d) by food and ca. 0.2-0.6 mg by drinking water [3].

Average daily intake of boron results in a boron blood plasma concentration of < 1 mg/l and in a urine concentration < 3 mg/l [4]. Few investigations imply that boron might exert positive effects for human health [5, 6].

However, from an occupational point of view mostly boron exposure is of interest and concern.

The mining of boron containing minerals in natural deposits and the processing into borax can cause occupational exposure of workers. Boron exposure can also appear in the above mentioned glass-, ceramic- or enamel related industries. Toxico-kinetic of boric acid has been extensively studied in animals and in humans. Absorption through the intact skin is low but after oral ingestion boric acid is absorbed rapidly and completely.

Following high oral ingestion, symptoms may include nausea, vomiting, abdominal pain and diarrhea, where stool or vomited stomach contents may be discolored blue-green. The central nervous system can be affected resulting in confusion, headache and convulsions, even coma and death could be faced after high intoxication [7]. Kidneys are likely to be damaged with a reduction or complete stop of urine production [8]. The lowest reported lethal dose for humans after oral administration was 640 mg boric acid/kg body weight; after ingestion of 5-20 g of boric acid fatal poisoning in adults was reported [9].

At an average workplace exposure of 28.4 mg boron per day decreased sexual function was observed for affected males [7, 10]. Exposed workers had lower sperm volume, less sperm motility and count of sperm. However, standardized birth rate was not reduced, but gender ratio of offspring was shifted toward females at a rate of 56.5 vs. 43.5. This effect, being significant only in some statistical tests [11], was due to an increased number of female offspring and not to a decrease of male children.

A detailed description of toxicology of boron and its compounds is shown in the MAK documentation from 2011 [11]. For boron in urine currently a biological tolerance value (BAT) of 8.5 mg boron/g creatinine (boric acid) and 3.5 mg boron/g creatinine (borates) is discussed, the latter corresponding to 3 - 3.5 µg boron/L for urine with averaged creatinine levels.

Boric acid or borates are excreted by the kidneys from the blood into urine almost completely unchanged. Urine-boron thus is regarded to reflect the daily exposure [7, 12, 13]. Therefore the content of boric acid or borates in biological materials is generally quantified via elemental boron (B) determination. Different element detectors such as atomic absorption spectrometry, inductively coupled plasma (ICP) optical emission spectrometry (OES) or ICP-mass spectrometry (ICP-MS) are available, however, with different detection sensitivity, different high-throughput capability and a big range in investment and operating costs.

Specifically for those laboratories working for governmental (or other) authorities in function of workplace safety and protection standardized, highly reliable and as possibly cheap determination methods are mandatory. For governmental and regulatory authorities such methods must be evaluated as reference methods. We developed such a method which had been evaluated recently by the method development and evaluation group of DFG.

Our aims for this method development were

a) set-up of an easy, reliable determination method for biomonitoring,

b) with simple sample preparation revealing low risk for artifacts,

c) as possible low costs, including lower costs for element selective detection

d) short total analysis time including quick sample preparation and analysis,

e) suitability for occupational health laboratories.

Based on these targets we chose the following strategy: For sample preparation only a simple dilution step of urine samples was performed (simple, fast). The dilution ratio was 1:20 which provided sufficient dilution for reduced matrix interference but keeping the relevant boron concentration still far above detection limits. For element detection an ICP-OES was employed: The element lines are not interfered, instrumentation is cheaper than ICP-MS at purchase and during operation and the concentration of diluted urine even from non- exposed sample donors is typically more than 50-fold above LOD. Therefore, there is no need for even more sensitive but more expensive boron detectors such as ICP-MS. However, for quality control and feasibility the developed method was finally compared also to measurements with quadrupole based ICP-qMS and ICP-sector-field mass spectrometry (ICP-sf-MS).

**Chemicals and Standards**

It must be stressed that any contact of solutions, samples or standards with glassware (boro-silicate) should be avoided for minimizing contamination. Therefore, quartz, polyethylene or Teflon was employed throughout.

HNO3 from Merck, Darmstadt, Germany, was subboiled distilled. Certified element standards for boron and rhodium were purchased from Perkin Elmer, Rodgau-Jügesheim, Germany. Argonliq was delivered from Air Liquide, Krefeld, Germany and vaporized in an evaporizer at the tank. Water (> 18 MΩ) for dilutions and solute preparation was prepared from a Milli-Q system. The certified reference material (CRM) “*ERM CD-281”* was delivered from the Joint Research Centre, Institute for Reference Materials and Measurements (IRMM) of the European Union.

From the certified boron stock standard (PE # N9303760, Perkin Elmer, 1000 mg/L) working concentrations were prepared for calibration (0=blank, 10, 20, 50, 100, 250, 500, 1000, 2500, each µg/L), instrumental drift control (250 µg/L) and for recovery experiments by standard addition (stock concentrations: 5000 or 15000 µg/L). For ICP-MS measurements calibration concentrations were (µg/L): 0, 0.5, 1, 5, 10, 20.

**Sample preparation**

Spot urine samples were collected from volunteers and stored for a maximum of ten days in polyethylene tubes at 4o C. Before being processed the samples were vortexed. 500 µL aliquots were pipetted into quartz vessel and mixed with 9500 µL 5% nitric acid (1:20 acidic dilution). For serial precision ten parallel sample preparations were performed. For day-to-day precision a sample was prepared on each of ten consecutive days. For recovery experiments 100 µL of the previously prepared standard addition solutions (5000 or 15000 µg/L) were added to 500 µL sample and mixed with 9400 µL 5 % HNO3 resultingin “+50” µg/L or “+ 150” µg/L additions in the 1:20 diluted urine. For comparing and validating ICP-OES measurements with ICP-MS techniques another urine sample (No. 2) was prepared as native, and with addition of 1000 or 2000 µg/L boron. For respective analysis samples were diluted 1/20 for ICP-OES or 1/1000 for ICP-MS determinations.

**Sample analysis by ICP-OES**

An ICP-AES „Spectro Ciros Vision“ system (SPECTRO Analytical Instruments GmbH & Co. KG, Kleve, Germany) was used for element determination in 1:20 diluted samples. Sample introduction was carried out using a peristaltic pump (flow rate: 1 ml/min) connected to a Meinhard nebulizer with a cyclon spray chamber. The inner diameter of the torch injector was 2.5 mm. The RF power was set to 1400 W, the plasma gas was 12 L Ar /min, whereas the nebuliser gas was approximately 0.6 L Ar/min after daily optimization. When starting optimization and check-out of possible interferences the measured spectral element lines for boron were 249.6677 nm and 249.773 nm. It turned out that the two element lines were not interfered: Both showed low blank levels and were not interfered when analysing standards or even 1/20 diluted urine, as shown in figure 1. Since the 249.773 nm line revealed approximately double intensity compared to the other line we chose this one for further analysis.

**Figure 1**

**Quality control (QC)**

1. **Recovery and measurement of certified reference material**

The ICP-OES method had been validated previously by laboratory inter-comparison studies. Routinely every ten measurements, three blank determinations and determination of a certified control standard (PE # N9303760, Perkin Elmer) was performed. Calculation of results was carried out on a computerized lab-data management system, relating the sample measurements to calibration curves, blank determinations, and control standards. There were no urine reference materials being certified for boron found, therefore analysis was checked with the certified reference material *“BCR-CD-281”* after digestion.

1. **Sample analysis by ICP-qMS and ICP-sf-MS**

For quality control and additional information whether the method is also applicable for ICP-qMS or ICP-sf-MS determination, both, a NexIon ICP-qMS system (Perkin Elmer, Rodgau-Jügesheim, Germany) and an ELEMENT *II*, Thermo-Electron (Bremen, Germany) ICP-sf-MS instrument were also employed for boron determination. However, for applying a more suitable concentration range to these more sensitive instruments 1:1000 diluted urine samples were used. 103Rh was administered to each sample at a concentration of 1 µg/L as internal standard (IS). Boron was determined at 10B and 11B isotopes. For both instruments, sample introduction was carried out using a peristaltic pump (flow rate at both instruments: 0.4 ml/min) connected to a Seaspray nebulizer with a cyclon spray chamber. The inner diameter of the torch injectors was 2.0 mm for the NexIon and 1.75 mm for the ELEMENT *II*. At both instruments the RF power was set to 1250 W, plasma gas was 15 L Ar /min, whereas the nebuliser gas was approximately 0.92 L Ar/min (NexIon) or 0.84 L Ar/min (ELEMENT *II*) after daily optimization.

**Results:**

**Calibration:**

Figure 2 shows the 9-point ICP-OES calibration curve which was checked for linearity up to 2500 µg/L, having r2=0.9999 and a slope “b” of ca. 260 cps per µg/l. The concentration range between 80 – 130 µg/L appeared to be specifically interesting as in preliminary investigations 1/20 diluted spot urine samples from non-exposed volunteers were found in this concentration range. The zoomed insert shows complete linearity also in this lower part of calibration curve.

**Figure 2**

**Limit of detection**

The limit of detection (LOD) was determined as three times the standard deviation of blank determinations and was calculated at 53.4 µg B/l for undiluted, native urine. Urine from non-exposed persons is reported to contain between 1500 -3000 µg/L [4], whereas values above 3000 µg/L are considered to origin from exposed persons. From these numbers we can deduce that the LOD of the developed method is about 28 fold lower than low, native boron concentration in urine and even ca. 56 fold below the limit value set for exposure, i.e. in any case by far sufficiently sensitive for the aimed task.

It is clear that ICP-MS systems provide even better LOD, reaching down to 10 ng/L for ICP-qMS or 4 ng/L for ICP-sf-MS, each related to undiluted, native urine.

**Determination of precision**

1. **Serial precision**

For serial precision three sets of samples (each n=10) were analyzed in consecutive analytical runs: a) ten 1/20 diluted urine samples *“U1”*, b) ten 1/20 diluted urine samples *U1* with 50 µg/L boron addition and c) ten 1/20 diluted urine samples *U1* with 150 µg/L boron addition.

Table 1 shows measured concentrations, standard deviations and recoveries of doped concentrations.

**Table 1**

Serial precision was considered being very good with values below 1.5%. From ten consecutive runs the concentration of the undiluted urine was determined as 2460 ± 34 µg/L (RSD= 1.38%). This is in the normal range for non-exposed individuals (< 3000 µg/L [4]).

1. **Day-to-day precision**

Further, urine samples (+ standard additions) were prepared and analyzed on ten different days for determining day-to-day precision. Table 2 shows concentrations, standard deviation and recovery of doped concentrations.

**Table 2**

From table 2 the concentration of the undiluted urine was determined at 2498 ± 41 µg/L (RSD= 1.64%). The results from day to day showed still very good precision < 2% and the total determination was only insignificantly different from total determination derived from the serial determination (U1: p<0.200). Measurements of the doped samples differed also only insignificantly (“U1+50 µg/L”: p<0.104, “U1+150 µg/L”: p<0.114).

1. **Accuracy**

Since no boron-certified urine based certified reference material (CRM) or reference material (RM), nor another RM based on other body fluids were available, accuracy was tested mainly according to recovery determinations using the doped samples. Additionally, boron-certified CRM “*ERM CD-281”* (IRMM/EU) was digested and diluted digests were analyzed. Recovery from the doped 1/20 urine samples with “+50 µg/L” or “+150 µg/L” additions interestingly were somewhat better from the day-to-day samples around 103% whereas from the serial measurements recovery ranged from 105-110 %, which was still considered as acceptable. The determination of *ERM-CD 281* resulted in 5.55± 0.2 mg/kg compared to 5.5 ± 0.5 mg/kg for the certified value. Accuracy calculated from CRM comparison resulted in 100.9% (+0.9% overestimation for the total analytical procedure, comprising digestion + ICP-OES determination).

**Method Comparison: ICP-OES, ICP-qMS and ICP-sf-MS determination**

For cross-checking the ICP-OES determination and to show the applicability of ICP-MS systems, ICP-qMS and ICP-sf-MS systems were applied for analysis of a second urine sample (“*U2*”), or *U2* + 1000 µg/L or *U2* + 2000µg/L. Each sample was 1/20 diluted for ICP-OES or 1/1000 diluted for ICP-MS. ICP-MS determinations were performed on both 10B and 11B. According to the “ICP-MS Interference Table” [14] (and confirmed by preliminary investigations) measurement signals from ICP-OES, 11B signals at both ICP-MS systems as well as 10B and 11B signals with medium resolution at ICP-sf-MS are practically not interfered. Therefore, the determined urine concentrations of such measurements were taken for the mean reference concentration of U2 (mean ± SD / (RSD)): 1458 ± 49 µg/L / (3.4%). Table 3 shows the analytical performance of ICP-OES compared to quantifications at 10B and 11B by ICP-qMS, by ICP-sf-MS at low resolution (as suggested from the operating software) and by ICP-sf-MS at medium resolution.

In this comparison ICP-OES determinations matched the U2 reference concentration as well as the doped concentrations exactly (99.0 – 100.1% recovery). A similar positive performance was established for ICP-sf-MS at medium resolution for both boron isotopes (97.2 – 103.5% recoveries). 11B measurements using ICP-qMS, having 93.4 – 98.4% recovery, or ICP-sf-MS at low resolution, with 104.6 – 106.4% recovery, provided still good analytical performance.

**Table 3**

However, 10B determinations with those low mass resolving approaches were not satisfactory, overestimating boron concentrations by about 13 or 20%.

This worse performance on isotope 10B of ICP-qMS and ICP-sf-MS in low resolution mode may be explained by the known Ne++ interference which is seen in m/z scans around this isotope, shown in figure 3.

According to [14] 10B is overlapped from Ne++ (exact m/z [14]: 9.9962, found: 9.99619) at an abundance of 90.92% with Ne being an impurity in the Ar plasma and nebulizer gas. The quadrupole mass filter and ICP-sf-MS in low resolution mode are unable to completely resolve the interference signal from the boron signal. This leads to an overestimation. Contrarily to 10B, no interference is seen around 11B (not shown). At a medium resolution of 4000 amu both isotopes are no longer interfered. In case only ICP-MS, but no ICP-OES is at hand, it is recommended to use the 11B isotope for ICP-qMS (and for ICP-sf-MS at low resolution mode) or operating with ICP-sf-MS at medium resolution, since then both isotopes are clear.

**Summary**

Summarizing, this simple boron determination method is applicable for ICP-OES and ICP-MS systems, the latter using 11B or medium resolution. The sample preparation needs only dilution, and for ICP-MS additionally internal standard.

However, with respect to the aimed features of this method development, i.e. high precision and accuracy, ease of handling, high throughput and low costs for instrumental investment and operation, as it is needed in routine laboratories, ICP-OES determination after 1/20 dilution of urine is superior. It fulfils all the necessary requirements regarding simplicity, high precision and high accuracy at least as ICP-MS systems, has easily sufficiently low LOD and charges considerably less the budget, the latter being an important factor for health authorities.

**Conflict of interest:**

None

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**Table 1:** Serial precision of boron determination by ICP-OES in 1/20 diluted urine, with/without doped standard addition (n=10 each). Recoveries are related to doped concentrations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| n=10 | Doped standard concentration (µg/l) | measured concentration mean ± SD (µg/l) | **relative standard deviation: serial precision (%)** | Difference to urine 1 1/20(µg/L) | recovery (%) |
| urine No. 1; 1/20 | 0 | 123.7± 1.7 | 1.4% | - | -  |
| urine No. 1; 1/20 +50 µg/L  | 50 | 178.6± 1.71 | 1.0% | 54.9 | 109.8% |
| urine No. 1; 1/20 +150 µg/L  | 150 | 281.7± 3.3 | 1.2% | 158.0 | 105.3% |

**Table 2:** Day-to-day precision of boron determination by ICP-OES in 1/20 diluted urine, with/without doped standard addition (n=10 each). Recoveries are related to doped concentrations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| n=10 | Doped standard concentration [µg/l] | measured concentration mean ± SD (µg/l) | **relative standard deviation: day to day precision (%)** | Difference to urine 1 1/20(µg/L) | recovery (%) |
| urine No. 1; 1/20 | 0 | 124.9± 2.1 | 1.7% | - | -  |
| urine No. 1; 1/20 +50 µg/L  | 50 | 176.5± 3.2 | 1.8% | 51.6 | 103.2% |
| urine No. 1; 1/20 +150 µg/L  | 150 | 278.5± 4.8 | 1.7% | 153.6 | 102.4% |

**Table 3: Performance comparison of ICP-OES, ICP-qMS and ICP-sf-MS**

\* The recovery and related difference of *U2* (without addition) relates to the mean value determined from non-interfered determinations (ICP-OES, 11B with ICP-qMS and ICP-sf-MS at low resolution and 10B or 11B with ICP-sf-MS at medium resolution (see text). Recoveries and related differences of doped samples relate to respective doped amounts.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Method** | **Element/****Isotope** | **Sample** | **Concentration** | **difference (µg/L)** | **Recovery**  |   |
| **ICP-OES** | **B** | ***Urine 2*** | 1460 | µg/L | 2 | **100.1%** | **\*** |
| ***Urine 2* + 1000 µg/L** | 2460 | µg/L | 1000 | **100.0%** |   |
| ***Urine 2* + 2000 µg/L** | 3439 | µg/L | 1979 | **99.0%** |   |
| **ICP-qMS** | **10B** | ***Urine 2*** | 1643 | µg/L | 184 | **112.6%** | **\*** |
| ***Urine 2* + 1000 µg/L** | 2776 | µg/L | 1133 | **113.3%** |   |
| ***Urine 2* + 2000 µg/L** | 3735 | µg/L | 2092 | **104.6%** |   |
| **ICP-qMS** | **11B** | **Urine 2** | 1418 | µg/L | -41 | **98.4%** | **\*** |
| **Urine 2 + 1000 µg/L** | 2352 | µg/L | 934 | **93.4%** |   |
| **Urine 2 + 2000 µg/L** | 3286 | µg/L | 1868 | **93.4%** |   |
| **ICP-sf-MS low resolution (300)** | **10B** | ***Urine 2*** | 1759 | µg/L | 301 | **120.6%** | **\*** |
| ***Urine 2* + 1000 µg/L** | 2950 | µg/L | 1190 | **119.0%** |   |
| ***Urine 2* + 2000 µg/L** | 4304 | µg/L | 2545 | **127.2%** |   |
| **ICP-sf-MS low resolution (300)** | **11B** | ***Urine 2*** | 1552 | µg/L | 94 | **106.4%** | **\*** |
| ***Urine 2* + 1000 µg/L** | 2599 | µg/L | 1047 | **104.7%** |   |
| ***Urine 2* + 2000 µg/L** | 3644 | µg/L | 2092 | **104.6%** |   |
| **ICP-sf-MS medium resolution (4000)** | **10B** | ***Urine 2*** | 1417 | µg/L | -42 | **97.2%** | **\*** |
| ***Urine 2* + 1000 µg/L** | 2415 | µg/L | 998 | **99.8%** |   |
| ***Urine 2* + 2000 µg/L** | 3409 | µg/L | 1992 | **99.6%** |   |
| **ICP-sf-MS medium resolution (4000)** | **11B** | ***Urine 2*** | 1446 | µg/L | -13 | **99.1%** | **\*** |
| ***Urine 2* + 1000 µg/L** | 2481 | µg/L | 1035 | **103.5%** |   |
| ***Urine 2* + 2000 µg/L** | 3439 | µg/L | 1993 | **99.7%** |   |

**Figure 1**

ICP-OES emission spectra of a blank, a boron standard (250 µg/L) and the urine sample *U1* (1/20 diluted). Two element lines are observed at 249.667 nm and 249.773 nm. Both element lines are clear from interferences.



**Figure 2**

9-point calibration curve by ICP-OES. The window shows complete linearity in the lower concentration range where low concentrated 1/20 diluted samples from non-exposed individuals could be measured.



**Figure 3:**

Mass scan of the urine sample around the 10B isotope using the ICP-sf-MS instrument at low resolution.

Vertical bars (top) are the actual measured intensities in 0.00177 m/z intervals. Curve over bars is the fitted line resulting from the fitted peaks (bottom) using PeakfitTM Software

The Ne++ interference is detected at 9.99619 m/z and 10B at 10.0159 m/z. ICP-qMS and ICP-sf-MS at low resolution do not resolve the element signal from the interference.

