
# PROFICIENCY TESTING SCHEME: FINAL REPORT

## INSTITUTE OF PUBLIC HEALTH
## SKOPJE, REPUBLIC OF MACEDONIA

LJUBLJANA 2013

## ✓ Introduction

Within the "Regional Quality Infrastructure in Western Balkans and Turkey" project, Proficiency Testing Scheme for Drinking Water was organized by INSTITUTE OF PUBLIC HEALTH Chemistry Group Laboratory under the auspices of University of Ljubljana, Faculty of Electrical Engineering – Laboratory of Metrology and Quality.

## ✓ Objective of the Proficiency PT2

Participants in PT 2 were asked to measure the amount content of elements: Al, As, Cd, Cr total, Cu, Fe, Mn, Ni, Pb, Zn and Hg, and anions: fluoride, chloride, nitrite, nitrate, phosphate and sulphate in drinking water.

Proficiency Test PT 2 was operated in accordance with ISO/IEC 17043.

## ✓ Participants

PT 2 was opened to laboratories from Montenegro and Republic of Macedonia Eighteen laboratories participated in PT 2: Six laboratories were from Montenegro and twelve laboratories were from Republic of Macedonia.

## ✓ Samples

Natural spring water was used in this PT scheme. Sample preparation procedure for trace elements and anions was made according to International standards (ISO/IEC:15586:2003; Mercury Preservation Techniques, EPA, 2003 ).

Stability and homogeneity tests for prepared samples were made according to the ISO 13258:2005.

✓ PROFICIENCY SCHEME SCHEDULE

| | |
|---|---|
| – Preparation and quality control testing of test materials | October/November 2012 |
| – Dispatching the samples and protocol with instructions to the participants | November 2012 |
| – Reporting the results | 28/12/2012 |
| – Sending the final report to the participants | May 2013 |

✓ All laboratories (18) submitted their results before the deadline.

✓ Each laboratory was marked by the unique code and the results were confidential.

## ✓ Methods used by the participants

Participants were free to use method of their choice as for routine analysis.

## ✓ Methods used by the participants for trace elements analysis

Participants have reported different methods/techniques for trace elements analysis as: ICP, ICP-OES, ICP-MS, ICP-AES, GF-AAS, FAAS, spectrophotometry and spectroquant tests; mercury analyzer and CV – AAS for mercury analysis.

## ✓ Methods used by the participants for anion analysis

Participants have reported different methods/techniques for anion analysis as: Ion Chromatography, Spectrophotometry, Volumetry and spectroquant tests.

✓ **Determination of assigned value (*X*)**

In this exercise the assigned (reference) values were determined from median of PT 2 participants' results and from accredited laboratories results.

✓ **Determination of standard deviation for proficiency testing assessment ($\sigma$)**

✓ $\sigma$ for manganese and lead was determined as 7.5 % of assigned values

✓ $\sigma$ for aluminium, arsenic, cadmium, chromium, nickel and zinc was determined as 10 % of assigned values; for iron was determined as 12 % of assigned value and for mercury was determined as 15 % of assigned values (TUBITAK UME) .

✓ $\sigma$ for anions was derived from the Horowitz equation (ISO 13258):

$$\sigma = 0.02c^{0.8495}$$

Where $c$ is the assigned value of the analyte expressed as a dimensionless mass ratio (e.g. 1 µg/g = 1 ppm = $10^{-6}$).

✓ **Calculation of participant's Z scores**

Participant's z-scores were calculated using the following equation:

$$Z = \frac{x - X}{\sigma}$$

Where; x= participant's result

X = Assigned value

σ = standard deviation for proficiency testing assessment

For z-score the following interpretation is given to results:

- ✓ $|z| \leq 2.00$ Satisfactory result
- ✓ $2.00 < |z| < 3.00$ Questionable result
- ✓ $|z| \geq 3.00$ Unsatisfactory result

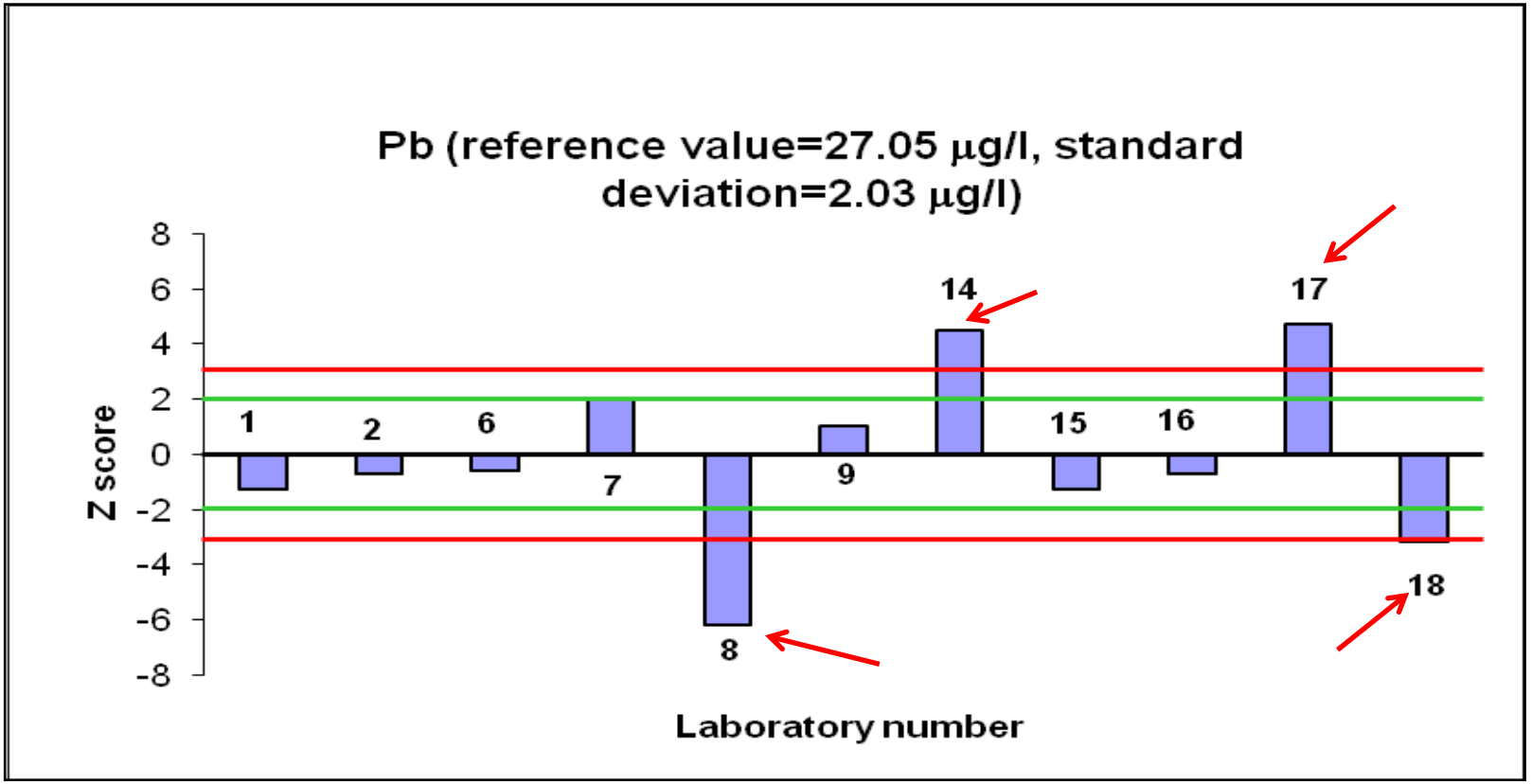


**Figure 1.** Z scores for Pb in drinking water

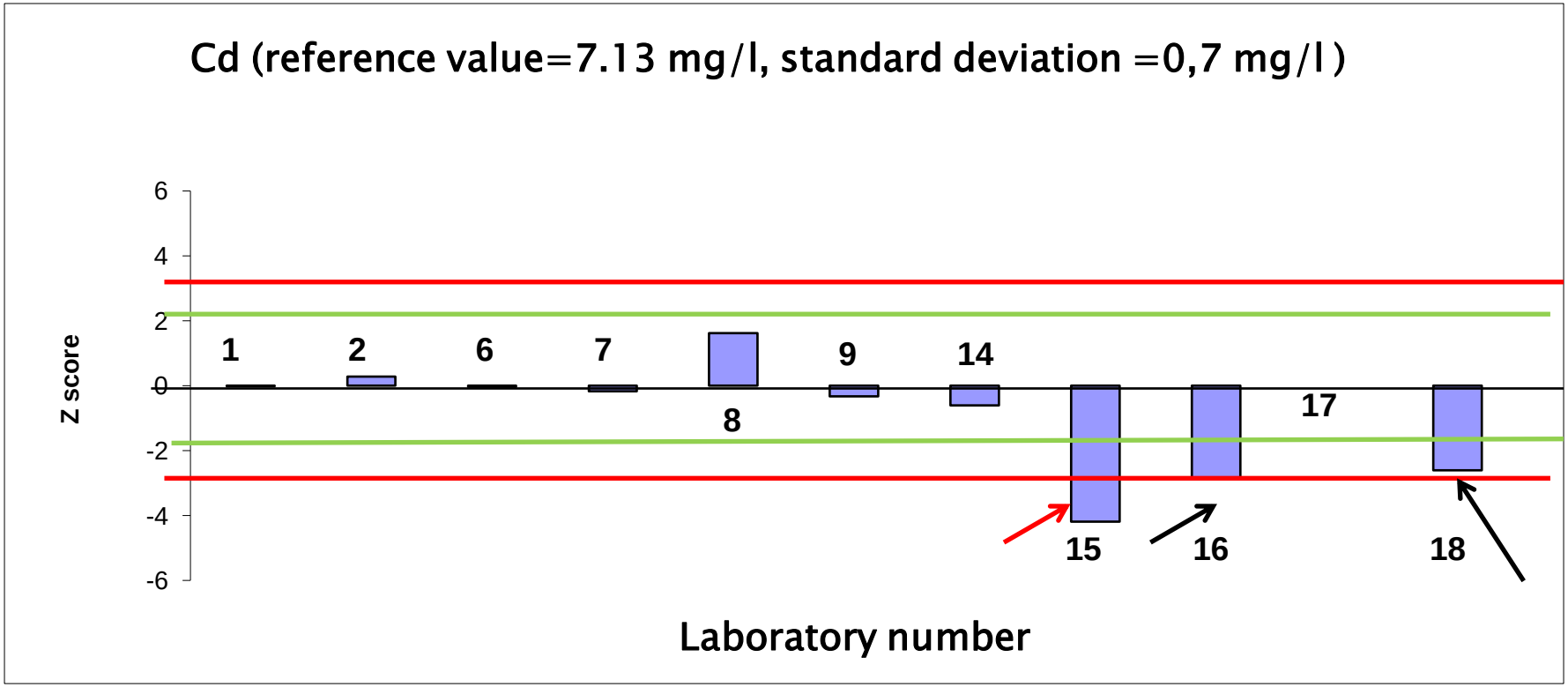


**Figure 2.** Z scores for Cd in drinking water

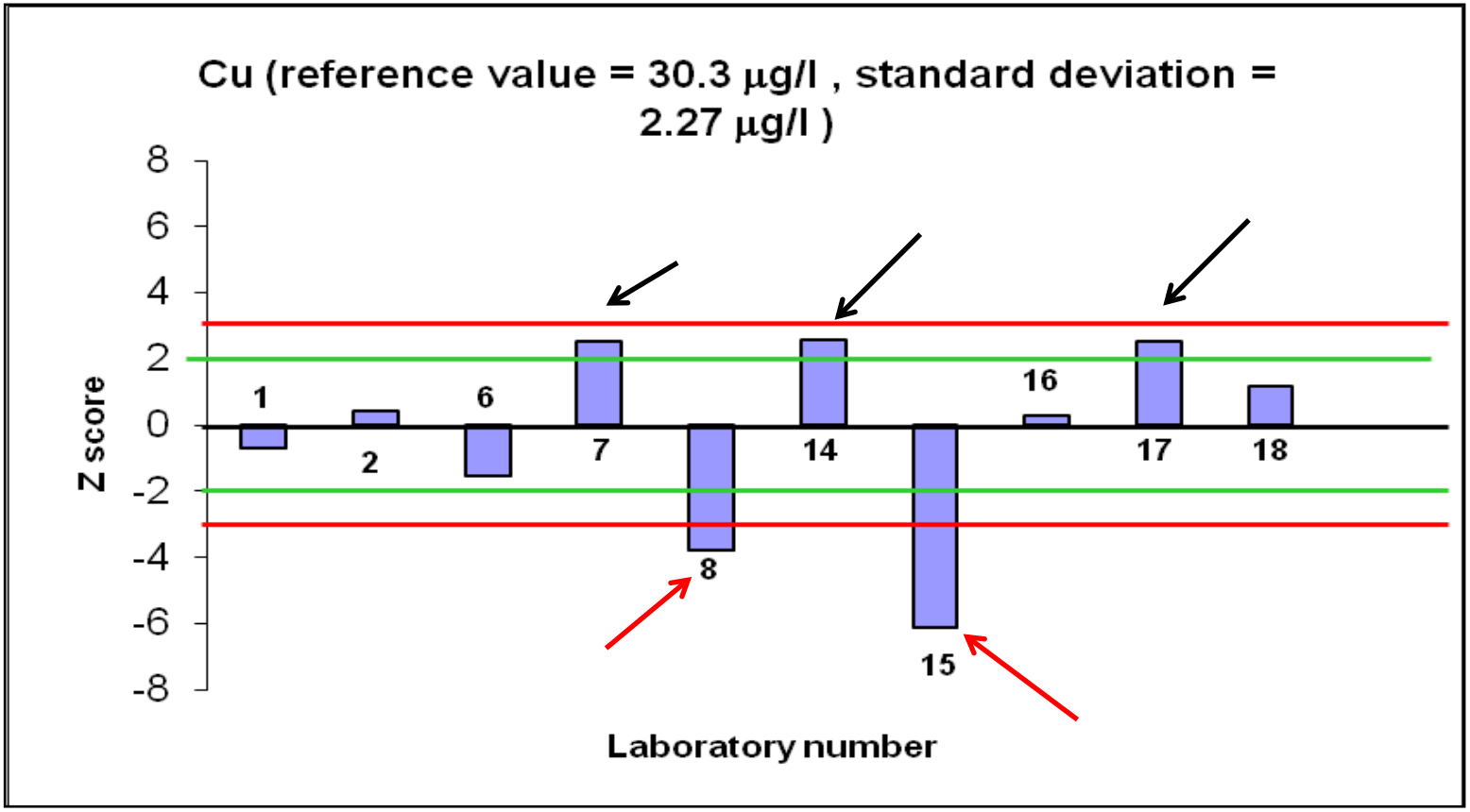


**Figure 3.** Z scores for Cu in drinking water

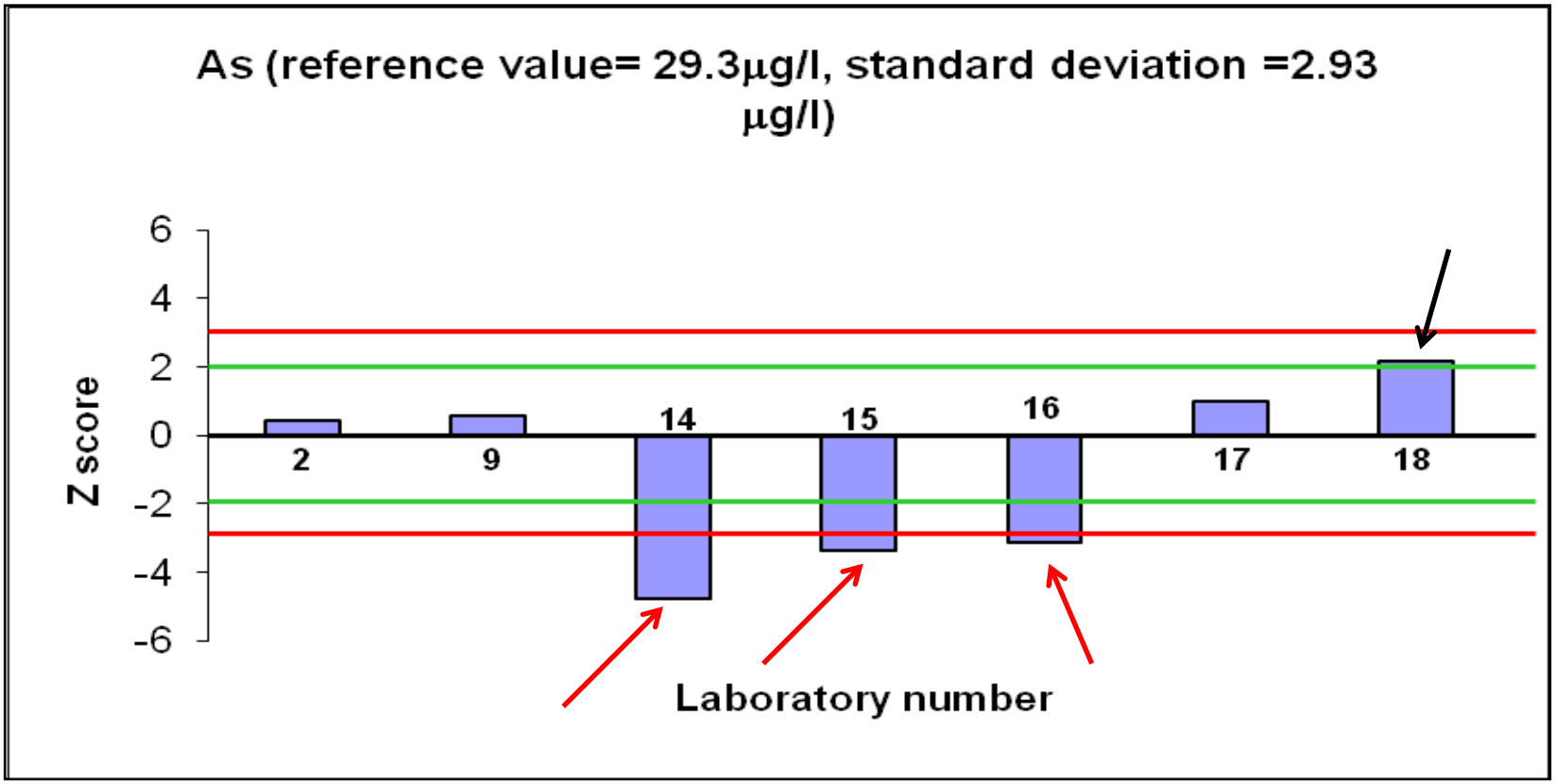


**Figure 4.** Z scores for As in drinking water

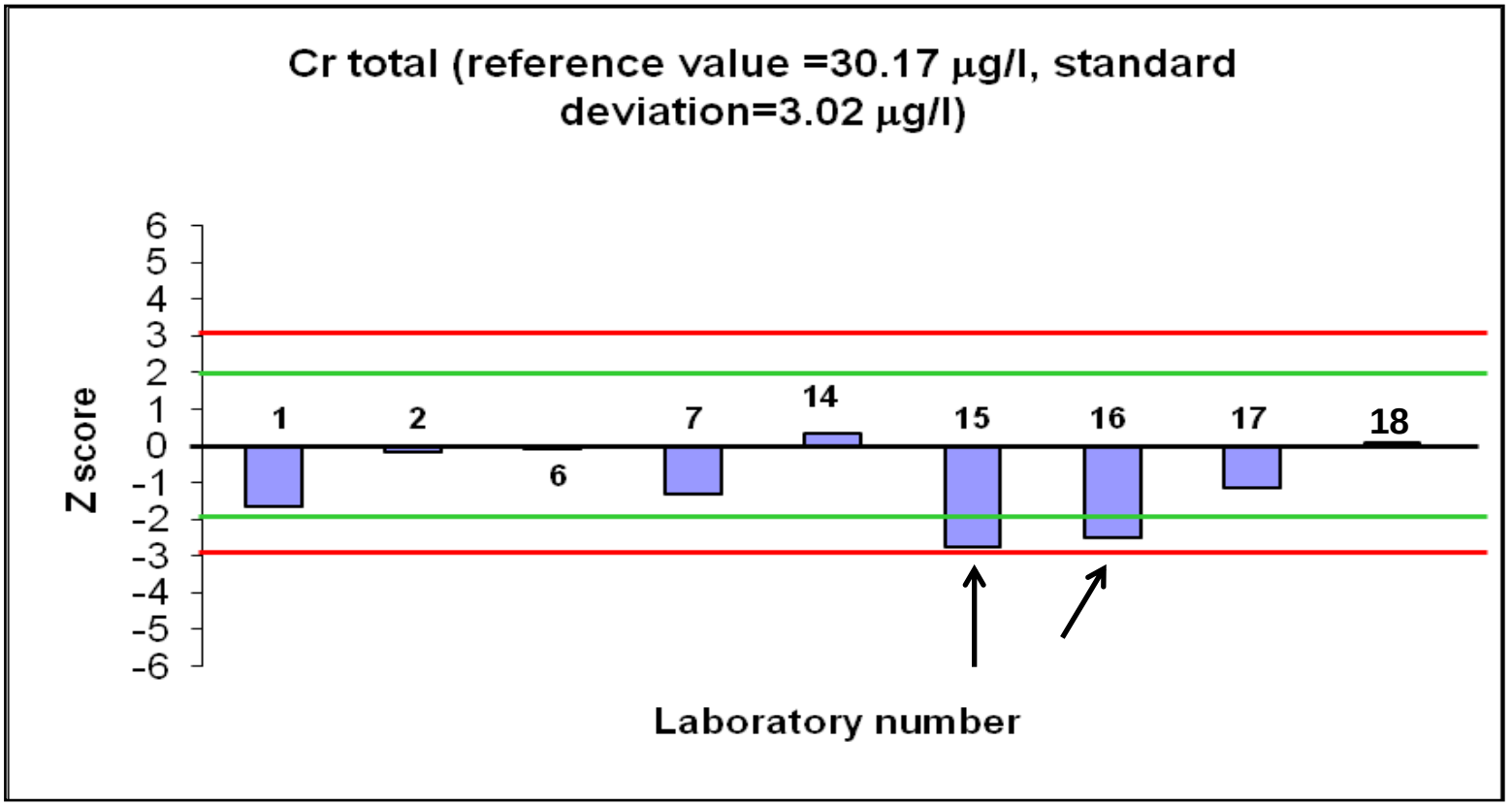


**Figure 5.** Z scores for Cr total in drinking water

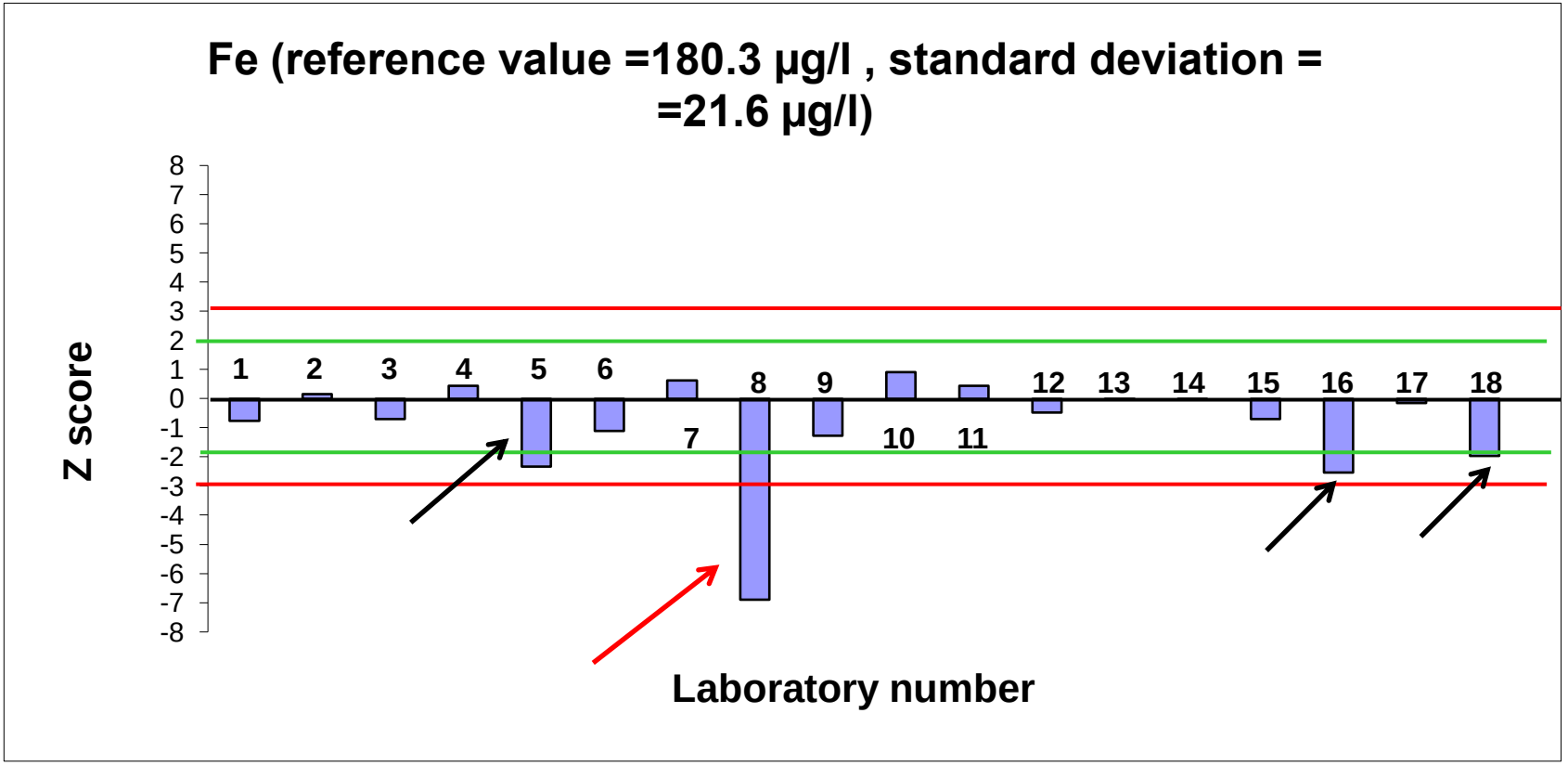


**Figure 6.** Z scores for iron in drinking water

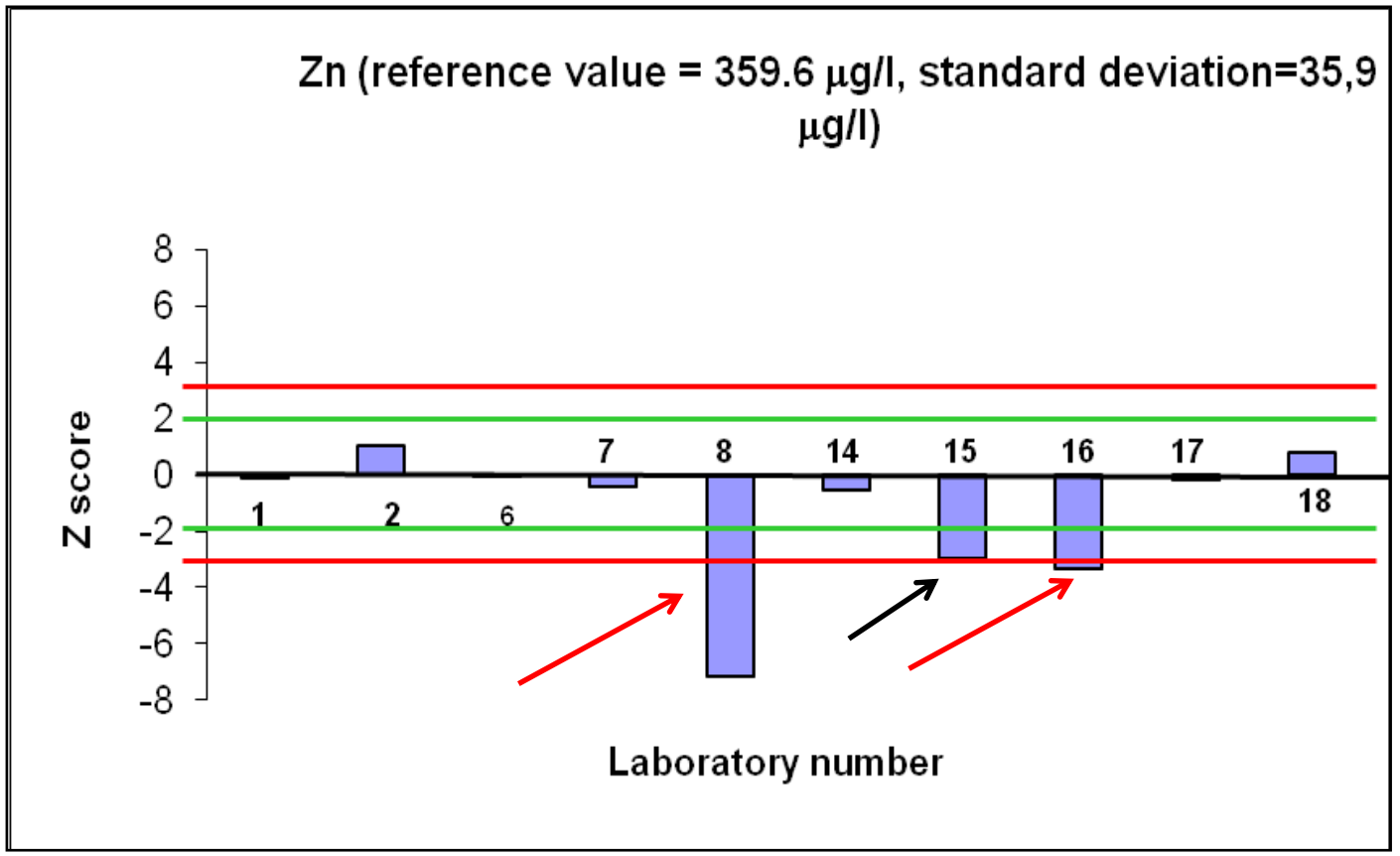


**Figure 7.** Z scores for Zn in drinking water

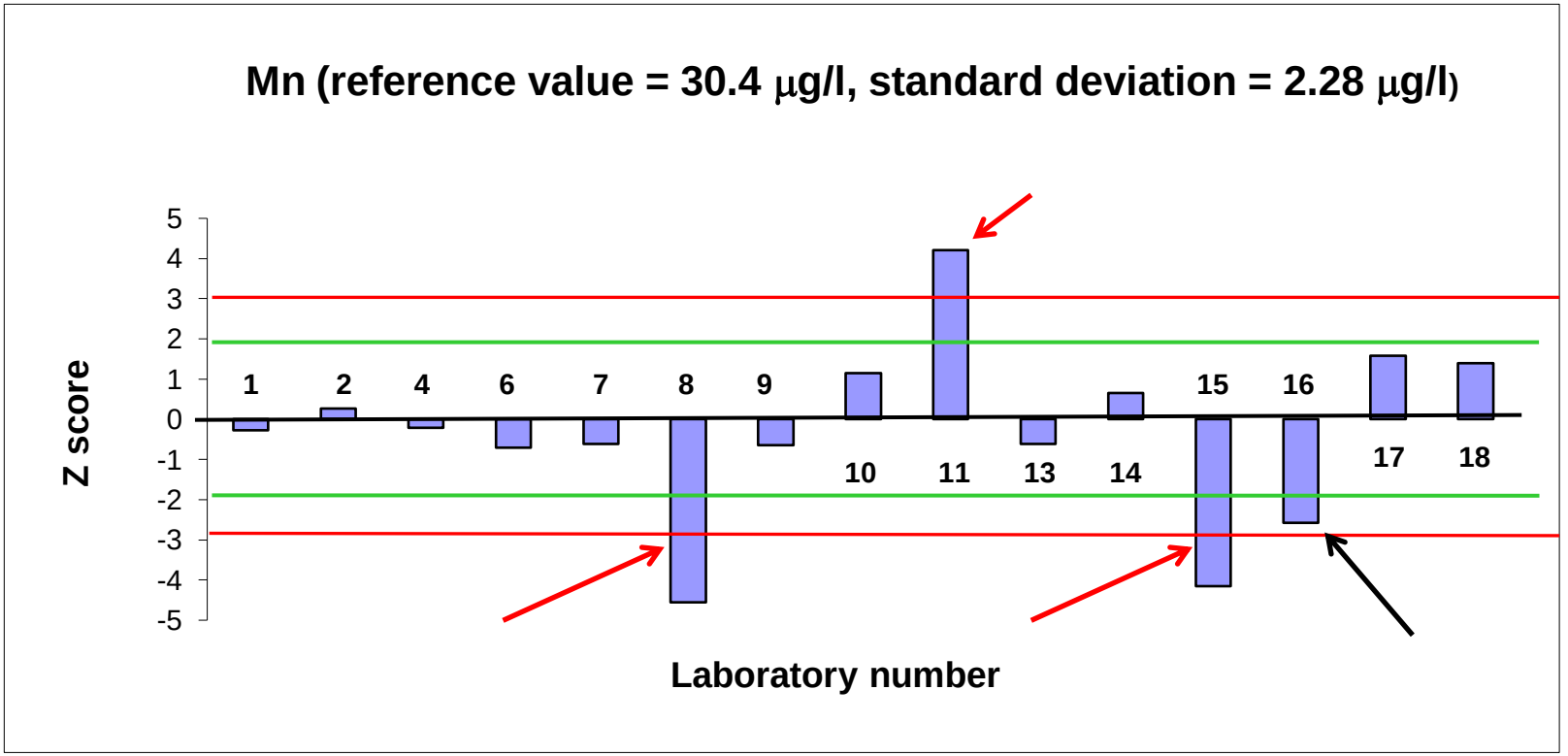


**Figure 8.** Z scores for Mn in drinking water

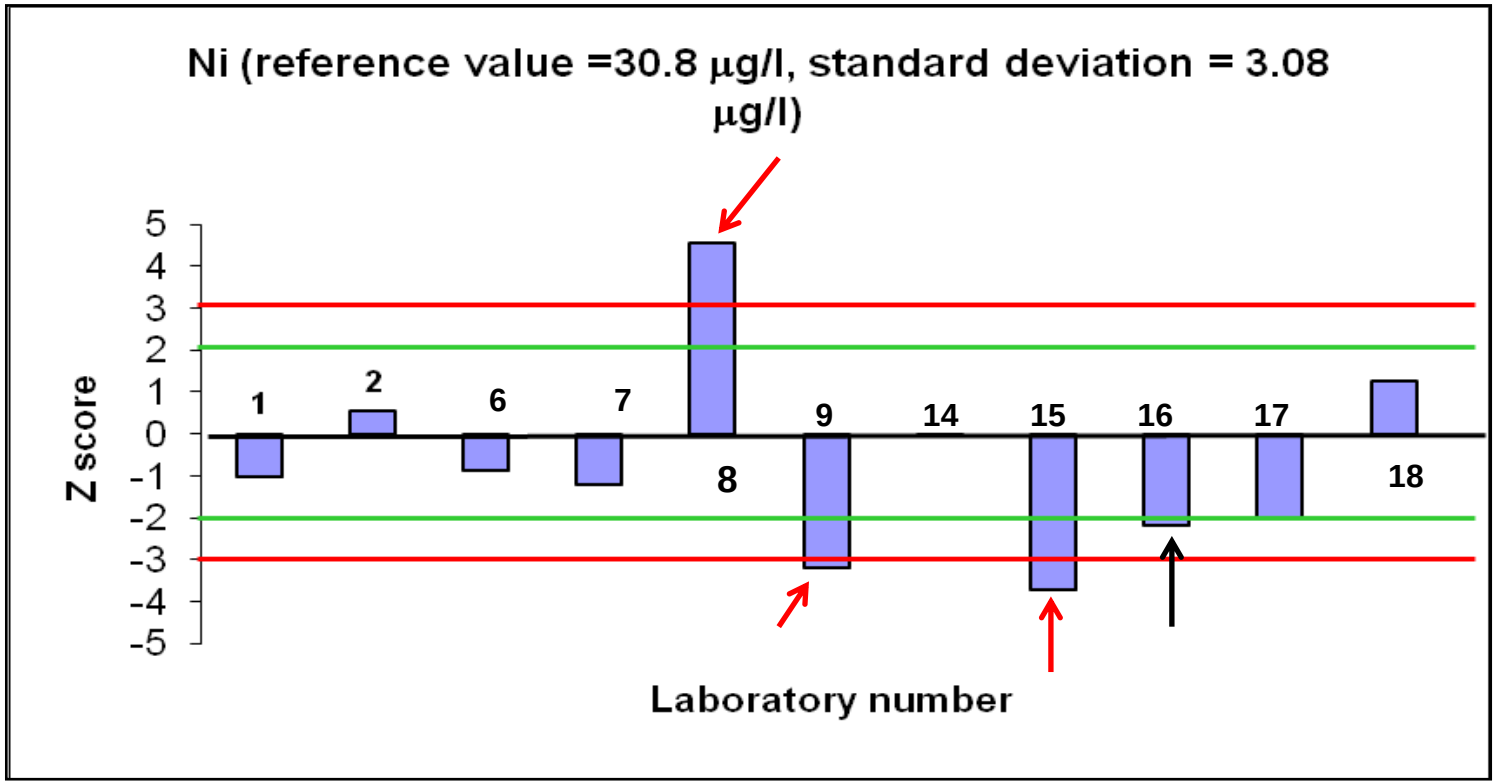


**Figure 9.** Z scores for Ni in drinking water

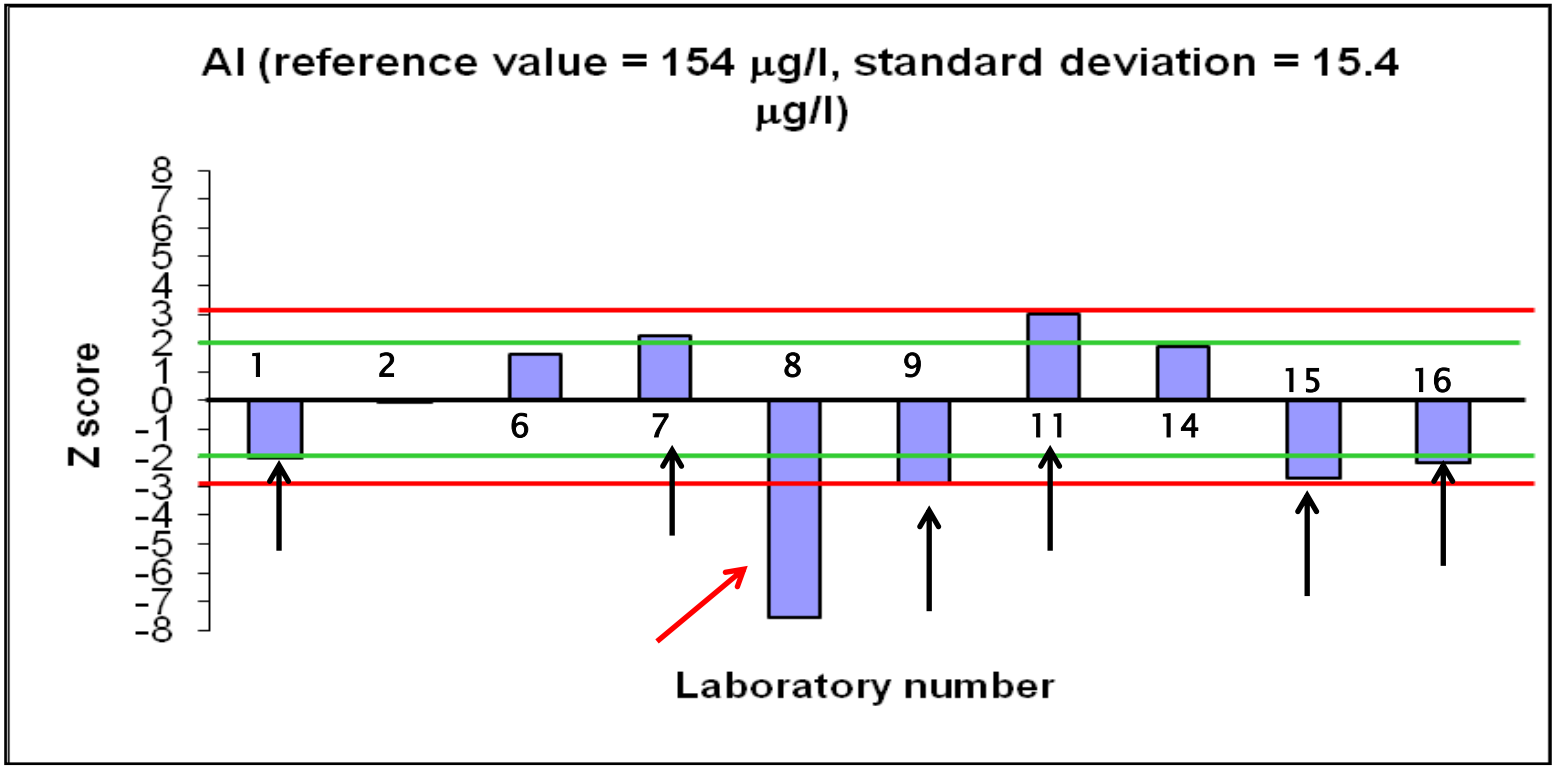


**Figure 10.** Z scores for Al in drinking water in drinking water

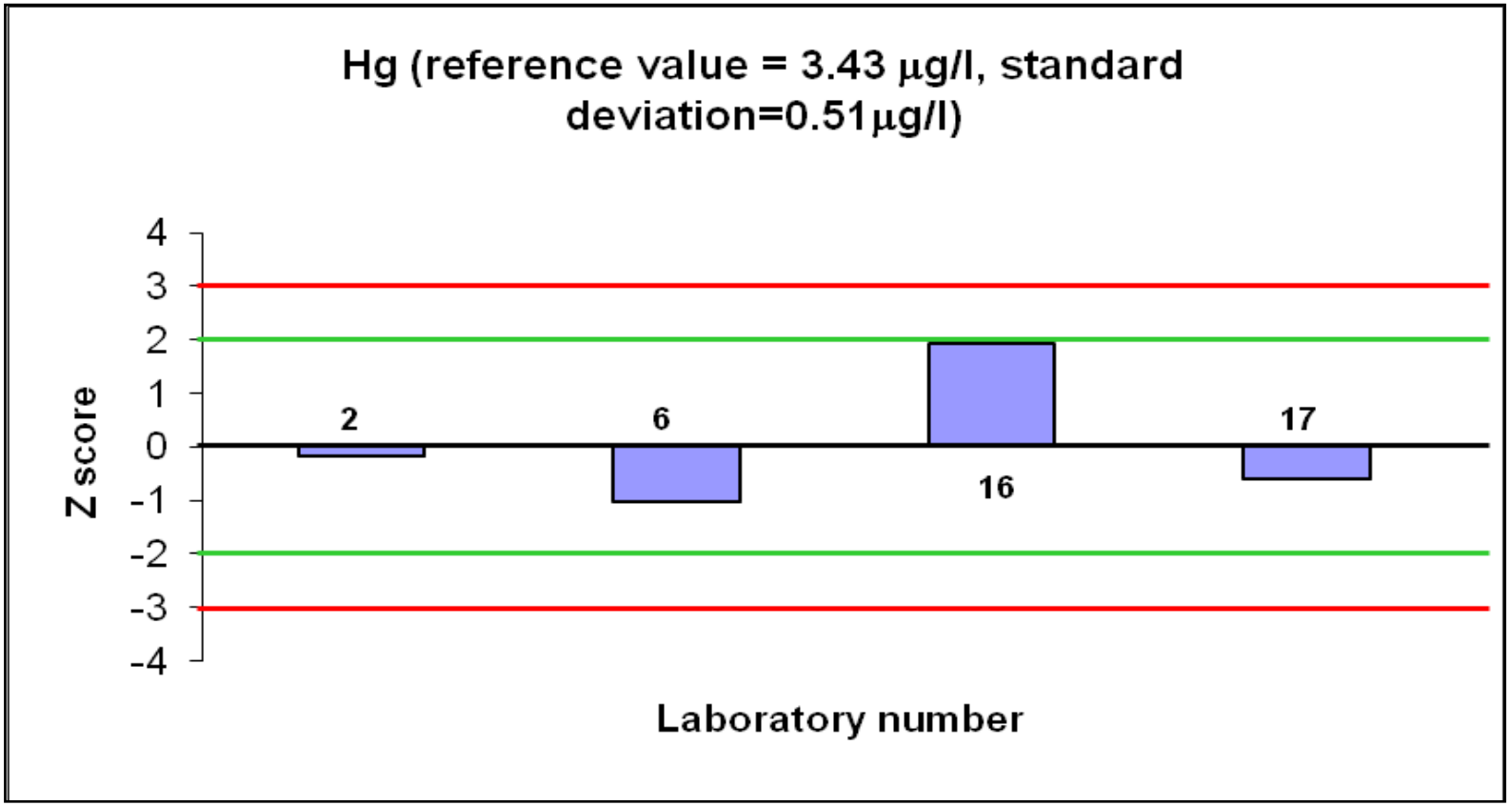


**Figure 11.** Z scores for Hg in drinking water

## Corrective measures proposed by the participants for questionable and unsatisfactory Z scores for trace elements analysis

- ✓ Laboratory number 8 – Purchasing new standard solutions for Pb, Cu, Fe, Al, Mn, Zn and Ni; maintenance and validation of the equipment, verification of the methods.
- ✓ Laboratory number 12 – Purchasing new standard solution for manganese; verification of the method
- ✓ Laboratory number 14 – Change of the method for Pb determination which will increase LOQ ; purchasing new standard solutions for Cu and As.
- ✓ Laboratory number 15 – Maintenance and validation of the equipment, validation of methods using certified reference materials; participations in more ILC schemes.

## Preventive measures proposed by the participants for questionable Z scores for trace elements analysis

- ✓ Laboratory number 7 – Maintenance and validation of the equipment.

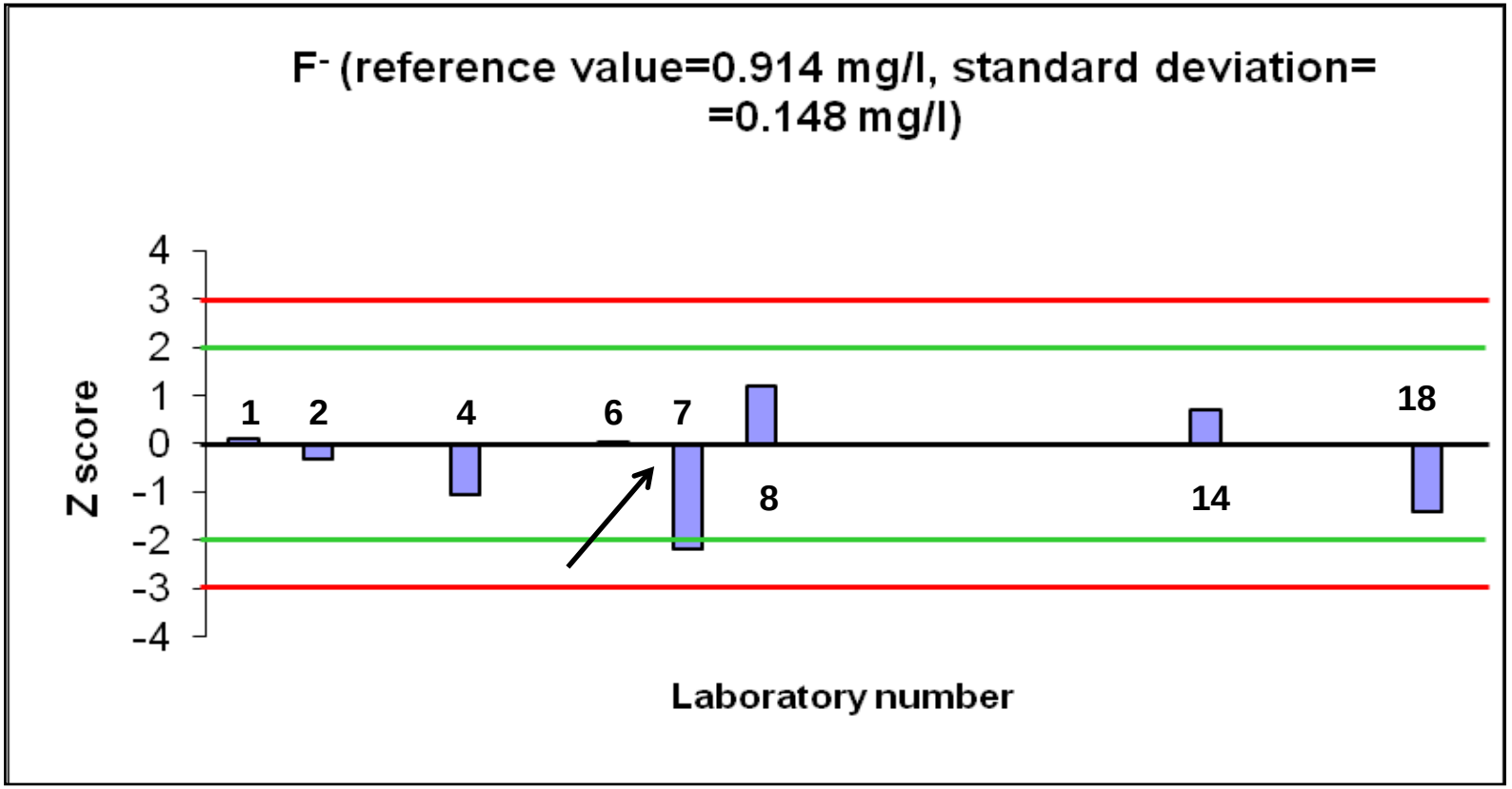


**Figure 12.** Z scores for $F^-$ in drinking water

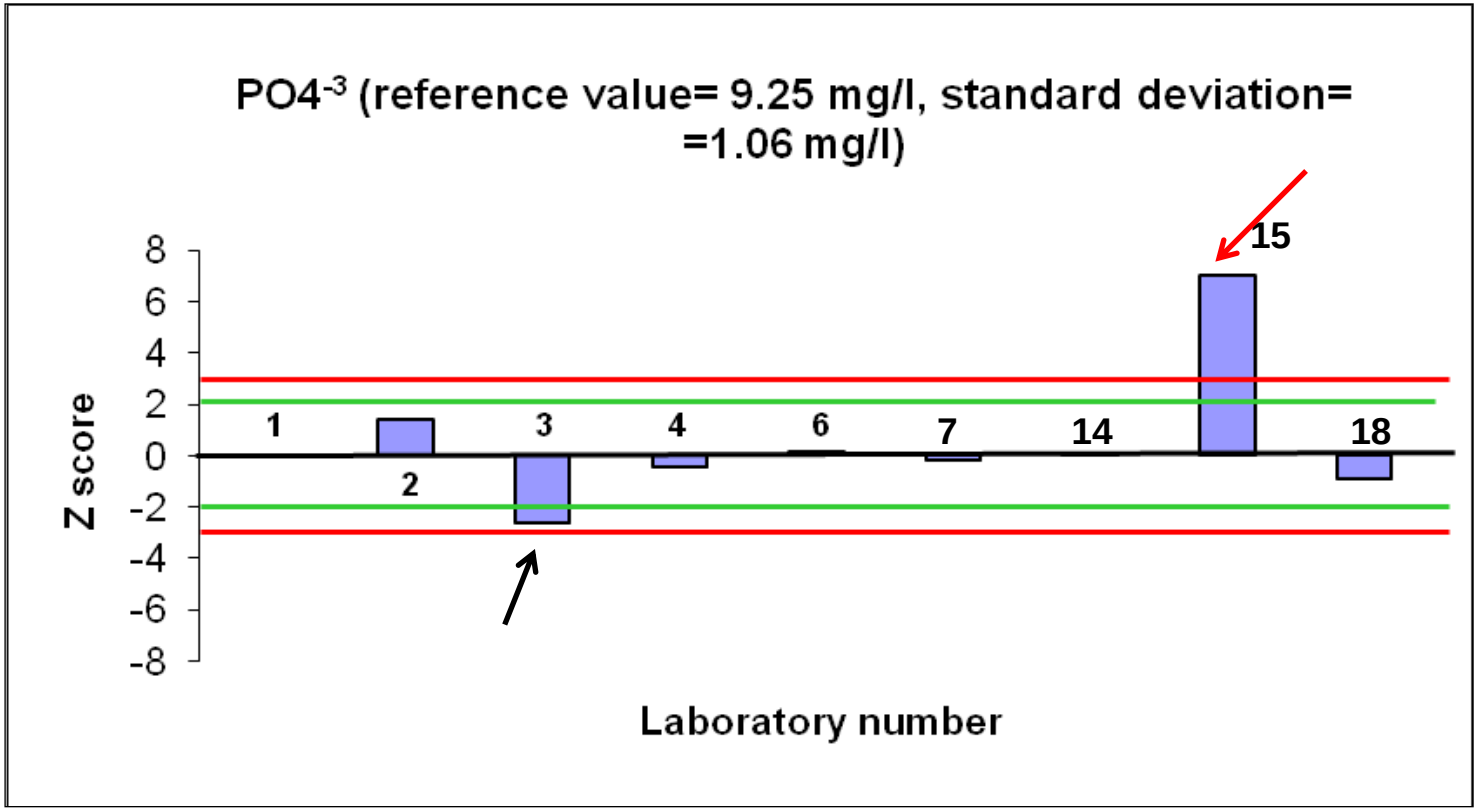


**Figure 13.** Z scores for $PO_4^{-3}$ in drinking water

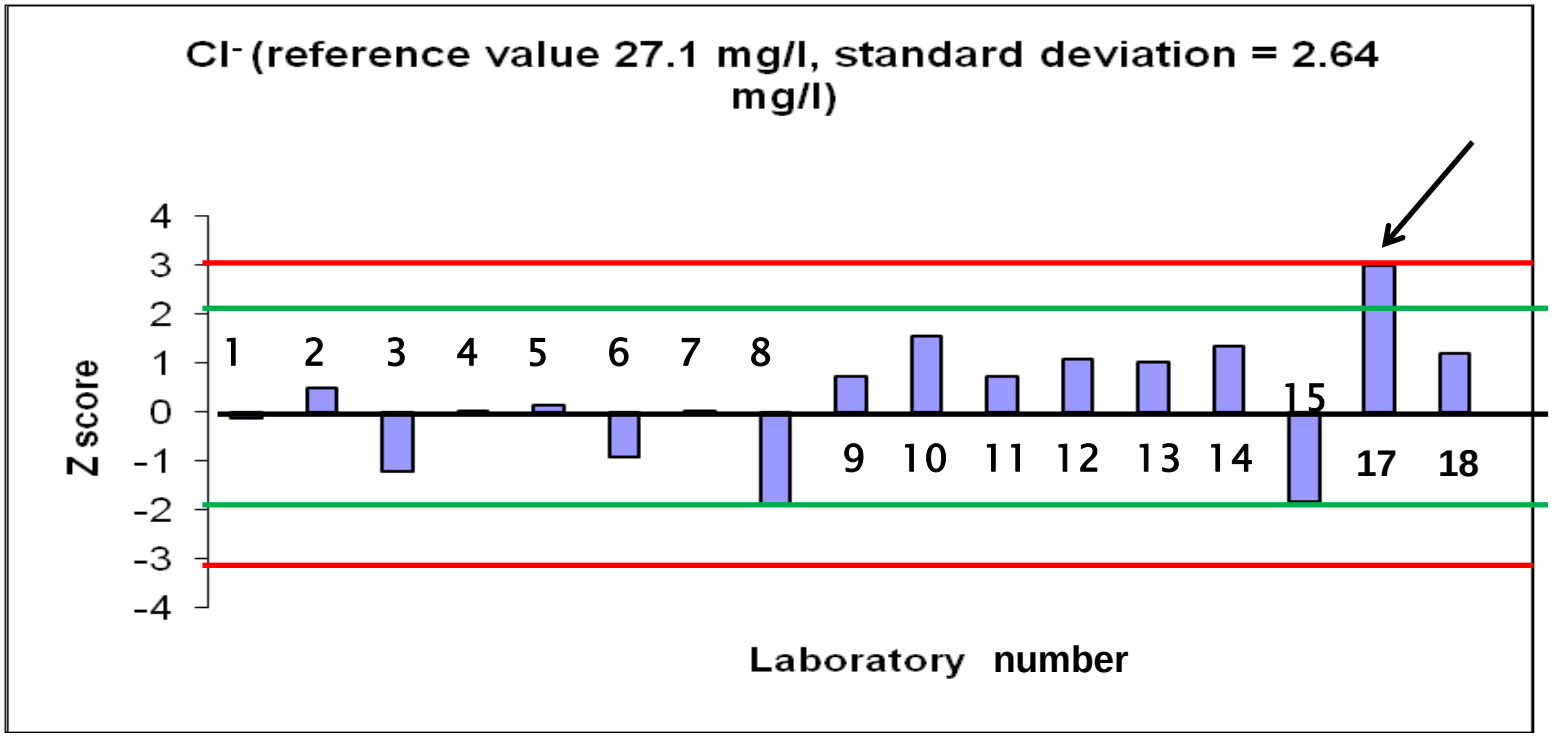


**Figure 14.** Z scores for $Cl^-$ in drinking water

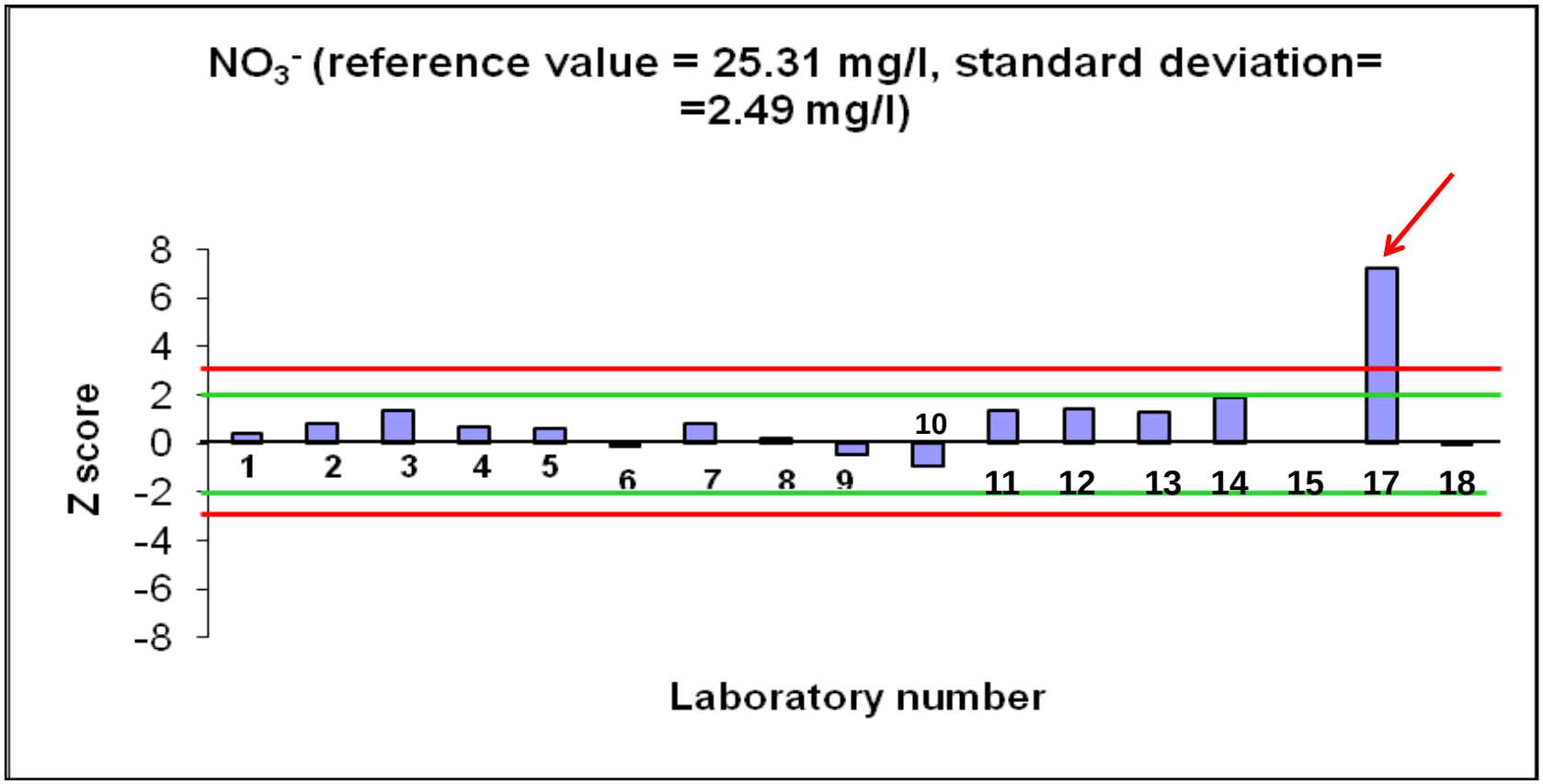


**Figure 15.** Z scores for $NO_3^-$ in drinking water

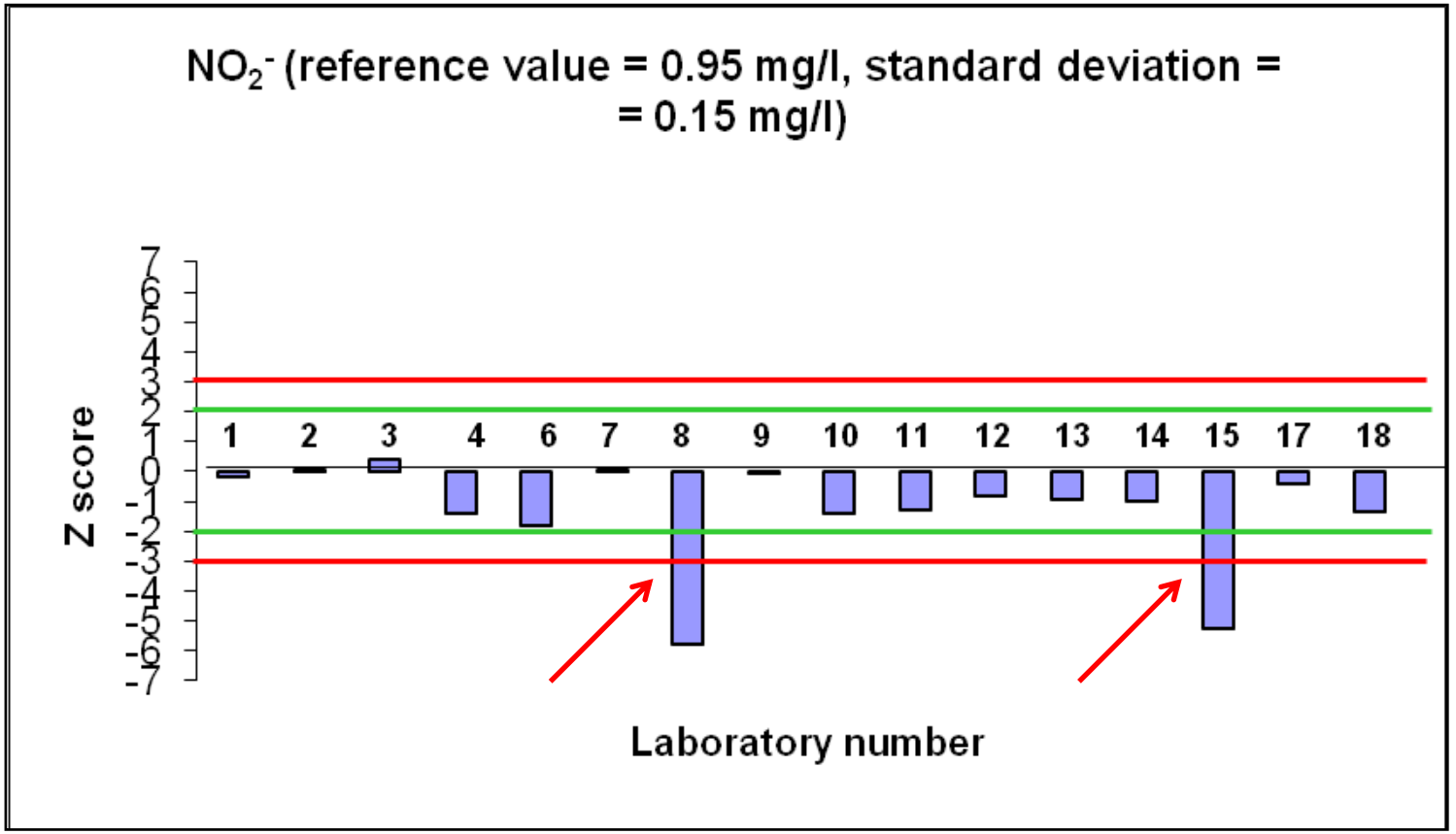


**Figure 16.** Z scores for $NO_2^-$ in drinking water

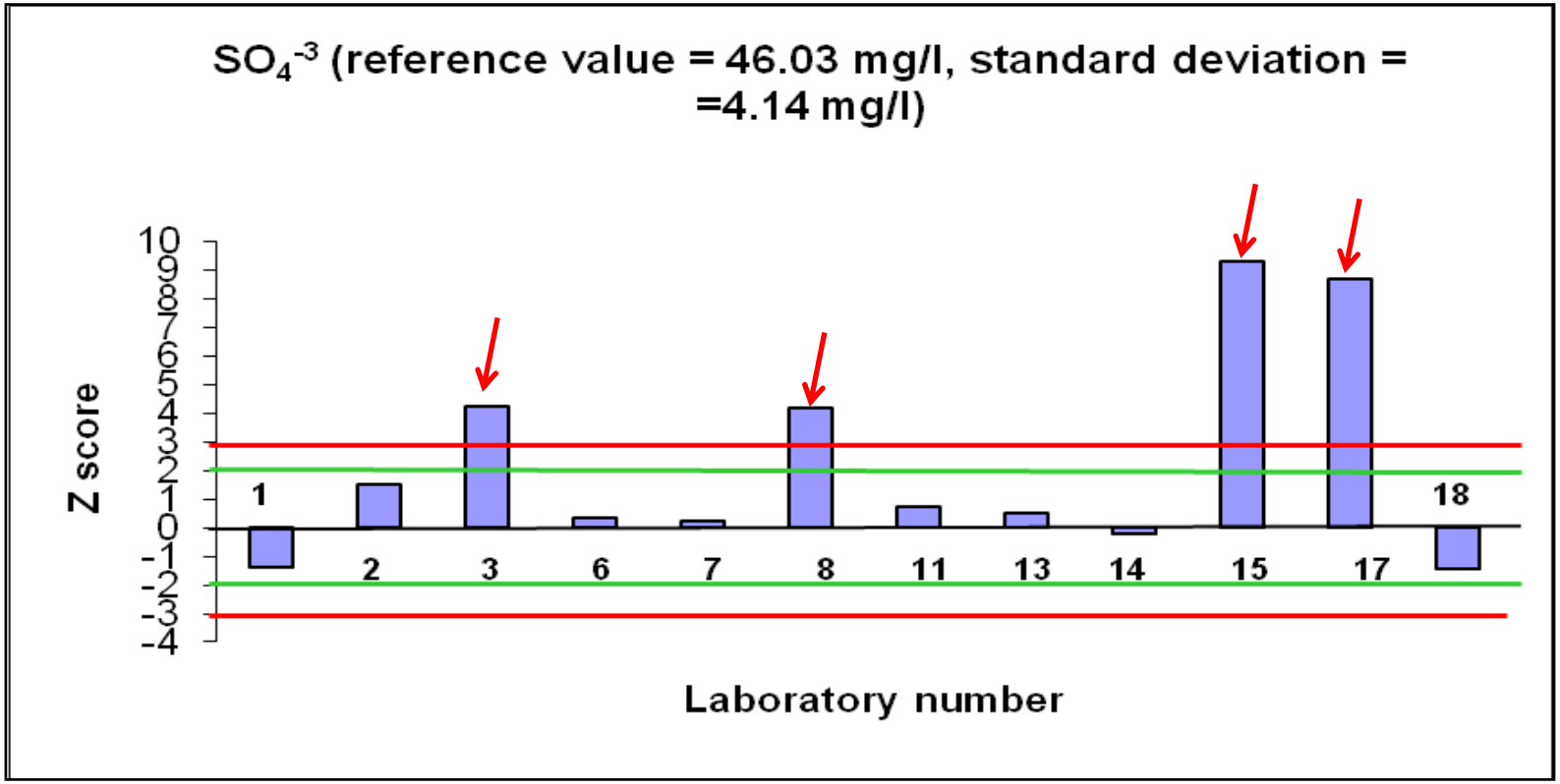


**Figure 17.** Z scores for $SO_4^{-2}$ in drinking water

## Corrective measures proposed by the participants for questionable and unsatisfactory Z scores for anion analysis

- ✓ Laboratory number 3 – Introduction of a new method for phosphate and sulphate determination in drinking water.
- ✓ Laboratory number 15 – Maintenance and validation of the equipment, verification of the methods.
- ✓ Laboratory number 17 – Maintenance and validation of the equipment, verification of the methods.

## Table 1. Distribution of the Z- scores for trace metals in drinking water

| | $\|z\| \leq 2$ | $2 < \|z\| < 3$ | $\|z\| \geq 3$ | |
|---|---|---|---|---|
| | Number of participants | Number of participants | Number of participants | Total number of participants |
| Pb | 7 (64 %) | – | 4 (36 %) | 11 |
| Cd | 9 (82 %) | 2 (18 %) | 1 (9 %) | 11 |
| Cu | 5 (50 %) | 3 (30 %) | 2 (20 %) | 10 |
| Zn | 7 (70 %) | 1 (10 %) | 2 (20 %) | 10 |
| Fe | 14 (78 %) | 3 (16 %) | 1 (5 %) | 18 |
| Mn | 11 (69 %) | 1 (6 %) | 3 (19 %) | 16 |
| Cr | 6 (60 %) | 2 (20 %) | – | 10 |
| As | 3 (43 %) | 1 (14 %) | 3 (43 %) | 7 |
| Hg | 4 (100 %) | – | – | 4 |
| Ni | 6 (55 %) | 2 (18 %) | 3 (27 %) | 11 |
| Al | 4 (40 %) | 5 (50 %) | 1 (10 %) | 10 |

# Table 2. Distribution of the Z- scores for anions in drinking water

| | $\|z\| \leq 2$ | $2 < \|z\| < 3$ | $\|z\| \geq 3$ | |
|---|---|---|---|---|
| | Number of participants | Number of participants | Number of participants | Total number of participants |
| $F^-$ | 7 (87.5 %) | – | 1 (12.5 %) | 8 |
| $PO_4^{-3}$ | 7 (77.8 %) | 1 (11.1 %) | 1 (11.1 %) | 9 |
| $Cl^-$ | 16 (94.1 %) | 1 (5.9 %) | – | 17 |
| $NO_3^-$ | 16 (94.1 %) | – | 1 (5.9 %) | 17 |
| $NO_2^-$ | 14 (87.5 %) | – | 2 (12.5 %) | 16 |
| $SO_4^{-2}$ | 8 (66.7 %) | – | 4 (33.3 %) | 12 |

# Table 3. Distribution of the results for trace metals in drinking water

| | Pb | Cd | Cu | Zn | Fe | Mn |
|---|---|---|---|---|---|---|
| *Number of participants (n)* | *11* | *11* | *10* | *10* | *18* | *16* |
| Median (µg/l) | 22.53 | 6.21 | 30.85 | 341.5 | 167.5 | 22.88 |
| Mean value (µg/l ) | 26.76 | 6.21 | 26.69 | 371.4 | 150.85 | 31.67 |
| Reference value (µg/l ) | 27.05 | 7.13 | 30.3 | 359.6 | 180.3 | 30.4 |
| Standard deviation of the proficiency (µg/l) | 2.03 | 0.7 | 2.27 | 35.9 | 21.6 | 2.28 |
| Maximum value (µg/l ) | 36.55 | 8.26 | 36.2 | 396.3 | 200 | 40 |
| Minimum value (µg/l) | 14.46 | 4.2 | 16.4 | 101.1 | 31 | 10 |
| Range (Max/Min) | 2.52 | 1.97 | 2.2 | 3.92 | 6.45 | 4 |

## Table 3. Distribution of the results for trace metals in drinking water (continued)

| | Cr | As | Hg | Ni | Al |
|---|---|---|---|---|---|
| *Number of participants (n)* | *10* | *7* | *4* | *11* | *10* |
| Median (µg/l) | 27.86 | 33.08 | 3.24 | 27.68 | 121.45 |
| Mean value (µg/l ) | 27.86 | 26.32 | 3.24 | 31.17 | 140.23 |
| Reference value (µg/l ) | 30.17 | 29.3 | 3.43 | 30.8 | 154 |
| Standard deviation of the proficiency (µg/l) | 3.02 | 2.93 | 0.51 | 3.08 | 15.4 |
| Maximum value (µg/l ) | 31.3 | 35.66 | 4.42 | 44.83 | 200 |
| Minimum value (µg/l) | 21.9 | 15.25 | 3.13 | 19.3 | 36.33 |
| Range (Max/Min) | 1.43 | 2.34 | 1.41 | 2.32 | 5.51 |

## Table 4. Distribution of the results for anions in drinking water

| | $F^-$ | $PO_4^{-3}$ | $Cl^-$ | $NO_3^-$ | $NO_2^-$ | $SO_4^{-2}$ |
|---|---|---|---|---|---|---|
| *Number of participants (n)* | *8* | *9* | *17* | *17* | *16* | *12* |
| Median (µg/l) | 0.89 | 9.77 | 29.0 | 26.83 | 0.80 | 48.5 |
| Mean value (µg/l ) | 0.87 | 9.21 | 28.53 | 27.28 | 0.75 | 55.14 |
| Reference value (µg/l ) | 0.914 | 9.25 | 27.1 | 25.30 | 0.95 | 46.03 |
| Standard deviation of the proficiency (µg/l) | 0.15 | 1.06 | 2.64 | 2.49 | 0.15 | 4.14 |
| Maximum value (µg/l ) | 1.19 | 16.70 | 35.0 | 43.19 | 1.02 | 84.40 |
| Minimum value (µg/l) | 0.58 | 6.45 | 23.9 | 21.90 | 0.15 | 40.0 |
| Range (Max/Min) | 2.05 | 2.59 | 1.46 | 1.97 | 6.78 | 2.11 |

# THANK YOU FOR YOUR ATTENTION