

Evaluation of proficiency test for the determination of total arsenic in fresh fish

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INTRODUCTION

Proficiency tests are inter-laboratory exercises in which the results of a particular laboratory arsenic in fish tissues. Therefore, this study describes a new protocol for the production of reference material compared to a reference value or with the results obtained from similar laboratories. A proficiency test item is required for the effective execution of these tests, which can be: a sample product or device, reference material, equipment, a standard set of data or other information. In Brazil there are currently no providers of proficiency testing for toxic metals such as materials for use in proficiency testing for arsenic in fish tissue. The reference materials produced for proficiency testing should be homogeneous and stable over the duration of the test, and must follow all the requirements of international quality standards used in the preparation of certified reference materials.

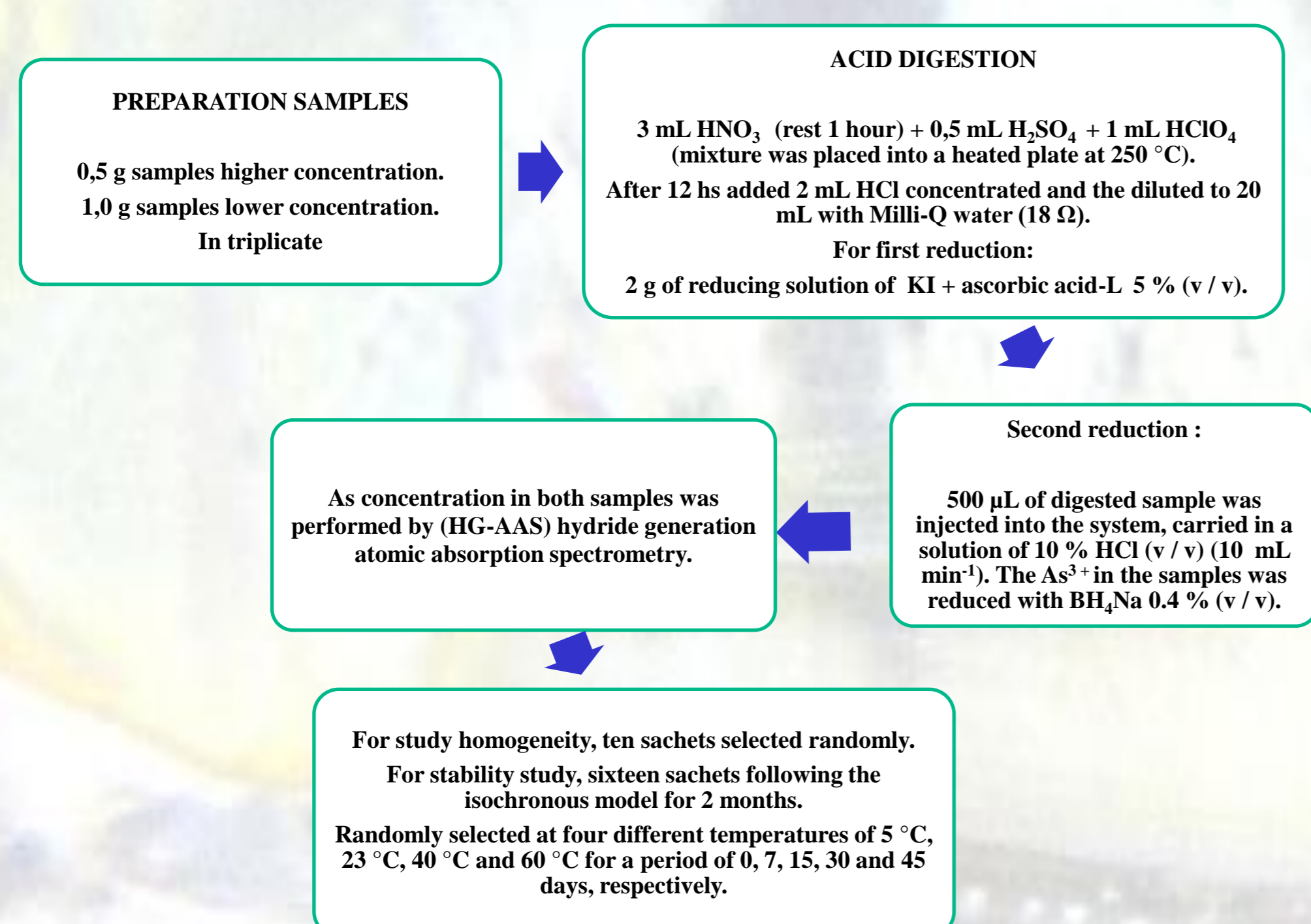
METHODOLOGY

The preparation scheme consisted of: selecting of individuals, cleaning of scale and skin, trituration, homogenization, and spiking with arsenic at two levels of concentration, irradiated with cobalt 60 at 10.00 ± 1.05 kGy and packed into sachets.

Preparation of samples



Determination of Arsenic



RESULTS AND DISCUSSIONS

Homogeneity study

The results obtained for the homogeneity test for arsenic at higher and lower concentrations of irradiation are shown in table 1. In both case the samples are homogeneity.

TABLE 1- Average values obtained in the determination of total arsenic in $\mu\text{g g}^{-1}$ by FIA-HG-AAS in higher and lower irradiation concentrations (wet basis) for the study of homogeneity (n = 30)

| Temperature 23 ± 0.3 °C | Concentration average As ($\mu\text{g g}^{-1}$) | |
|--|---|-----------------|
| | Lower | higher |
| Average \pm S.D. | 0.72 ± 0.06 | 1.30 ± 0.10 |
| Variance | 0.0032 | 0.0092 |
| RSD % | 7.8 | 7.4 |
| F _{calc} | 0.73 | 2.55 |
| F _{crit} | 3.88 | 3.88 |
| | gl(total)=14 | gl(total)=14 |
| valor-P (b1) | 0.25 | 0.09 |
| u _{pb} $\mu\text{g g}^{-1}$ (%) | 0.06 (6.0 %) | 0.04 (4.0) |

RSD-relative standard deviation, F-value obtained for Fisher's test, P (X1) P-value for variable X1 (slope b1), gl-degree of freedom, As-total arsenic, F-calc –calculated, F-crit –critical.

ACKNOWLEDGEMENTS



Stability study

The results are shown in Figure 1, samples exposed to higher and lower concentrations. In both case the samples are stable.

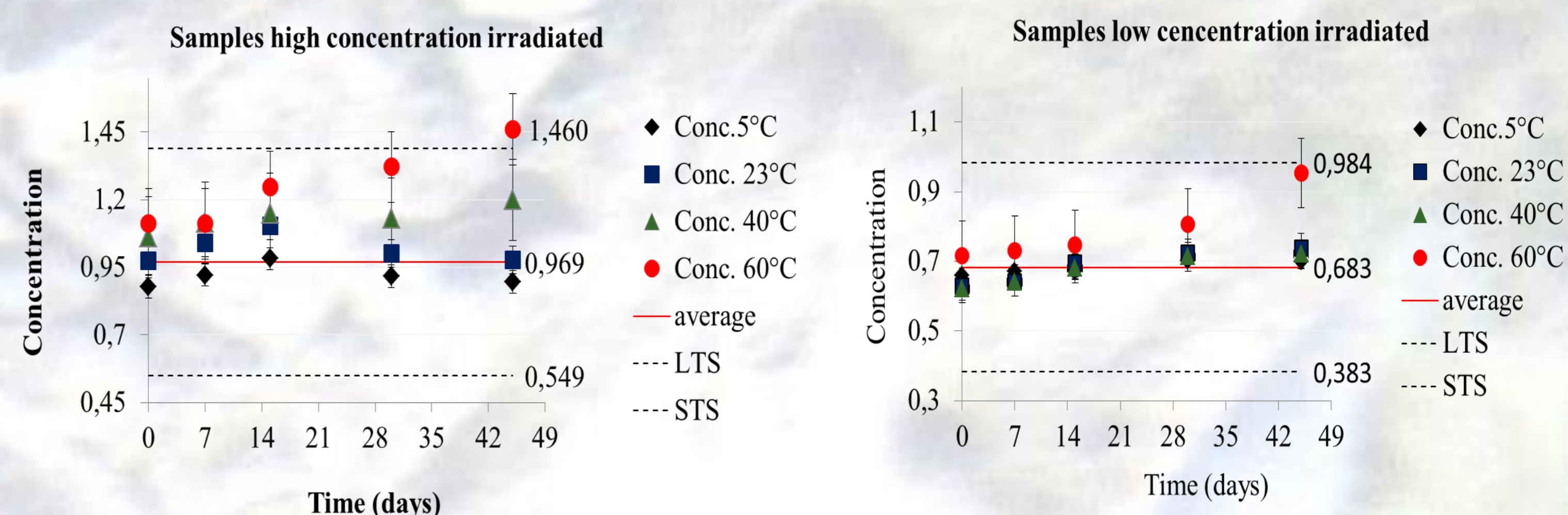


Figure 1-Samples high and low concentration

The value of reference obtained with the estimated expanded uncertainty associated was:

Table 2 - Estimated expanded uncertainty in $\mu\text{g g}^{-1}$ for As-total

| Element | ^a Average \pm U _{MR} ($\mu\text{g g}^{-1}$) | U _{MR} % |
|-------------|--|----------------------|
| As (higher) | 1.09 ± 0.42 | 39 |
| As (lower) | 0.64 ± 0.30 | 46 |

^aAverage-obtained in the characterization, represents the average of 45 replicates of each material.

Proficiency test

The proficiency testing for the determination of total arsenic in muscle tissue of fresh fish relied on the participation of ten governmental and private laboratories. The participating laboratories received two samples at different concentration levels that were analyzed on three different days in order to check the robustness of their results. The time for performing the tests and to return the results was 30 days. All results were statistically evaluated using procedures based on standard ISO/IEC 17043:2010 and the International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories. The assigned value used in proficiency testing program was obtained for robust mean of the results reported by all participants in the round, computed using the algorithm A and the standard deviation for evaluation of the proficiency test was derived from a general model with Horvitz curve Table 3.

TABLE 3- Estimate for the assigned values and standard deviation, in $\mu\text{g g}^{-1}$ for the results of pilot proficiency testing (wet basis)

| Concentration Element | Robust Statistical ($\mu\text{g g}^{-1}$) | |
|-----------------------|--|------------|
| | H15 Huber | uH15 Huber |
| As high | 1,05 | 0,11 |
| As lower | 0,72 | 0,01 |

H15 = Huber robust mean; uH15 Huber robust = standard deviation of Huber;

The evaluated laboratory performance is summarized in the Fig. 2. Considering the results obtained to date, all laboratories obtained a satisfactory z-score.

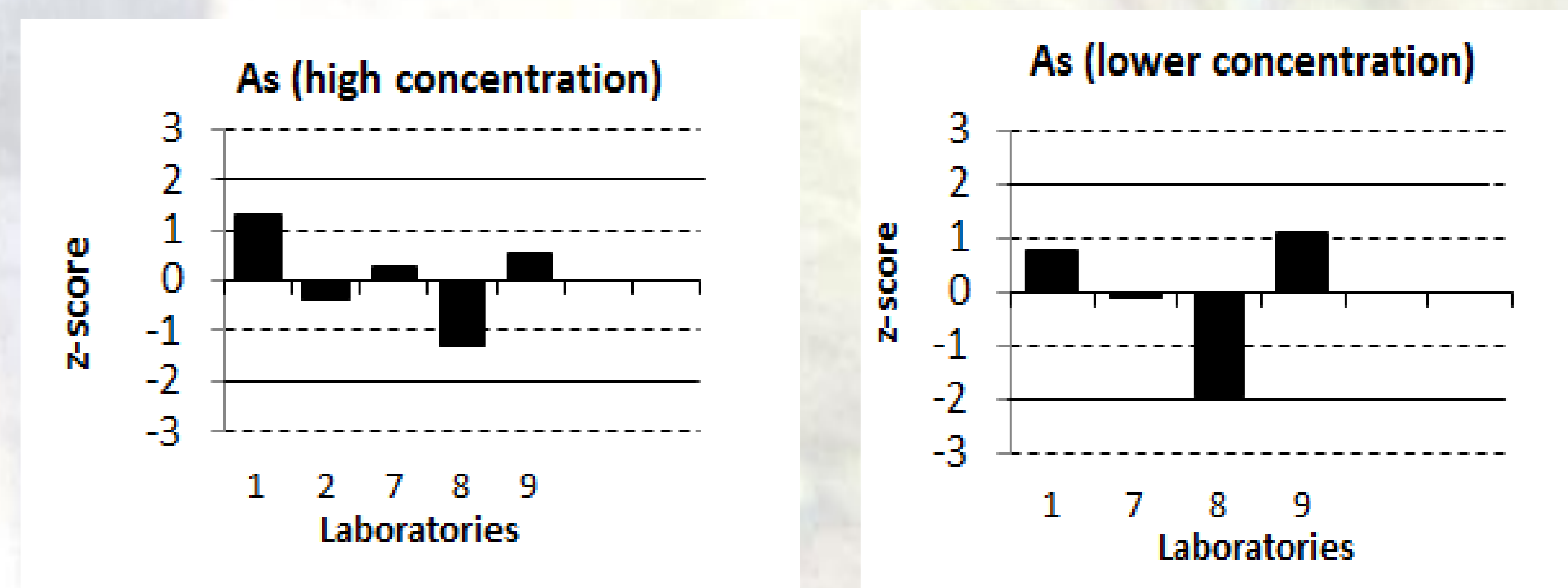


Fig. 2: z-scores of the laboratories participating in the EP / MP 11/12 for determining the total arsenic in fresh fish

CONCLUSION

As a first analysis, it should be noted that the small number of laboratories was further reduced because some participants did not submit their results due to internal analytical problems, which made it difficult to statistical analysis as indicated in ISO 5725-2. However, no inference or deviation in the value of consensus was observed. In this case, for safety reasons we consider this comparison as a pilot study to development of a future proficiency test program.