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PROF TEST SYKE

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- Native matrix PT samples are of high importance when accuracy and precision of the method of analysis is tested.
- Native matrix PT samples of extended stability could be used as PT or ILC items during longer period without additional testing, or for internal quality control samples in laboratories.
- The combined uncertainty of the reference value should be taken into consideration when the standard deviation for the proficiency assessment is established.

Stability of the native wastewater matrix samples for PTs of metal analyses

PT samples which are natively of similar matrix as the daily samples in the laboratories provide thorough information of the performance of the method with the matrix present. A stability study for native wastewater PT matrix samples was conducted and sample preparation as well as storage procedures were optimized.

Background

For the synthetic PT samples for e.g. metal analyses, prepared from NIST traceable CRM and stored appropriately, the stability is fundamentally good.

In addition to the synthetic samples, native matrix samples, which simulate the daily samples within the laboratories better than the synthetic samples, provide information of the accuracy and precision of the method with the matrix effect present. In such samples, the matrix composes a challenge for, among other things, the stability of the sample.

PT provider Proftest Syke stores the PT samples until the publication of the final report and the participants may order new samples to, for example, resolve problems within their analyses or to test their methods of analyses. The samples of stable measurands are stored for longer time and those can be utilised also by non-participants, for example, for internal quality control purposes.

Longer stability of the PT samples increases the versatility of using the samples. Further, better stability of the samples increases cost efficiency as possibly less testing would be needed.

Therefore, the sample preparation procedure and storage conditions were optimized for the native matrix PT samples of industrial wastewater for metal analyses. The stability of the concentration of metals in the matrix material and the uncertainty raising from the storage were studied.

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Results

Figures 1-4 show the results of the stability test for Al, As, Cd, Cr, Mo, Pb, Se, and Sn over more than 1.5 years of storage. No trends were observed during the test period, the observed variation of the results was random.

For the reference value of the measurands the average of the homogeneity test results conducted by the expert laboratory was calculated. Further, the analytical and between-sample uncertainty components were calculated.

The uncertainty raising from the storage was calculated using the modified formula for the storage time and the relative standard deviation of the results of the stability test [1].

$$u_{stability} = \frac{RSD}{\sqrt{\sum(x_i - x_{mean})^2}} \times t$$

RSD = relative standard deviation of the point on the regression line

x_i = time point for each replicate

x_{mean} = mean of all time points

t = maximum time suggested for storage

For the uncertainty of the reference value the combined uncertainty of analytical, between-sample, and storage uncertainties was used.

Conclusions

The native matrix PT samples of industrial wastewater for metal analyses were proven to be stable for at least one and half years and, thus, the given reference values with their uncertainties remain valid.

When evaluating the PT results, the reference value could be used as the assigned value, but also other assigned value could be selected. The combined uncertainty of the reference value should be taken into consideration when the standard deviation for the proficiency assessment is established.

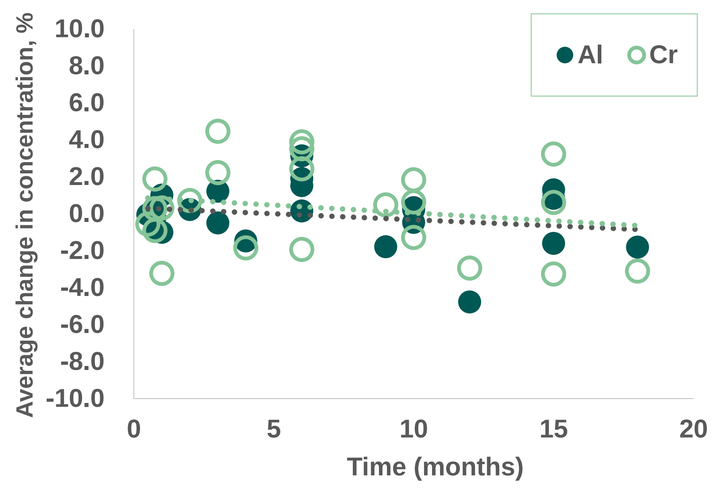

Figure 1. Stability test results for Al and Cr.

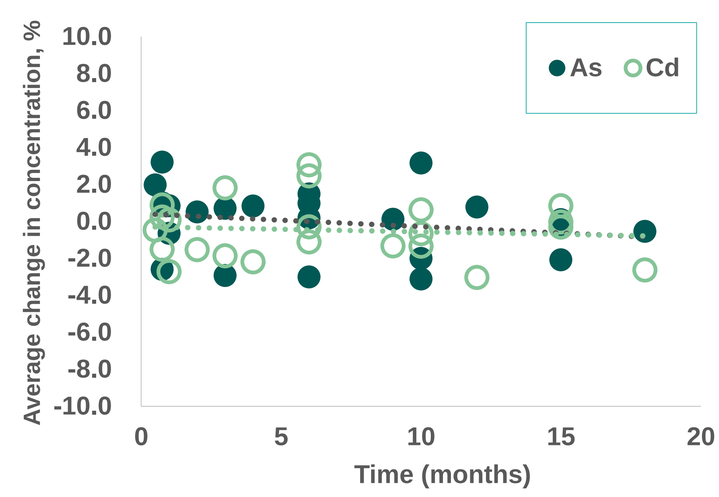

Figure 2. Stability test results for As and Cd.

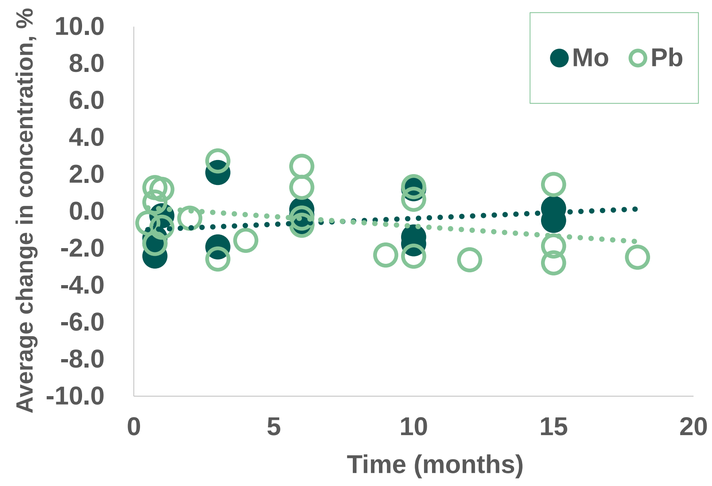

Figure 3. Stability test results for Mo and Pb.

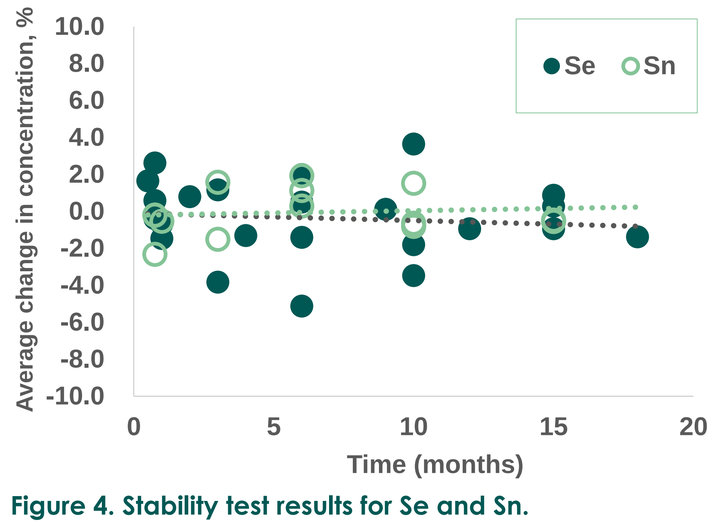

Figure 4. Stability test results for Se and Sn.

References:

[1] Alper İşleyen et al. 2019. Certification Report, Element in River Water, UME EnvCRM 02, www.ume.tubitak.gov.tr