Round Robin Cuvette Test: Quality Control at an International Level

More than 94 % of all submitted measurement results are correct! This is the excellent outcome of an international round robin test carried out by the independent Dutch institute, Kiwa Water Research, in late 2007. Almost 300 HACH LANGE users in 18 European countries took part. Municipal sewage treatment plants, research laboratories, industrial plants – no matter what the sector, they all performed well. The parameters COD, ammonium-nitrogen, nitrate-nitrogen, total nitrogen, orthophosphate and total phosphate were analysed using LANGE cuvette tests. The analyses were carried out and evaluated in accordance with the Youden methodology.

Organisation and implementation

Kiwa Water Research spiked real wastewater samples with two different concentrations of the parameter to be analysed (COD, TN, NH_4-N, NO_3-N, Ortho PO_4-P and P_{tot}). The participants therefore determined two different concentrations, which differed by a known amount, for each parameter. This concept enables a quick error analysis to be carried out afterwards, e.g. to determine whether deviating results from individual participants were due to systematic or random errors. The prepared round robin test solutions were preserved and then express mailed to the various countries. The participants had to carry out the analyses within three days of receiving the samples, then submit the results to the institute no later than 14 days after receiving the samples.

Evaluation and Representation of the Results

After receiving the results, Kiwa Water Research evaluated the data per parameter. As the difference in concentration between the two samples of each Youden pair was known, the accuracy of the values could be checked. The reproducibility of the individual results in the laboratory and/or the repeatability of the results were not tested.

Assessment of the Methods

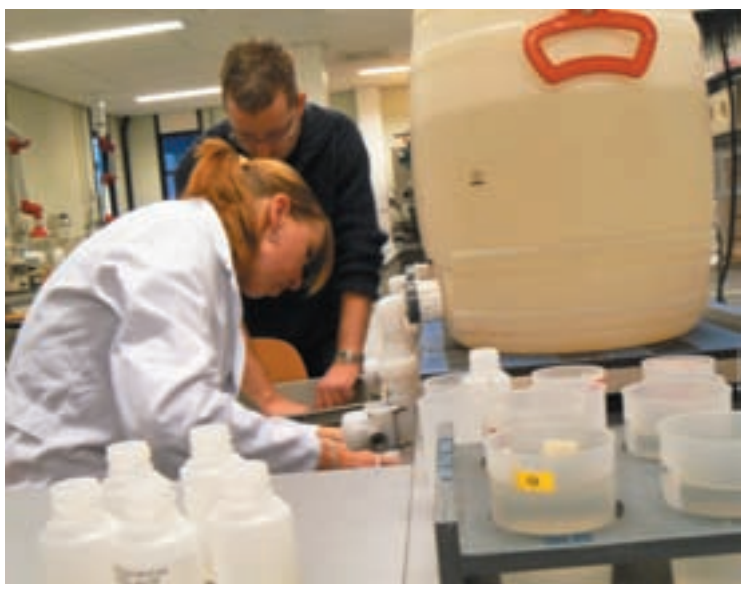

Fig. 1: Preparation of the round robin test samples for the 2007 international round robin test in the Dutch institute Kiwa Water Research

In addition, in order to obtain an impression of the performance of the whole group of participants, alternative evaluation marks were calculated for the analysis of each parameter. The marks range from 0 (very poor) to 10 (excellent), so that it is immediately obvious whether action needs to be taken to improve analysis methods. The mark is derived from the scores of the following factors: outlier percentage; the efficiency with which the difference in concentration between the two samples of the Youden pairs is detected (recovery rate); and the coefficient of variation. The effectiveness of the LANGE cuvette tests was again clearly demonstrated. A comparison with the round robin test results of the standard methods (ISO) shows that HACH LANGE users obtained equally good values.

Kiwa Water Research is a leading independent institute for drinking water, wastewater and associated ecological aspects. It is headquartered in the Netherlands and has three fully equipped laboratories for chemical analysis, microbiology and materials research. Gonny de Jong (laboratory research coordinator) and Marieke ten Broeke (Assistant) both work in the Kiwa Water research laboratory for materials research and inorganic analysis. They are responsible for research, method development and carrying out round robin tests.

Gonny de Jong: "Quality assurance is very important for all laboratories. It consists of several steps:

1. *Analysis of standard solutions of known concentration.*
2. *Internal round robin tests (other departments supply unknown samples).*
3. *External round robin tests."*

Marieke ten Broeke: "Besides the first two steps, regular participation in external round robin tests is highly advisable, as these give the participants even more information about their analysis."

Gonny de Jong: "The advantage of an external round robin test is that the participants can check the quality of their own analysis using real samples. Unlike standard solutions, these have a real sample matrix, just like normal wastewater samples."

Marieke ten Broeke: "Regular participation in such round robin tests provides a continuous overview of analysis quality."

Gonny de Jong: "If a participant's round robin test results deviate, this is usually due to errors during the determination.

The most common errors are:

- Sample mix-ups

- Sample preparation (temperature, homogenisation)

- Wrongly adjusted pipettes or wrong use of pipettes

- The manner of working

Round robin tests quickly highlight these errors so that they can then be avoided in future."

Marieke ten Broeke: "The results of this round robin test with HACH LANGE users are very good – just like those of two previous round robin tests. They are a credit to the work of the participants."

Representation of the Results

Figs. 2 + 3: The diagram is a graphic representation of the results obtained by all participants from the two samples of a Youden pair. The continuous lines represent the target values, and the broken lines represent the maximum permissible upper and lower deviation (or 95th and 5th percentiles). This diagram can be used to compare the result obtained by each individual participant with the results of the other participants.

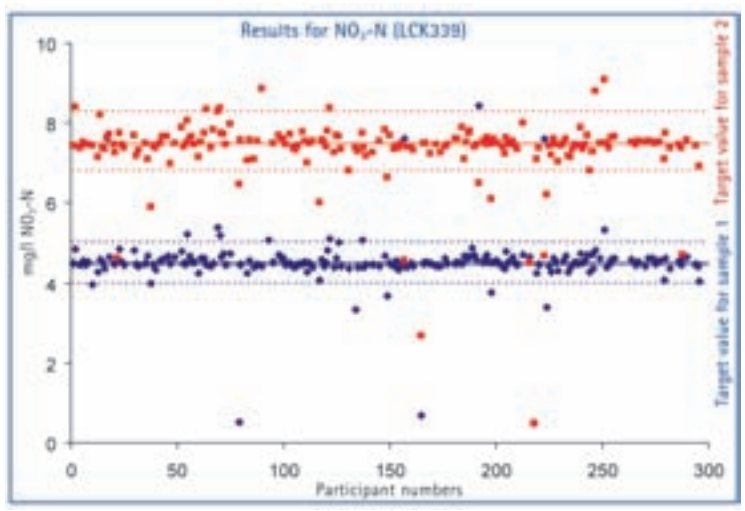

Fig. 2: Distribution of the individual nitrate-nitrogen results around the target values: Sample 1 = 4.5 mg/l NO_3-N, sample 2 = 7.5 mg/l NO_3-N.
More than 95 % of the results are correct!

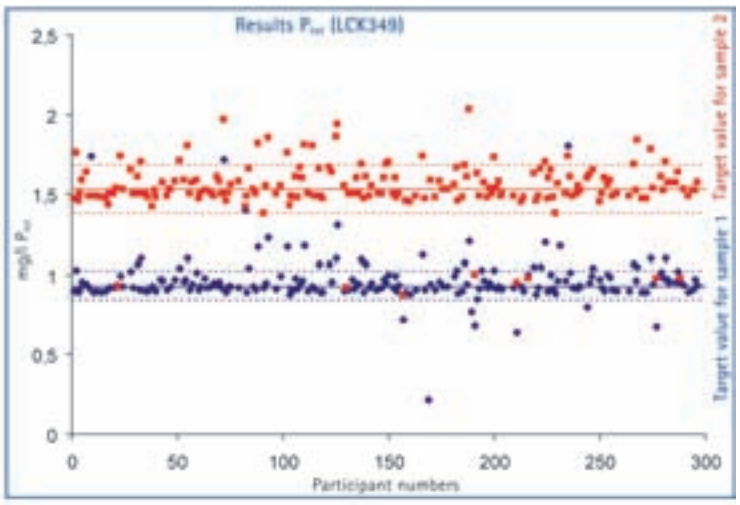

Fig. 3: Distribution of the individual total PO_4-P results around the target values: Sample 1 = 0.93 mg/l P_{tot}, sample 2 = 1.53 mg/l P_{tot}
More than 95 % of the measured values are correct!

Learning from Errors

Ammonium-nitrogen: Why are "only" 85 % of the results correct?

This is the question Kiwa Water Research and HACH LANGE asked themselves after analysing the data. In comparison with a total result of more than 94 % correct measured values, 85 % was a surprisingly low percentage. Moreover there were a disproportionate number of outliers, especially from sample 2. Targeted investigation soon revealed the cause. Instead of LCK303, many participants used a cuvette test with a measuring range that was unsuitable for the sample concentration unless the sample was first diluted. As a result, a number of faulty results were obtained, which were usually not recognised as such by the users. A revised evaluation, dividing the results into two groups (LCK303 and "not LCK303"), gave a very different result: The participants who used LCK303 had a success rate of 94 %!

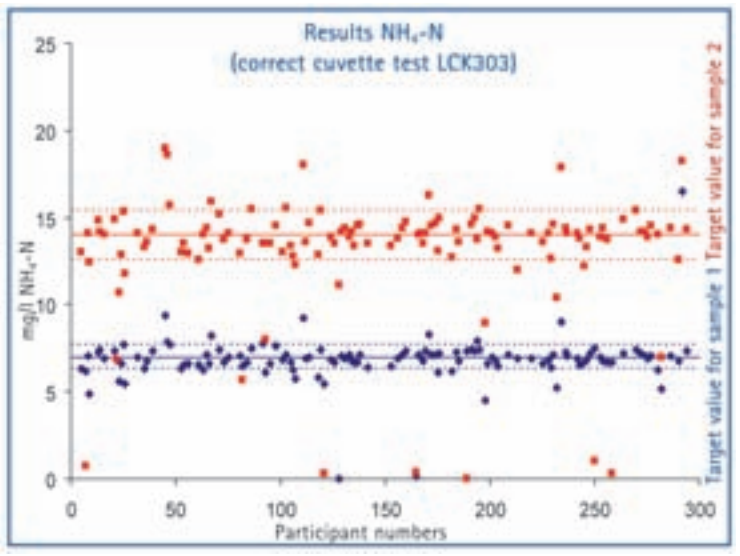

Fig. 4: Results of the 2007 international round robin test, NH_4-N, properly measured using LCK303: 94 % of the measured values are correct!

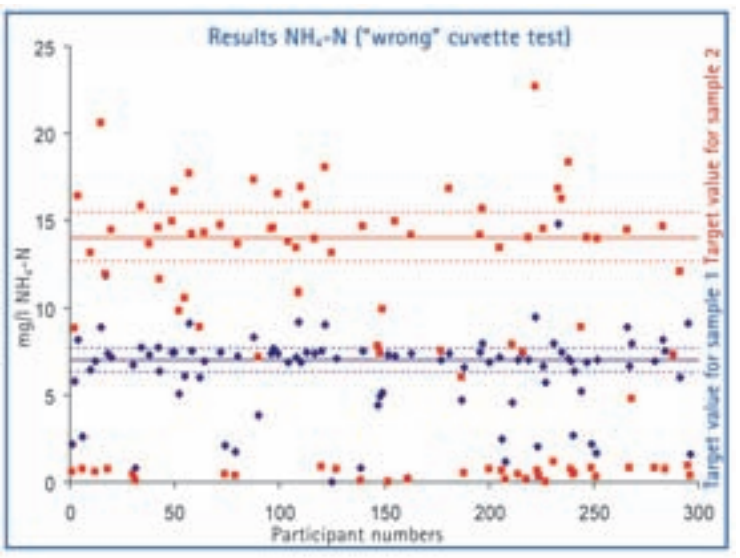

Fig. 5: Results of the 2007 international round robin test, NH_4-N, cuvette test with wrong measuring range used: Only 66 % of the measured values are correct!

Method Optimisation

Non-recognition of concentrations in excess of the measuring range is unfortunately a problem associated with the determination method (indophenol blue in accordance with DIN 38406 E5) and occurs independently of the analysis system used. When measured values are well outside the measuring range, results are displayed. A solution to this "indophenol blue shortcoming" is now available to all users of HACH LANGE spectrophotometers, in the form of an additional evaluation option for the LANGE ammonium cuvette tests, which immediately recognises and signals that the concentration is above the measuring range.

Analytical Quality Assurance (AQA)

Quality assurance and analysis are inseparably linked. Only documented and verified measured values are officially recognised. This means that standard determinations, participation in round robin tests and plausibility checks (diluting and/or spiking the sample) are fixed elements of all analysis procedures. The purpose of AQA and the fact that it is worthwhile are illustrated by the round robin test results for ammonium-nitrogen. Plausibility checks would immediately have revealed that the concentrations were above the measuring range. If the measurement had then been repeated with a diluted sample, the correct results would have been obtained. In fact, the error only came to light through the Kiwa round robin test and targeted investigation. But what if such faulty measurements remain undetected, perhaps even when an important wastewater sample is analysed?

Fig. 6: ADDISTA with standard/spiking solution and two round robin test solutions for checking the precision and accuracy of results

Conclusion

By participating in a round robin test, users can check their analysis method, and how well they use it, under real conditions. Systematic or random errors are immediately revealed by deviations in the results and can therefore be avoided when measurements are carried out in future. HACH LANGE users have participated in round robin tests with great success for more than 20 years. One of these was the first international analysis comparison organised by the accredited Dutch institute Kiwa Water Research in late 2007.

More than 94 % of the results submitted by the almost 300 participants from Europe were correct, irrespective of the sector in which the users operate (sewage treatment plants, laboratories, industrial plants) and the parameter (COD, NH_4-N, NO_3-N, TN, Ptot and Ortho-PO_4-P).

Errors have their uses! When the cause of the unusual numbers of deviating results for NH_4-N was identified, HACH LANGE reacted immediately. An additional, optional, evaluation feature for LCK304 in DR spectrophotometers eliminates this source of error.

Fig. 7: LANGE cuvette test LCK349 Phosphate, measuring range 0.05–1.5 mg/l PO_4-P

Fig. 8: DR 3800 sc spectrophotometer with touchscreen, automatic cuvette test identification, outlier elimination and optional linkage with process data

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