PT’S FOR QUALITY ASSURANCE ON WASTE WATER TREATMENT PLANTS

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Abstract

For the protection of surface waters in Germany the cleaning capacity of waste water treatments plants (WWTP) must fulfil high requirements. There are strong limits for the ingredients of purified waste water, especially for the concentration of nutrition parameters. The operators of the WWTPs usually control the quality of the purified waste water by using rapid test methods based on photometrical detection (cuvette tests) instead of the time-consuming standardized chemical analysis in regular laboratories. The quality of these measurements in the WWTPs is controlled by additional measurements commissioned by the water authorities. In 2003 a notification system for WWTP laboratories was installed in Baden-Wuerttemberg (Southwest Germany) in order to reduce the necessary surveillance of municipal WWTPs by the authorities. However this requires the implementation of a quality assurance (QA) system in the WWTP laboratories. The requirements for such a system is described in the guideline DWA-A 704 [1]. In addition to the installation of a QA system the operators of the purification plants must successfully participate in two proficiency test rounds within three years. Since 2000, the AQS Baden-Wuerttemberg, a provider of PTs in Germany, offers a PT scheme particularly for the water analysis with rapid test methods in WWTP laboratories with one round per year for the parameters COD, ammonium nitrogen, nitrate nitrogen, total phosphorus and total nitrogen. This paper gives an overview of this quality assurance system for WWTPs and experiences with this PT system from six years.

Key words

Rapid test, waste water treatment, quality assurance, proficiency test
Frank Baumeister, Michael Koch: PT’s for quality assurance on waste water treatment plants

1 INTRODUCTION

Some years ago, the environmental ministry in Baden-Württemberg initiated a project “Quality assured self-control for the support of the official monitoring on municipal waste water treatment plants” in Baden-Württemberg, a federal state in Germany. The aim of this project was to check the possibility to include the operational self-control on WWTP’s into the sovereign monitoring by the authorities. This requires additional measures with the self-control, like the installation of a quality management system according to the guideline DWA-A 704 [1] (DWA - the German Water Association), which must be proofed by inspections as well as the participation in special proficiency tests. In the context of this project, seven PT’s were already provided by the AQS-Baden-Württemberg, the biggest PT provider in Germany in the water sector, since 2000. Additionally in March 2003 recommendations of the environmental ministry in Baden-Württemberg were published. According to these, the operator of a WWTP can demand the recognition of equivalence of its self-control with the official monitoring by the responsible water authority. The requirement for the confirmation by the responsible water authority is among other things, the successful participation in two PTs within three years. Thus the aim of these PTs is to proof the quality of the measurements in the context of self-control analysis on WWTPs by an independent third party.

By the majority the participants come from laboratories of WWTPs using rapid test methods (cuvette tests) for their analysis and want to check the plausibility of their measurements by an external quality assurance procedure.

2 PT DESIGN

2.1 Basis of the PTs

The PTs are performed according to the German standard DIN 38402 – A45 [2] and to LAWA-guideline A-3 [3]. Both describe the requirements for PTs for external quality control in the water sector in Germany. Beside these national requirements several international standards [4,5,6] must be fullfilled.

2.2 Parameters

The parameters for this PT scheme are fixed in cooperation with the environmental ministry of Baden-Württemberg. At the moment the following parameters are included: COD, Total-nitrogen (N_{tot}), Ammonium-Nitrogen, Nitrate-nitrogen, Total-phosphorous (P_{tot}).

2.3 Matrix and concentrations

The samples of the PT’s are based on a real waste water matrix from the waste water treatment plant for research and education in Stuttgart-Buesnau and are spiked with the desired analytes.
Table 1 – Concentration range in WWTP-PTs

<table>
<thead>
<tr>
<th>Concentration in mg/l</th>
<th>COD</th>
<th>N$_{\text{tot}}$</th>
<th>Ammonium-Nitrogen</th>
<th>Nitrate-Nitrogen</th>
<th>P$_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>effluent</td>
<td>10 - 150</td>
<td>2 – 40</td>
<td>1 - 15</td>
<td>1 - 40</td>
<td>0,2 - 5</td>
</tr>
<tr>
<td>influent</td>
<td>100 - 600</td>
<td>30 - 60</td>
<td>10 - 50</td>
<td>1 - 10</td>
<td>3 - 15</td>
</tr>
</tbody>
</table>

Each laboratory receives three sample with different concentrations. Two samples are prepared in a concentration range of the effluent and one sample of the influent quality of a WWTP (see Table 1.). The concentrations are aligned to the requirements of the German Waste Water Ordinance.

### 2.4 Sample Preparation and analysis

The samples are based on purified waste water. After withdrawal of the matrix from the effluent, the waste water is stored over night for settling of suspended particles. The supernatant is transferred into a stainless steel tank, in which it is pasteurised with 80°C over night to stabilise the matrix and to protect the co-workers from risks of infections during sample production. Meanwhile it is aerated with a mixture of nitrogen and carbon dioxide in order to suppress calcium carbonate precipitation.

The stock solutions for spiking the matrix are produced in accordance to the calculation of the final concentration with certified chemicals on high-precision balances. Thereby great importance is attached to the complete and exact documentation of all steps.

For additional preservation, all samples are stabilised with acids and are autoclaved after bottling. This procedure avoids biodegradation of the analytes by microorganisms from the matrix.

The samples are dispatched simultaneously by an express service within 24 hours to the laboratories on the WWTPs and must be analysed within two weeks. The analysis is restricted to rapid test methods (cuvette tests). In smaller WWTPs the analysis is usually executed by the technical personnel, who is primarily responsible for the attendance and function of the WWTP and is not usually educated in chemical analysis. In bigger WWTPs the analysis is often done by laboratory assistants.

### 2.5 Evaluation and report

The data sets are evaluated according to DIN 38402-A45 “Interlaboratory comparisons for proficiency testing of laboratories” [2] with robust statistical methods. In a first step for each concentration level, the relative standard deviation $s_R$ is calculated by the Q-method and the consensus mean by the Hampel-estimator, which is then used as assigned value ($x_a$). For evaluation of the results, $Z_{U}$-Scores are calculated according to chapter 10.5 of the above mentioned standard, which is a modified $Z$-Scores with a factor $k$ that considers an asymmetry of the statistical distribution. The $Z$-Score is calculated according to Eq. 1:

$$Z \text{ Score} = \frac{\text{result} - x_a}{\hat{\sigma}}$$ (1)

$\hat{\sigma}$ is the standard deviation for proficiency assessment and is determined out of the calculated standard deviations by fitting a variance function according to chapter 10.4 of the above mentioned standard.
The measurements for a parameter is assessed as successful, if $|Z_{ul}| \leq 2$ for two of three values. According to LAWA-guideline A-3 [2] the complete PT participation is successful, if 80 % of the parameters and 80 % of all values are confirmed. After finishing the evaluation, the participants receive a sheet with the result evaluation, a certificate and a report with detailed informations about the PT.

3 EXPERIENCES

3.1 Participation

Figure 1 illustrates the number of participating laboratories in the PT’s since 2000 and the proportion of successful participants for each PT. As it can be seen, the number of participants increased until 2003, decreased in 2004 but since then the number is nearly constant.

![Figure 1 – Characteristics of the participant numbers and success ratio in the PT scheme](image)

Figure 1 shows, that the percentage of successful laboratories has been improved continuously and is now on a high level. This can mainly be explained by a steady improvement of the rapid test methods by the supplier of the test kits and better user skills due to a training effect from the PTs.
Figure 2 – Distribution of the participating WWTPs and success rates in dependence on the size of the WWTP

Figure 2 illustrates the distribution of the participating laboratories in dependency on the size of the WWTPs, which is described by the total number of inhabitants and population equivalents (EW), is shown. Additionally the success rate for each size range is characterised by the line and the values represent the success rate within the size range. Both informations are average values from five PTs (2000 - 2005). Most of the participating laboratories come from WWTPs with 10001 – 100000 EW. In general the success rate is increasing with the size of the WWTP. This is due to better equipped laboratories, more and better instructed staff the bigger the WWTP is.

REFERENCES