Measuring low limit values for ortho-phosphate using the Phosphax sc Low Range analyser

Problem

Due to a tightening of the phosphate effluent limit values, much lower concentrations will be mandated in the future and the demand for precipitants will increase as a result. The online measurement technology deployed is subject to exacting requirements in order to ensure that the low limit values can be reliably adhered to at all times while maintaining the economical use of precipitants.

Two photometric methods are normally used for continuous orthophosphate analysis: the molybdenum blue method and the vanadate-molybdate method (yellow method).

Solution

In order to increase the measurement accuracy in the low measuring range and to eliminate the influence of self-colouration, Hach® has refined the measurement method with a new measuring instrument, the Phosphax sc LR (Low Range). The main changes made compared with the previous measuring instrument are as follows: The mixed reagent used in the medium and high measuring range has been divided and the dosing sequence has been changed. In the low measuring range, the acid is dosed first, after which a zeroing process is performed; only then is the colour reagent dosed (yellow method 2.0). This eliminates the influence of any possible self-colouration of the wastewater. There is also a standard solution and the photometric unit has been redesigned and now has a longer path length.

Benefits

The yellow method 2.0 offers advantages over the molybdenum blue method. The required chemicals can be stored for several months and do not require cooling. In addition, maintenance costs are comparatively low. As yellowish substances in water can influence the measured value when this measurement method is used, the effect is compensated for through automatic calibration procedures. The molybdenum blue process had previously been considered the more accurate measurement method at low concentrations.

Background

A large, regional wastewater partnership in Germany operates a total of 59 wastewater treatment plants, with numerous measurement technologies being used across the facilities they operate. In-depth testing of technical equipment that will subsequently be used in the plants is a must, in order to ensure that the latest requirements for wastewater treatment are always satisfied. Hach has been collaborating with this partnership for many years, with a recent initiative being a beta test of the new Phosphax sc LR analyser.

The Solution in Three Different Locations

Over a period of three months, a number of parallel measurements using various measuring instruments were carried out at three different wastewater treatment plants; there were also laboratory-based comparative measurements for the blue method and the yellow method.

Treatment Plant 1:

A Phosphax sc analyser is used at the first wastewater treatment plant in the in-depth testing project, focussing on the PO_4-P concentration in the effluent from the aeration tank. Samples are pre-treated using Filtrax-type filtration.

The new Phosphax sc LR was installed parallel to this measurement. The following chart plots the measurement results against each other. **The graph from the Phosphax sc LR shows a lower fluctuation range and provides slightly lower measurement results in the very low concentration range**.

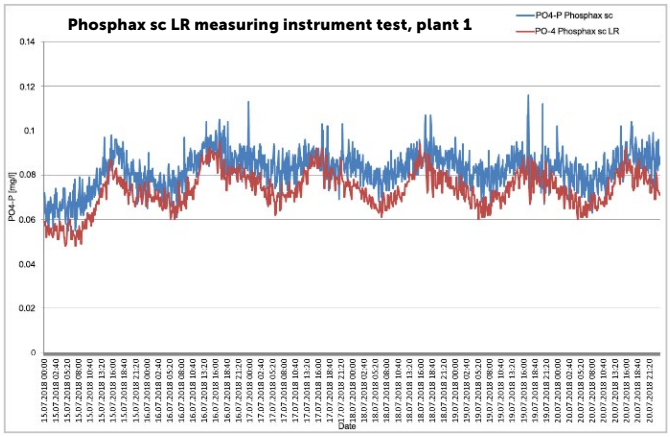

Figure 1: Graph of the PO_4-P concentration in mg/L from 15th to 20th July 2018

Treatment Plant 2:

The second plant is the location for a test to determine the phosphate concentration in the effluent. The Phosphax Sigma analyser uses the molybdenum blue method (blue method) to determine the total phosphorus concentration (P_{tot}) and the orthophosphate concentration (PO_4-P) at intervals. The P_{tot} value is determined with the solids that are still in the sample being taken into account, which means there is no sample filtration. As the PO_4-P concentration can be distorted by particles in the sample, an additional Phosphax sigma was installed for this test and a Filtrax sample filtration system was connected upstream. This allowed the blue and yellow methods to be tested directly next to each other. The following chart plots the measurement results against each other.

Figure 2 shows the comparatively balanced curve of the PO_4-P concentration as measured by the Phosphax sc LR. The PO_4-P concentration measured using the blue method is comparable, but the curve is slightly more uneven. **No advantage in the precision of the blue method compared with the yellow method could be identified**. The sample is analysed unfiltered by the measuring instrument at the wastewater treatment plant. Here, the influence of the turbidity included in the measurement is clearly visible. The higher the proportion of turbidity, the higher the deviation of the measured PO_4-P concentration compared with the measuring instruments with upstream sample filtration.

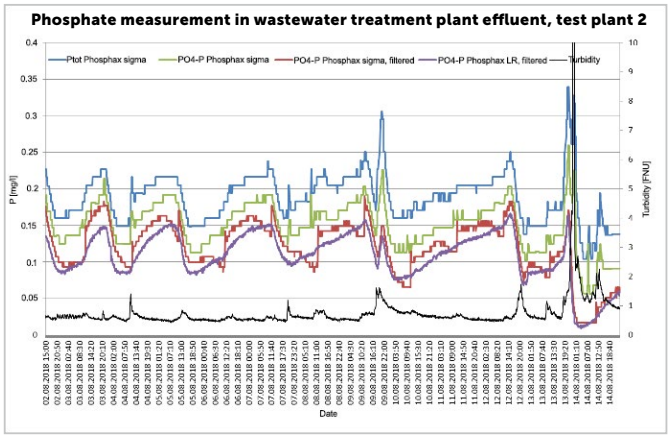

Figure 2: Graph of the PO_4-P concentration in mg/L from 2nd to 14th August 2018

Treatment Plant 3:

At the third plant total-P is measured in the effluent with the Phosphax Sigma (blue method). Ortho-P is measured with a tried-and-tested Phosphax inter (yellow method). The sample is filtered using Filtrax sample conditioning for this purpose. The Phosphax sc LR was placed immediately next to this instrument and supplied with the same sample.

The measured values from the PO_4-P analysers correlate very well with each other (see chart information). **It can also be seen here that the graph for the Phosphax sc LR has a more stable progression**. The total phosphorus concentration is correspondingly higher due to the co-determination of the undissolved phosphorus content in the sample.

During cleaning work several days after the testing period began, particles entered the sample inlet in the sample receiver. This led to a short-term increase in the phosphorus concentration measured (see Fig 3) but had no effect on the effluent from the wastewater treatment plant.

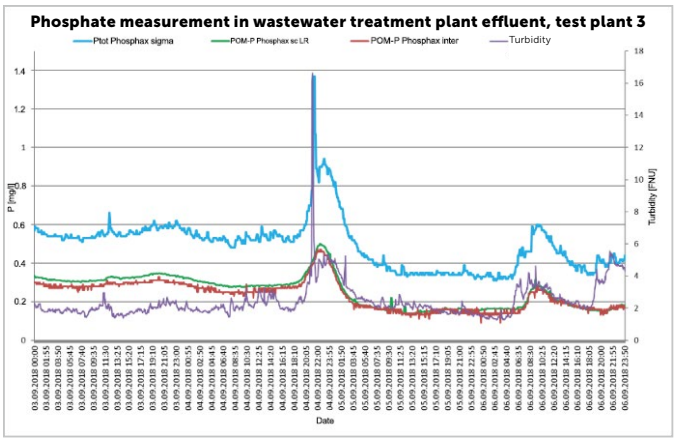

Figure 3: Graph of the PO_4-P concentration in mg/L from 3rd to 9th September 2018

Assessment of the measurement results

During the test phase, comparative measurements were taken in the laboratory by conducting Hach cuvette tests in accordance with the standard method: DIN 38405 D11-4 (blue method). The chart in Figure 4 illustrates how well the measured values compare to the results of the cuvette tests. Figures 5 and 6 show the measured values in scatter diagrams. The charts illustrate that **the linear regression line for the new Phosphax sc LR measuring instrument features better congruence with the laboratory results with a coefficient of determination of $R^2 = 0.98$ than the previous measurement method, where $R^2 = 0.90$.**

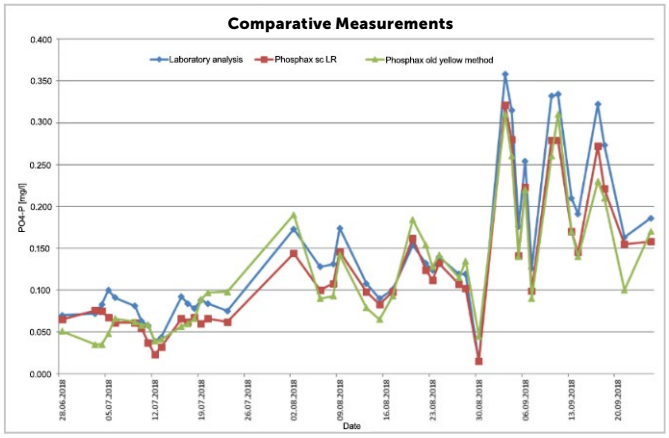

Figure 4: Comparative measurements in the laboratory using cuvette tests, in mg/L

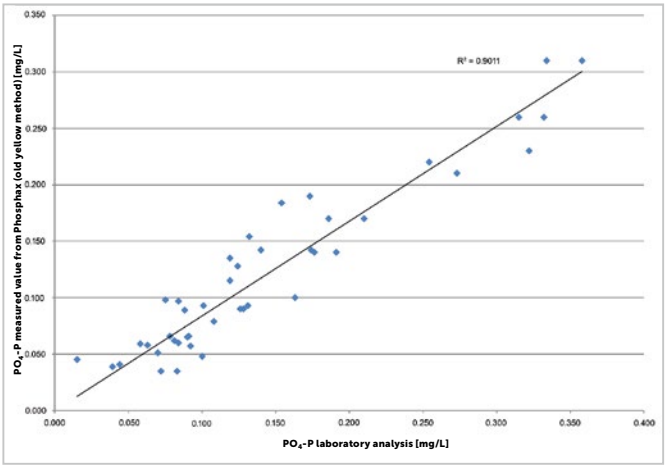

Figure 5: Scatter diagram of measured values from the laboratory and Phosphax sc (old yellow method), in mg/L

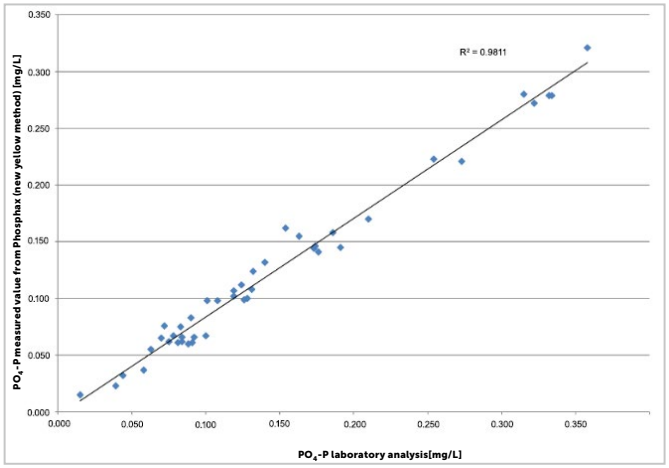

Figure 6: Scatter diagram of measured values from the laboratory and Phosphax sc LR (new yellow method), in mg/L

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Maintenance and operating supplies

During the test period of approx. three months, no maintenance work was performed on the analyser except for visual inspections. Refilling or replacement of reagents and wear parts was not required. The chemical consumption can be used to estimate an annual consumption of two reagent sets at a measurement interval of ten minutes. The new process analyser is approximately 20% more expensive than the Phosphax sc; the cost of a reagent set and the chemical consumption rate have also increased. The molybdenum blue method is significantly more expensive by comparison. In contrast to the yellow method, the Phosphax sigma can also be used to determine the total phosphate concentration in the effluent from the wastewater treatment plant. However, the total phosphate concentration is not relevant for phosphate precipitation.

	Phosphax sc	Phosphax sc LR	Phosphax sigma (P_{tot} or PO_4-P)
Measurement method	Double-beam photometer, yellow method		Molybdenum blue method acc. to DIN
Measuring range	0.05 - 15 mg/L	0.015 - 2 mg/L	0.01 - 5.0 mg/L
Meas. interval	5 - 120 mins	10 - 120 mins	Approx. 10 mins
Measurement uncertainty	2% + 0.05 mg/L	2% + 0.015 mg/L	2% + 0.02 mg/L
Annual wear parts	€224		€640
Reagent set	€151	€337	€568
Reagents per year	€200	€674	€2375

Table 1: Technical data and costs, as of December 2018

Conclusion

In the future, operators of wastewater treatment plants will have to adjust their operations to comply with lower limit values for the discharge of phosphate into bodies of water. This places more stringent demands on the cleaning processes as well as on the accuracy of the measurement technology. Accurate measuring instruments for low measuring ranges are required in order to achieve economical dosing of the precipitants. With this in mind, Hach has developed a new PO_4-P online process analyser for the low measuring range using the yellow method. This measuring instrument has now been tested at a number of wastewater treatment plants.

The new measuring instrument exhibited **lower deviations** from the comparative values from the laboratory testing than the existing measuring instruments, which use the yel low method. There was also a **consistently lower fluctuation range** in the graph. The **maintenance burden is very low**; no faults occurred. The Phosphax sc LR measuring instrument is recommended for monitoring and adhering to low PO_4-P effluent concentrations. Due to the strong measurement accuracy and the low fluctuation range of the measurement results, the precipitant can be used more economically, as the dosing threshold values can be more narrowly defined.

Despite the slightly higher outlay to cover purchase costs and chemicals, there is a cost advantage over a process analyser based on the blue method.

DOC043.52.30496.Feb19