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Diploma Thesis

Integration of a Phosphate Analyzer in a Pro-active Maintenance Concept for Water Quality Monitoring

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Table of contents

Figure index

Table index

Short Summary

During the past years a trend towards online-analyzers can be observed, leading to a significant increase in the total amount of measurements. The problem with the currently used online-analyzers is that they are not able to give information about the measurement quality. Therefore grab sample are still taken and analyzed in the laboratory to check for the quality of the measurements. Online-analyzers are also not able to give sufficient information about their current state. This often leads to unexpected shutdowns and to an increase of maintenance effort and costs.

To improve the measurement quality of online-analyzer more information about the processes within the analyzer’s system and more signals are needed. The output of most online-analyzer is only one signal, sending the measured concentration. Therefore a phosphorus online-analyzer was examined to study the already available signals and to search for a way to improve the evaluation of these signals. During the measurement of one concentration the analyzer creates a frequency curve with approximately 600 individual measurements which are not shown. The analyzer only uses 10 individual measurements to calculate the concentration. During the experimental period the reaction of the frequency curve on intentionally triggered failures was examined to find typical patterns for the faults. The three modes that the analyzer runs in and the used spare parts were examined too. With the information about the existing capabilities of the analyzer and with the additional information that was gained through the experiment a concept was developed to point out the failure causing part. With the development of a matlab based program a tool was developed that follows the frequency curve and checks whether the curve takes a normal course or not. Further, with the program an optimization of the time that is needed for the measurement is possible.

With the results of the experiments and with the knowledge about the analyzers abilities a sensor self-diagnosis concept has been developed. If the analyzer detects a failure, state of the art still is a warning message that signalizes a problem somewhere within the system, not specifying any detail. With the sensor self-diagnosis concept a step towards detection, isolation and identification of the failure was made. The concept also led to an increase of the number of detectable malfunctions. To reduce the cost and the effort, spent on maintaining online-

analyzers a dynamic maintenance concept was developed. In this concept the static maintenance cycles were reduced to a minimum and a dynamic maintenance manager was implemented optimize the maintenance cycles.

Both concepts were then combined to a “pro-active” maintenance concept. The assembly of the two concepts allows an increase of detectable errors and a detection of malfunctions before the data quality decreases. In this concept first automatic maintenance actions will be triggered to remove a failure. If the automatic action does not succeed the dynamic maintenance manager will demand for manual maintenance.

1 Introduction

1.1 Problem analysis

During the past years, the way of monitoring the urban water quality has changed drastically. State-of-the-art was and still is to take grab or composite samples and analyze them in the laboratory (Thomann et al., 2002). The procedure of sample collection, transport, storage and analysis is highly standardized and the methods to assess the uncertainties of the measurement are an inherent part of the laboratory practice. Therefore, the quality of the measurements is known and mostly sufficient for the application in the urban water field.

The disadvantage of lab measurements is that only a low frequency of measurements is possible. To get a better knowledge of the dynamic processes that take place in a river section or to introduce real time control at waste water treatment plants (WWTP) or of sewer systems a high frequency of measurements is needed. Otherwise, for example high concentrated combined sewer overflows into a river can not be detected (Nopens, 2007). They can contribute a significant mass load to the overall pollution of the river. Therefore on-line analyzers were developed, allowing higher measurement frequencies (depending on the device up to one measurement per few seconds).

The problem with on-line analyzer is that they are currently not able to give information about the data quality. To check the accuracy of the measurements, reference samples are still a common and reliably way (e.g. in form of control charts, e.g. Thomann et al., 2002). But it is impossible to do it for every measurement.

This generation of analyzers delivers a great amount of data, which can be unusable because of the unknown accuracy of the measurements (Rieger et al, 2005). This way, so called data graveyards are produced by just collecting data and not evaluating them (Rieger and Vanrolleghem, 2008).

The data that is taken by those analyzers is just one signal that delivers the measured concentration. While in use, clogging of the analyzer’s system, aged reagents or contaminated standards can lead to inaccurate measurements. Drifts and shifts take place slowly. They lead to a slow reduction of the measurement accuracy and are often first detected after days or even weeks. The drawback conclusion is that further information about the processes, conditions of the measurement system and the environment are urgently needed to produce high quality data. For the evaluation of the measurements, only high quality data gives valuable information, usable for process optimizations, control, water quality checks etc.

An increase of quality leads to an increase of maintenance effort. Since maintenance is already the main cost factor for the sensors, a new concept needs to be developed to optimize the maintenance effort and costs.

Chemical analyses just like on-line measurements are expensive. Besides chemicals (e.g. reagents, calibration standards, cleaning solutions) and spare parts mainly the labor costs are responsible for the annual expenses to operate an analyzer. A reduction of the maintenance effort and an optimization of the use of chemicals will decrease the annual costs significantly.

Static maintenance cycles are still state-of-the-art. Experience has shown that a maintenance cycle of once every week is realistic and a common practice. Even though no decrease of the measurement quality has taken place the sensor will be checked. Therefore, man power is needed to accomplish the time consuming maintenance tasks so that the analyzers deliver a satisfying quality. To get an impression about the significance of the maintenance compared to the investment costs, the author calculated both for a time range of 2 and 10 years (average time of usage). It becomes clear that the investment for the analyzer itself is not the main cost factor (Winkler et al., 2004). In the example for an ammonium analyzer, the maintenance costs almost exceed the investment costs after two years (Figure 1).

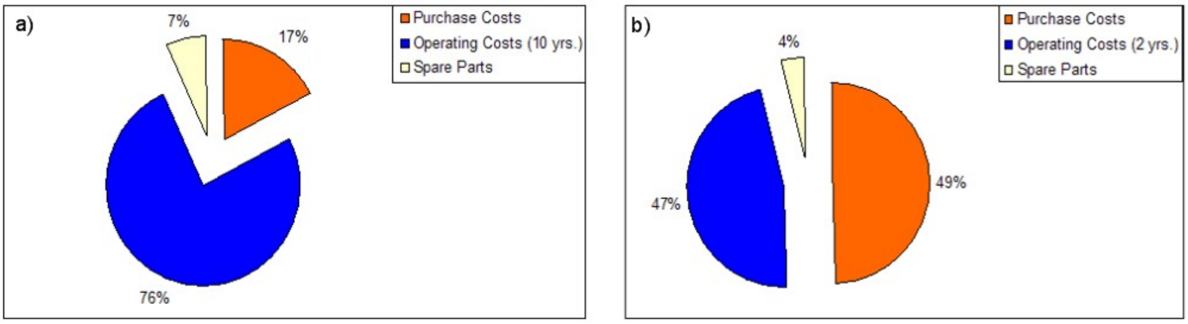


Figure 1: Pie chart for an ammonium analyzer: showing the relations of purchase costs, operating costs and the costs of spare parts; time range: a) 10 years, b) 2 years

In most cases, the maintenance interval of once every week is not enough to ensure a smooth procedure because from experience it is obvious that unexpected shutdowns will appear and result in further maintenance effort.

1.2 General monitoring concepts

The optimization of maintenance efforts, the reduction of unexpected shutdowns, the increase of the data quality, etc. can not be achieved by just improving the analyzing device. The goal should be to implement the analyzer in a monitoring concept that allows communication between the analyzer and a higher level (e.g. a monitoring station or a central server). At the higher level data are collected and evaluated for its quality. On the level of the base station the results of different analyzers are compared and errors can be detected. The base station also demands for maintenance, once a malfunction of an analyzer is detected. Examples for such a framework are the monitoring project at the Dorneburger-Mühlenbach (Mietzel, 2008) and the mon*EAU* (Figure 2) monitoring network (Rieger and Vanrolleghem, 2008):

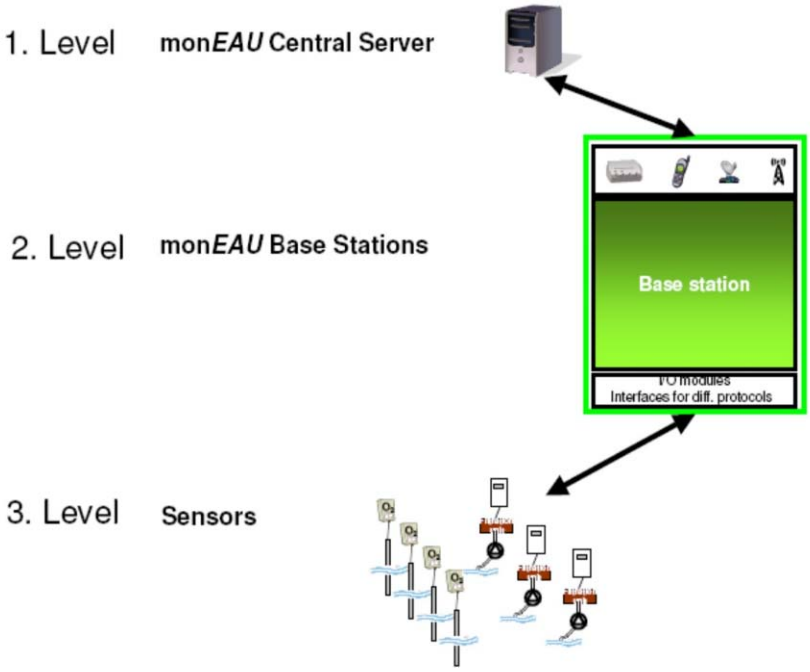


Figure 2: Three levels of the data quality evaluation concept in the mon*EAU* vision

To keep the usage of the concept as simple as possible, it is envisioned to create a software framework which allows the end user a simple addition of further analyzing devices.

Even though the base station and the server level are needed to have a reliable monitoring system, the sensors need to deliver the information. Therefore, a single measurement signal is not enough. Every concentration should be sent with additional meta-data (data about data) (APHA et al., 2005). Meta-data is a generic term, describing different information concerning the influences on the measurement. Without any additional information, the sent concentration is only a number. State-of-the-art is that the additional information is manually added to a data base. Combined with the meta-data, the signal becomes valuable information. The problem with those kinds of data bases is that the information is static and changes on side of the analyzer will not automatically be changed in the data base. In the author’s opinion, further information about the measured concentration should be provided by the analyzing device. So, changes in the application or the status of the device will automatically be related to the measurement.

In first place, this meta-data should provide such information as the location where the measurement has taken place, as well as information about the unit of the measurement and the compound that was measured.

With the improvement of the analyzing device to run the self-diagnosis, further information can be available and be attached to the meta-data, such as:

- accuracy and precision
- numerical precision
- data quality flag
- response time/delay
- measuring range (min/max concentration)
- time interval

Since controlling the analyzer (evaluation of grab samples, great maintenance effort) is cost intensive and time consuming a concept has to be developed to advance an analyzer to check the accuracy of its measurements and the current status. The improvement of an analyzer to run a self-diagnosis is a way to achieve this. With self-diagnostic, the analyzer is able to detect drifts and shifts, a loss of the measurement accuracy and the need for maintenance. Detected drifts and shifts can then automatically be corrected by recalibrating or by maintaining the system. In those cases, maintenance will be demanded and the customer will be informed.

The results of the self-diagnostic will be a part of the data quality flag. The data quality flag gives information about the accuracy of the measurement by referring to reference point measurements, statistical analysis, the analyzer's condition, etc. The outcome of the evaluation of this information will allow a qualification of the measurement.

1.3 The goal of this paper

This paper's goal is to create a new concept for self-diagnosis on the analyzer level. The existing capabilities of the analyzer will be examined and enhanced to increase the number of detectable errors.

For this, experiments will be created to simulate possible errors which could also appear under field conditions. With the use of the calibration data, meta data, etc. the author will create a concept to advance the analyzer to be able to run self-diagnosis. The analyzer will then be able to detect, isolate and identify malfunctions in the system. With the knowledge about an occurred failure, appropriate service actions can be triggered. Since some malfunctions can be solved by the analyzer itself, e.g. by flushing the system with the cleaning solution, man power is not always necessary to fix the problem.

Further goal of the work is to use the information of the fault detection concept to develop a “Pro-active Maintenance” concept. This concept leads away from static maintenance routines. The author will use the information of the self-diagnosis and will combine this concept with the maintenance concept to create a cost and time effective “pro-active” maintenance concept. In this concept, the analyzer delivers information about its current state and a “dynamic maintenance manager” will then trigger necessary service actions. Tasks, like scheduling the service actions and ordering spare parts are taken care of within this “Pro-active Maintenance” concept.

Maintenance effort is one of the most important facts for the end-user. An increase of maintenance is always related with rising costs. Hence, it is very important to get rid of the static maintenance cycles and to implement maintenance demanding analyzer.

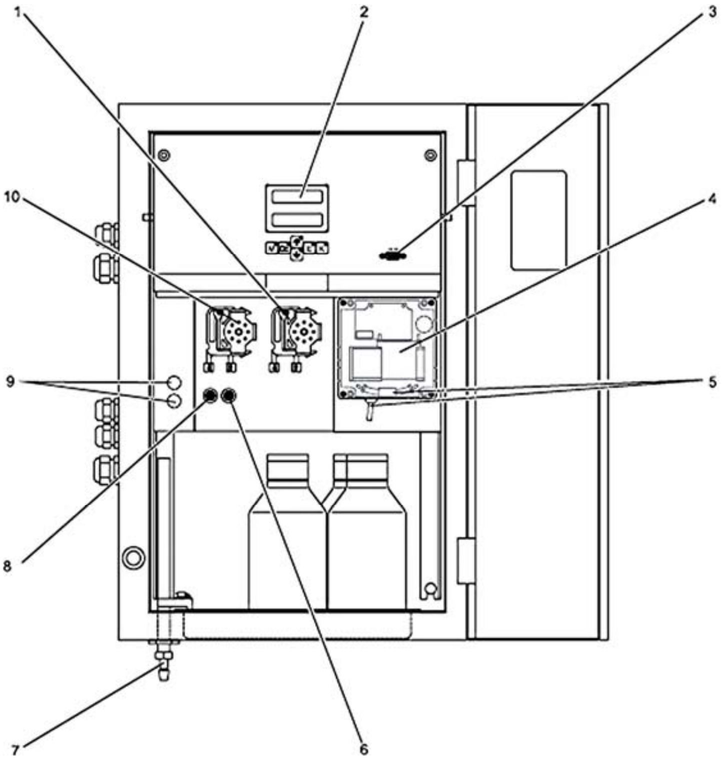
The request for maintenance will occur before the data quality falls below a certain tolerance level and will then be a “pro-active” action.

2 Material and Methods

The build up and the function of the analyzer will be explained in this chapter. To get a good impression of its abilities the three modes, the available signals and the readout software will be described in detail. This will be followed by the introduction of the experiments to exceed and improve the analyzer's signals.

2.1 Phosphorus analyzer

The Stamolys CA71PH, from Endress and Hauser, is a phosphorus analyzer that measures the concentration of orthophosphates in a river, sewer system or WWTP. The analyzer's measuring range is between 0.05 and 2.5 [PO_4-P mg/l].



1. Reagent pump (P2)
2. Display
3. Serial interface RS 232
4. Photometer cell
5. Static mixer
6. Valve (V2)
7. Outlet for sample or reagent mixture
8. Valve V1
9. Chanel switchover: top channel 1, bottom channel 2
10. Sample pump (P1)

Figure 3: Design of the Stamolys CA71PH, without hoses

The phosphorus analyzer (Figure 3), using the molybdenum blue method (see 3.1.1) (APHA et al., 2005) needs two reagents that react with the phosphates in the sample, one standard solution that provides a solution with a known concentration of phosphate and a cleaning solution. Two pumps take care of the transportation of the liquids. All parts are connected with exchangeable tubes to keep the maintenance effort low. Furthermore the analyzer is equipped with a level meter monitored inlet. Two valves support the pumps to provide the right reagents. A RS 232 serial interface allows the user the access to the measured data. With the usage of the AnaWin 0.96 software further data can be accessed. Through a display the user can read off the measured concentration as well as go through the settings of the analyzer.

2.1.1 Measuring principle of the analyzer

A photometric cell, such as used in the Stamolys CA71PH, measures the light intensity that passes through the sample. Therefore the phosphor to be measured must be transformed into a measurable coloring. The used phosphorus analyzer does this by using the “molybdenum blue method”. The orthophosphate ion reacts with ammonium molybdate and potassium tartrate under acid conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex that absorbs light at 880 nm (APHA et al., 2005). The intensity of the color is depending on the phosphorus concentration.

A measuring sequence begins with the measurement of the basis frequency. Therefore the intensity of the light source after passing through the uncolored sample will be measured. The reagents will then be added and the measuring cell measures the intensity of the light after traversing through the colored sample (plateau frequency). The analyzer automatically converts both light intensities into frequencies. Then the difference of the plateau- and the basis frequency will be calculated. Through the linear coherence of the frequency and the absorbance, the absorbance can be calculated. And since the concentration is a linear function of the absorbance the concentration can be calculated (Figure 4). Eventually, the concentration can be calculated through the light intensity.

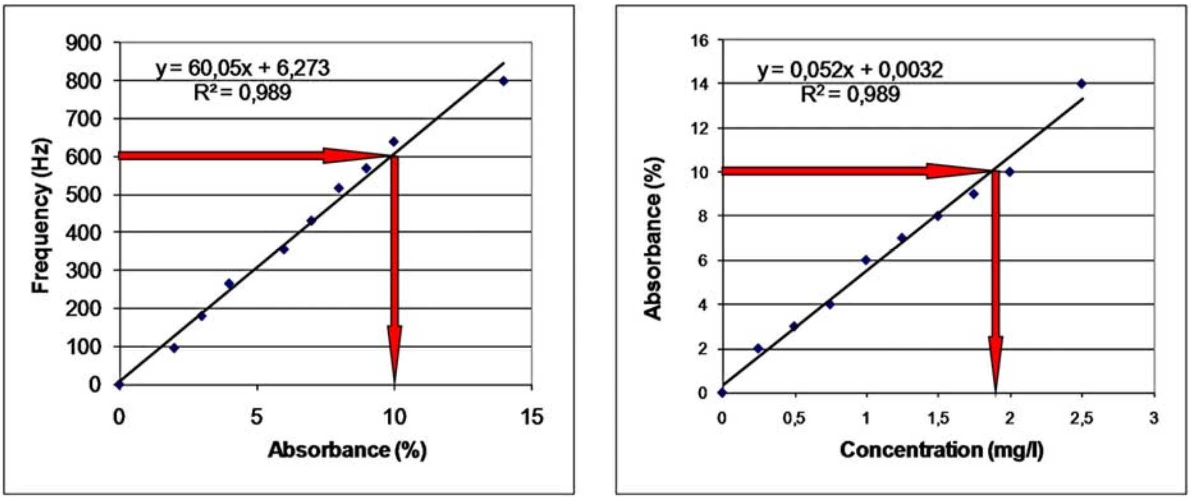


Figure 4: a) Shows the linear coherence between the frequency and the absorbance. b) Shows the linear coherence between the absorbance and the concentration. The red arrows show the way the concentration can be valculated out of the frequency.

2.1.2 Modes

The Stamolys CA71PH is able to run three different modes to ensure the highest data quality:

- cleaning mode
- calibration mode
- measurement mode

Each mode consists of a sequence of pre-defined actions (Table 1). The order of actions cannot be changed but the given duration for each action can be modified by the user.

Table 1: List of the modes and default settings (Endress+Hauser)

Mode	Function	Duration [s]
Measurement	Flushing (sample)	3 x 15
	Delay to sample	20 to 999
	Stabilization	8
	1. measurement (basis)	n/a
	Fill mixture	30
	Reaction	see technical data
	2. measurement (plateau)	n/a
	Flushing (sample)	30
Calibration	Flushing (standard)	3 x 15
	Delay to standard	20 to 999
	Stabilization	8
	1. measurement (basis)	n/a
	Fill mixture	30
	Reaction	see technical data
	2. measurement (plateau)	n/a
	Flushing (sample)	20
Cleaning	Pump cleaning solution	1/2 flushing duration
	Allow to react	5
	Pump cleaning solution	1/2 flushing duration

To visualize the differences between the three modes, concerning the involved parts and the mechanism, the scheme of the three modes will be presented (Figure 5 to Figure 7).

The cleaning mode, (Figure 5) has one basic duty. It should prevent or remove any sedimentation or clogging in the system. If not possible wrong measurement results or error messages will occur.

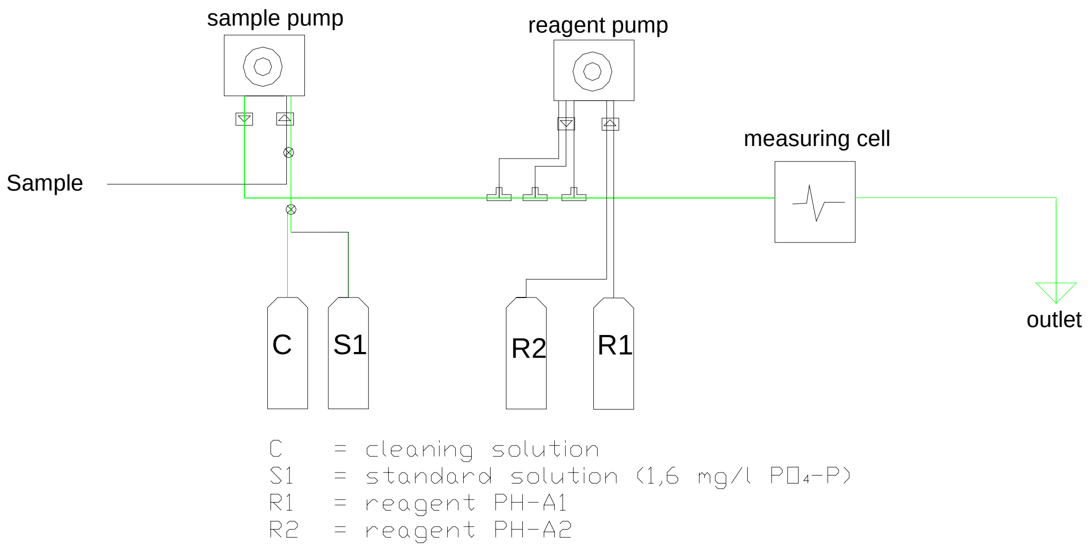


Figure 5: Scheme of cleaning mode

The calibration mode (Figure 6) is an important mode to ensure a high accuracy of the measurement and a high data quality. Here, the analyzer measures the phosphorus concentration of the standard solution. The standard solution's concentration, used in this study, is 1.6 mg/l PO_4-P. Due to the influences of reagent aging, aging of constructive components, etc. the result of the measurement can differ from the actual amount. To compensate these influences, the results will be multiplied by the calibration factor (cf). This factor is the ratio of the measured concentration of the calibration standard to the predefined concentration of the standard.

To avoid a malfunction during the calibration the Stamolys CA71PH checks the registered calibration factor logically. Is the calibration factor outside a defined tolerance range the calibration will automatically be repeated. If, after the second calibration, the calibration factor is still outside the range, an error message appears.

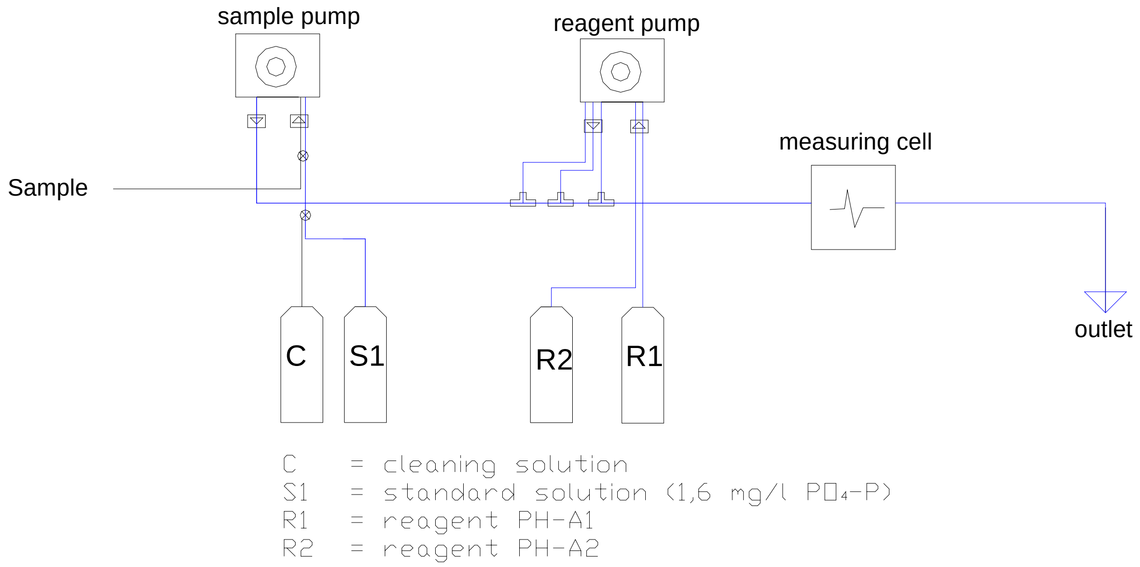


Figure 6: Scheme of calibration mode

The measurement (Figure 7) is the main mode. Here, the concentration of the sample's phosphate is measured.

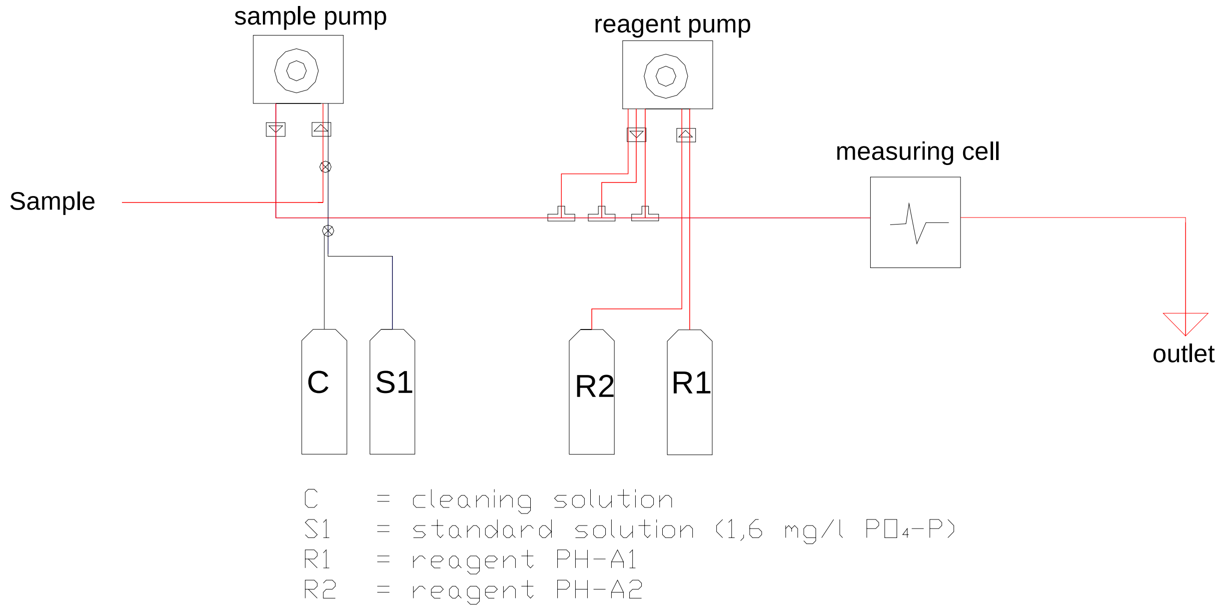


Figure 7: Scheme of measurement mode

In case of a malfunction during the measuring mode, the analyzer can run the calibration- and the cleaning mode. If both modes work properly, the functionality of many parts, also used in the measurement mode, has been proven. Many parts of the analyzer are utilized in more than just one mode. Hence, the defective part can be located. This is the basis of the sensor self-diagnostic, in which the sensor detects the failures itself (see 6.1).

2.2 Available Signals

To improve a measurement device it is essential to know about the device’s capability. The light intensity, which is measured before each measurement and then converted into a frequency, varies around 6300 Hz. This frequency is the so called basis frequency and should not fluctuate. During a measurement the measuring cell indicates the light intensity passing through the colorized sample. Then the light intensity will also be converted into a frequency (plateau frequency) which should be lower than the first. The plateau frequency is depending on the concentration. Out of the subtraction of both frequencies the phosphorus concentration in mg/l can be calculated. To avoid an aberration from the actual concentration, the photometric cell makes five measurements for each sample and then calculates the average. This way an aberration of one measurement will not automatically lead to an error. As it is shown (Table 2), every concentration is assigned to a specific frequency.

Table 2: Standard calibration curve

	Measuring range	**Concentration [mg/l]**	**Frequency [Hz]**
Phosphate, molybdenum blue, lower measuring range PH-A	0.05 to 2.5 [mg/l]	0.00	0
		0.25	96
		0.50	180
		0.75	265
		1.00	355
		1.25	430
		1.50	516
		1.75	568
		2.00	638
		2.50	798

Concentrations between the given data can be calculated through a linear interpolation, such as the Stamolys CA71PH automatically does.

To send the signal to the user or to a data base, the concentration will be converted into milliampere [mA]. Therefore, the beginning of the measuring range (0.05 [mg/l]) will be converted into 0/4 [mA] and the end of the measuring range (2.5 [mg/l]) into 20 [mA]. Every concentration is linked to certain amperage and has to be between 0/4 and 20 [mA]. State of the art on WWTP's is still the analog data transfer but the trend goes towards digital protocols like Profibus, Foundation Fieldbus, Hardt, etc.

An additional signal that is available from the analyzer is the inlet control. It gives information about whether enough sample is available for the upcoming measurement or not.

2.2.1 Frequency offset ("blank value")

The coloring of the reagents, used for the analyzer can influence the measurement and the calibration. The measured phosphorus concentration then is higher than the actual concentration. The photometric cell measures the blue coloring that appears by reacting with the phosphates plus the coloring of the reagents itself. To compensate these influences, every time the reagents are changed, an offset is necessary.

The frequency offset ("blank value") is a setup to eliminate these influences. For this, the analyzer makes a measurement with deionized water. By measuring the absorbance of the mixture, the blank value can be calculated:

$$\text{Basis frequency of offset measurement} - \text{plateau frequency of offset measurement} = \text{Frequency offset}$$

To visualize the influence of the blank value on the measurement Figure 8 shows the shift of the graph after considering the frequency offset. The offset should be in the range of 0 – 10 [Hz], otherwise the reagents should be replaced.

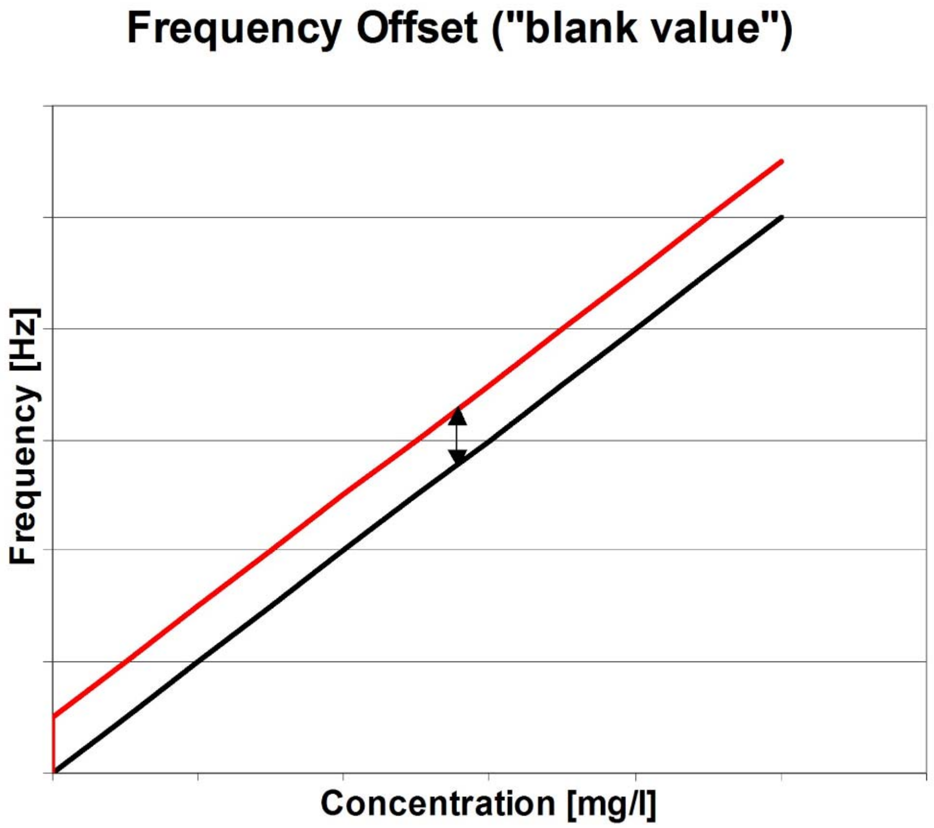


Figure 8: Frequency offset („blank value”)

2.3 Available self-diagnosis

The analyzer has already the capability to detect some basic malfunctions within its system. But the quantity of the detectable errors is limited. It can for instance detect, that a calibration failed, when the measured calibration factor is out of an “acceptable” (pre-defined) range. A specification of the source of the error is not possible on the sensor level and will remain the task of the user. The following list shows the available error messages and the possible causes (Table 3).

Table 3: Available error messages, given in the operating instructions of the Stamolys CA71PH (Endress+Hauser)

Error message	Possible cause	Test and/or corrective measures
Calibration failed		If a calibration fails, you can enter a new calibration factor manually (CONFIGURATION menu, "calibration factor"). Cancel the error message by switching the analyzer off and on briefly. If the error occurs frequently, you will have to search for the cause.
	Air bubbles in the system	Start calibration manually (PARAMETER ENTRY, "1.calibration", change the date accordingly, start measurement) or enter a new calibration factor.
	Incorrect concentration of standard	Check the concentration in the laboratory. Adjust the standard accordingly ("PARAMETER ENTRY", "Calibration solution") or replace the standard
	Reagents contaminated or aged	Simple check: Mix 5-10 ml of standard solution and 5 ml of reagent in a beaker. If it does not change color after max. 10 min, replace the reagents.
	Standard dosing defective	Check the valves for contamination, obstructions (visual inspection). Replace valve hoses if necessary.
	Incorrect photometer	Check the setting in the CONFIGURATION menu.
Cell dirty	Not enough light intensity at receiver, e.g. due to sedimented particles	- Flush with 12.5 % bleaching lye (monthly maintenance) - When using a CAT 430: Check the filter
Incorrect photometer	Incorrect photometer	Check the setting in the CONFIGURATION menu, "Photometer".
No sample	No sample	Establish sample transfer.
	Level measurement defective	Check level measurement at the sample collector.
Spillage error	Leak at canisters or hoses	Replace defective components and clen and dry the analyzer or those components affected by the leak.
No measuring signal	Cell filled with air	Pump sample for 1 minute. (SERVICE)
	Photometer defective	Inform Service
	Electrical connection	Check all electrical connections and make sure the fuses are firmly seated.
	Fuse defective	Replace fuse F4 or F5 (semidelay 0.2 A)

The operating instructions also give a variety of further errors that can appear. These errors can not be detected by the analyzer itself, but need man power to be detected.

2.4 Readout software

The readout software AnaWin^{TM}_0.96 (Endress+Hauser, 2005) is based on the labview software (national instrument coorp.). The user interface of AnaWin^{TM} offers three modes to read out information from the analyzer:

- frequency control
- parameter
- data storage

The frequency control mode displays the current frequency in form of a graph (Figure 9). The time (s) is displayed on the x- and the frequency (Hz) is displayed on the y-axis. In addition to the frequency curve the value of the measurements can be read in a window (not shown). During a measurement, the different phases of the cycle are marked.

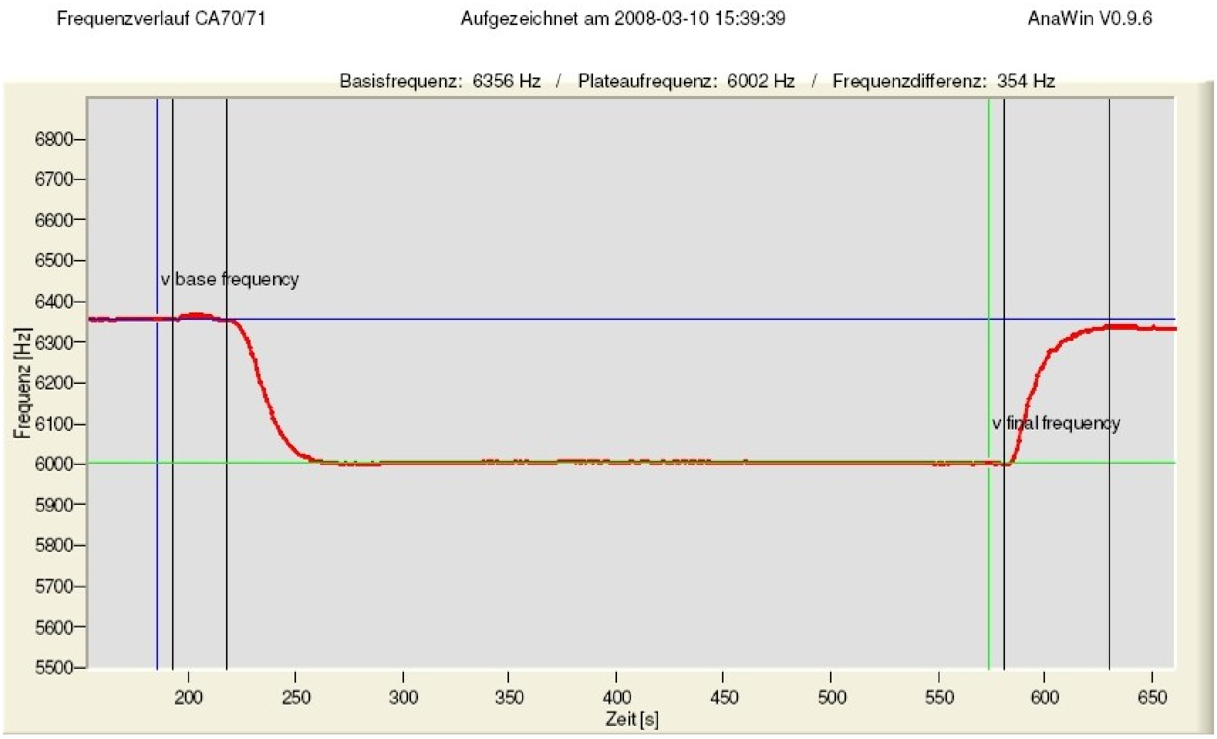


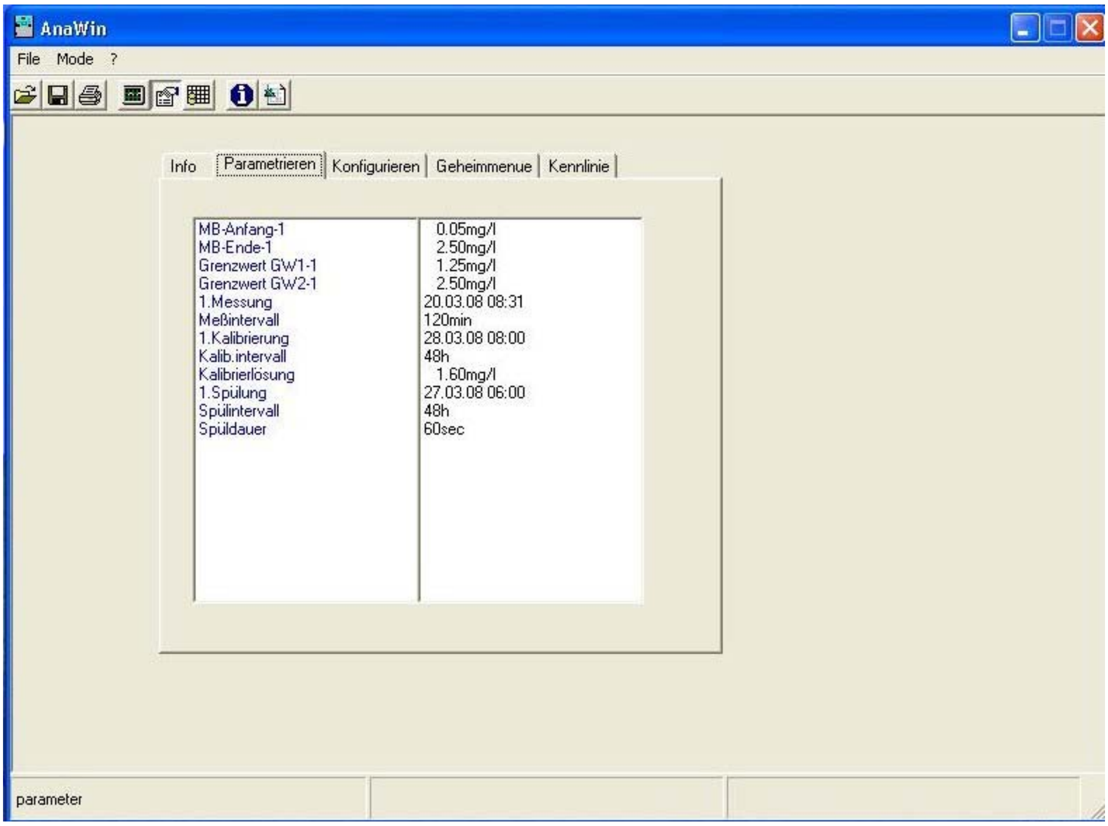
Figure 9: Display of the frequency curve in AnaWin^{TM}

At the end of each measurement or calibration, the base frequency, the final frequency and the difference of both frequencies is given.

The AnaWin^{TM} software does not allow storing the frequency curve. In the presented work the experiments were video taped and a screen shot of each experiment was taken and stored as a PDF-file.

In the parameter mode, five different categories of information can be selected:

- info
- parameter (Figure 10)
- calibration
- secret menu
- characteristic curve



MB-Anfang-1	0.05mg/l
MB-Ende-1	2.50mg/l
Grenzwert GW1-1	1.25mg/l
Grenzwert GW2-1	2.50mg/l
1.Messung	20.03.08 08:31
Meßintervall	120min
1.Kalibrierung	28.03.08 08:00
Kalib.intervall	48h
Kalibrierlösung	1.60mg/l
1.Spülung	27.03.08 06:00
Spülintervall	48h
Spüldauer	60sec

Figure 10: Screen shot of the user surface in AnaWin^{TM}

In the submenu info, general information like software version and serial number are stored (Figure 10). The user has the ability to check the setups, like measuring range, time of the next measurement, time of the next calibration, cleaning interval etc. The secret menu delivers information about the duration of the phases as well as the rotation speed of the second pump. The last submenu of this mode is the calibration curve. This curve defines the frequency of ten different concentrations from 0.05 mg/l to 2.50 mg/l-PO_4-P.

The data storage mode reads out the memory of the analyzer. With this mode, the measured concentrations (with the appropriate unit) can be shown on the computer. This information can be copied into a .txt file and then be stored or printed.

3 Experimantal activities

3.1 Experimental setups

For the planned experiments, samples with three different concentrations were prepared by diluting a high concentrated phosphorus solution (1000 mg/l PO_4-P) in a beaker (capacity 2l) to the aimed concentrations. The reached concentrations were 1.02 mg/l PO_4-P, 1.59 mg/l PO_4-P and 2.05 mg/l PO_4-P. All concentrations were checked twice with cuvette tests (HACH).

Further equipment needed for the experimental procedure is nano-pure water, three clamps, a medical injection needle and a waste container for the outflow. To avoid the loss of information the right software tools should be installed on the computer (AnaWin^{TM}, PDF-converter).

Before the testing series was started the frequency off-set was defined. This was followed by calibrating the system which was done with a 1.6 mg/l PO_4-P standard solution. With these setups the effects of external influences were reduced.

The pre-set durations (Table 1) of the measurement phases were not changed. To ensure the consistency of the results every experiment was repeated six times with all three concentrations.

To reduce the environmental influences experiments were performed at a room temperature of 24° C (+/- 1° C).

3.2 Experimental procedure

Due to a limitation of the experimental time frame it was decided to focus on the following experiments:

- **“normal” measurement:** Failure free measurement under lab conditions. Serves as a reference for the detection of faulty measurement cycles.
- **plugged sample tube:** Measurement with an intentionally plugged sample tube. In this experiment no sample was added to the regents.
- **failure of reagent pump (pump 2):** Simulation of a reagent pump break down. In this experiment no reagent was added to the sample.

- **no reagent PH-A1:** Here, the tube of reagent PH-A1 was blocked to examin the effects of the missing reagent on the measurement.
- **no reagent PH-A2:** Blockage of the reagent PH-A2 tube to examin the effects of the missing reagent on the measurement.
- **air bubbles in the system:** The effect of air bubbles on the measurement cycle was in the focus of this experiment.
- **comparison of “no concentration” and “no sample”:** Two different failures can cause the same result. Here, the possibility to distinguish between both failures was examined.
- **measurement with high concentration:** The accuracy of measurements at the limit of the detectable measuring range was examined in this experiment.

For the experiments, the phosphorus solutions were filled into a beaker (500 ml) which was placed inside the analyzer. Every measurement was triggered manually to start a full measuring cycle.

During the experiments the frequency curve was observed to detect abnormalities in the course of the curve.

4 Results

4.1 “Normal” measurement

The goal of the testing series was to detect, isolate and identify abnormalities of the frequency curve. Before a detection of an abnormality is possible a “normal” status has to be defined. Therefore, the first experiment of the testing series was the definition of a “normal” measurement. The phosphorus solution was given into the beaker and the measurement cycle was started.

Figure 11 shows the development of the frequency during the failure-free measurements for three different concentrations. The y-axis of the graph displays the frequency and the x-axis displays the number of measurements during one measurement cycle. After dosing the reagents, the characteristic reaction curve appears. Depending on the phosphorus concentration the time until the steady state is reached varies. The black frequency curve (1.02 mg/lPO_4-P) reaches the steady state longe before the blue frequency curve (2.02 mg/lPO_4-P). With rising phosphorus concentration the time until the steady is reached increases. For concentration at the limit of the measurable range it is possible that the steady state will not be reached during the pre-set reaction time (see 4.7).

The fact that the frequency curve reaches the steady state is an indicator of a failure-free measurement. After the reaction time the system will be flushed with sample. This is visible by the fast increase of the frequency curve.

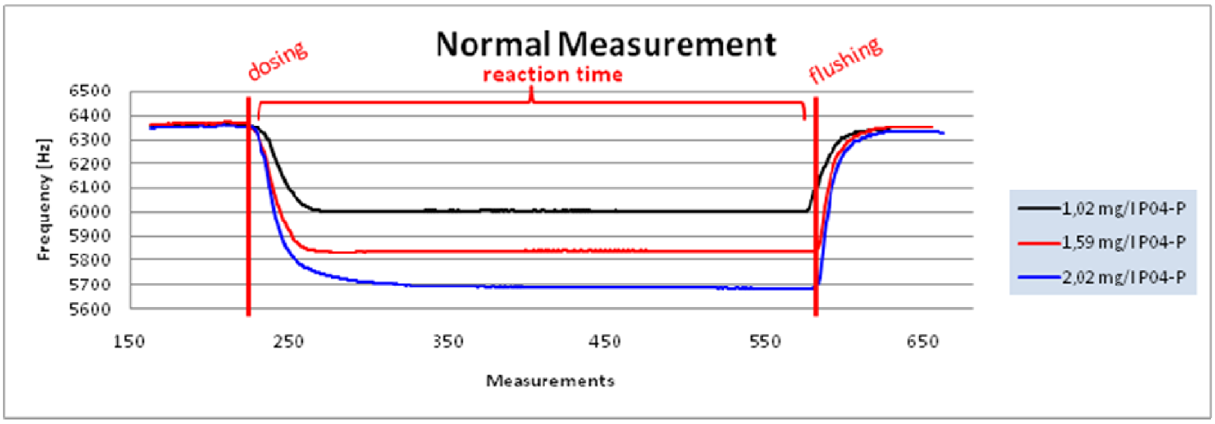


Figure 11: Frequency curve under normal conditions with three concentrations

4.2 Plugged sample tube

After a normal measurement cycle the sample tube was pinched off with two climps (Figure 12) to simulate a clogged or buckled sample tube. For this experiment, first a normal measurement cycle was performed. Then the tube was taken out of the beaker and pinched off with two climps. The fact that the tube was taken out of the beaker allows detecting possible leakages. In case the tube is not totally blocked, air bubbles would be visible in the system.

Figure 12: Pinched-off sample tube for experimental series

The result of this experiment is shown in the (Figure 13). Already during the first measurement after pinching off the sample tube the development of the frequency curve changed. The beginning of the first measurement is similar to the normal measurement. The first indicator for a failure is that the frequency curve does not reach a steady state. The second abnormality is that at the end of the first measurement cycle, at this point the system should be flushed with sample, the characteristic increase caused by the flushing is missing. The following measurement cycles show a more or less horizontal development.

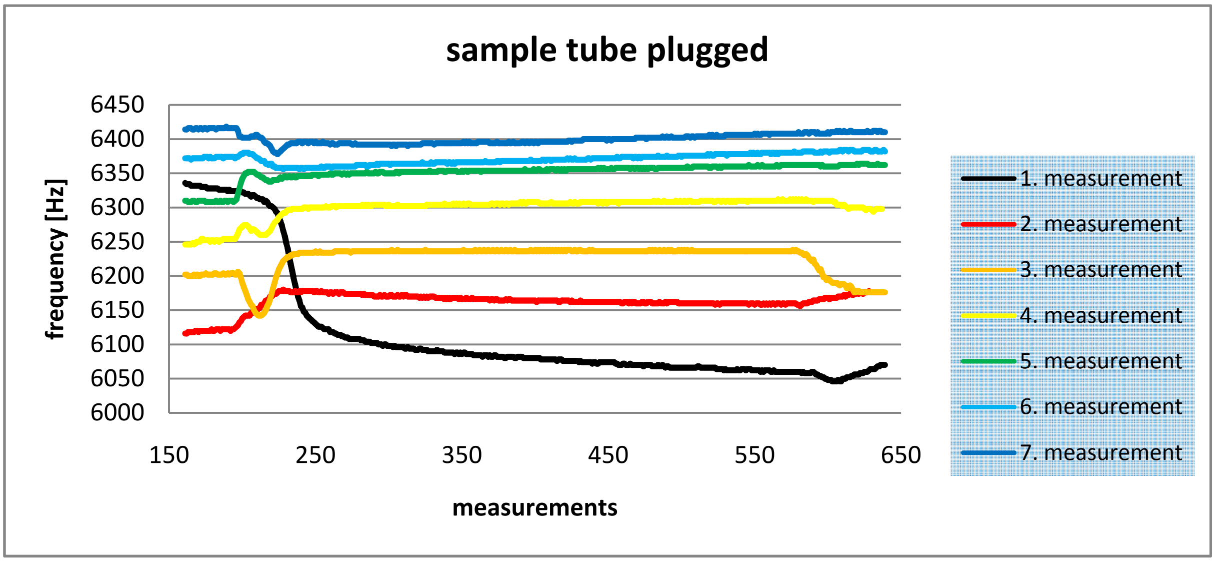


Figure 13: Development of measurements with a plugged sample tube

4.3 Reagent pump (pump 2) failure

In the analyzer software it was not possible to shut down the reagent pump. Thus, the hose boxes of the reagents were taken off the pump and the tubes were pinched off. With this setup, not allowing the reagents to be mixed with the sample, the measurement was started. With this experiment a breakdown of the reagent pump (pump 2) was simulated (Figure 14).

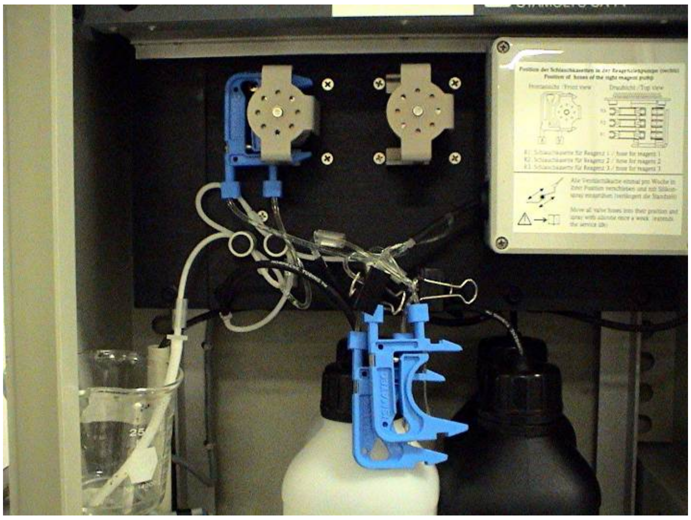


Figure 14: Simulation of reagent pump failure

The simulation of the reagent pump failure delivered the expected result. Since no reagent can be added to the sample no reaction can take place. Therefore the result of this experiment was a horizontal line. Figure 15 shows the differences between a normal measurement and a measurement with a pump failure.

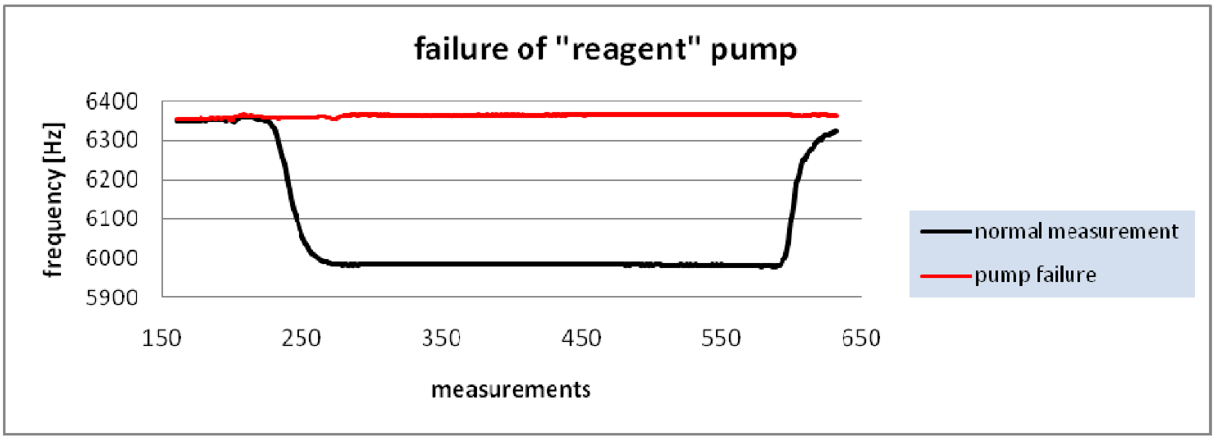


Figure 15: Simulation of a “reagent“-pump break down

4.4 No reagent PH-A1/PH-A2

It is possible that the tube of one reagent is clogged, buckled or bent and subsequently the reagent is not mixed with the sample. To examine this effect the tube of reagent PH-A1 was pinched off and the tube cast was hanged off (Figure 16). Then the measurements were taken. In between the experimental repetitions a normal measurement cycle was performed. The same experimental procedure was repeated with reagent PH-A2.

Figure 16: Simulation of a clogged reagent PH-A1 tube (similar buildup for reagent PH-A2)

A clogged reagent tube, an empty reagent canister or a bent tube can reduce the reagent supply. Hence, the reaction will be disturbed. The frequency curve shows a delayed S-shaped reaction curve (Figure 17). The first measurement is still close to a normal measurement, because there is still some sample left in the tube. The following measurement cycles show a delayed reaction. The delay increases with every measurement cycle because with every cycle fewer reagent is left in the system. Not only is the reaction curve delayed. The further development of the curve is disturbed as well. The curve does not reach the steady state for a sufficient time.

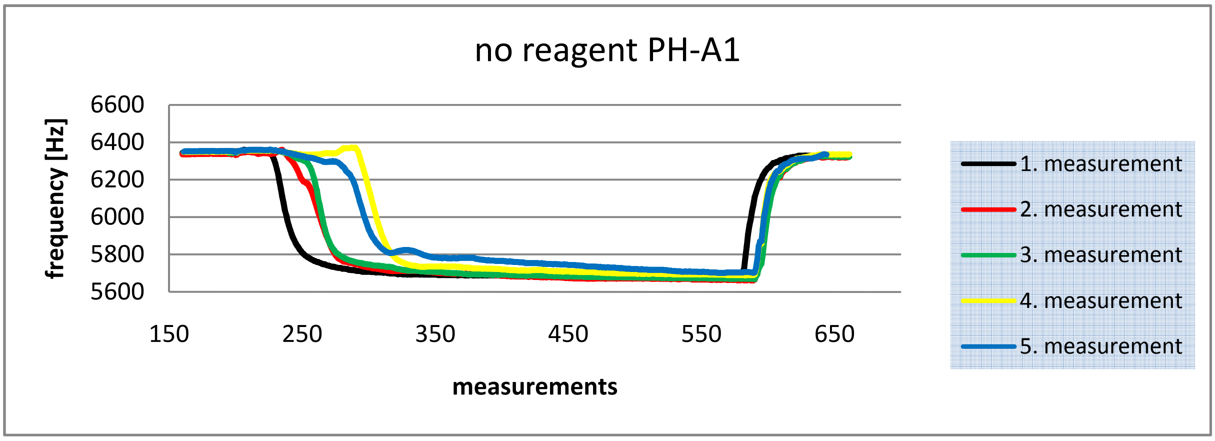


Figure 17: Reduced reactivity through excluding reagent PH-A1 from the mixture

Even though a malfunction is certainly affecting the analyzer, the measured concentrations in this experiment were not far off the real value (Table 4). The reaction with the phosphor takes place but is slowed down.

Table 4: Comparison of the measured concentrations of a normal measurement and a measurement with a clogged PH-A1 tube

experiment	concentration (normal measurement)	concentration (clogged tube PH-A1)	difference	accuracy (%)
81-85	1.05	1.08	0.03	97.2
	1.05	1.07	0.02	98.1
	1.05	1.11	0.06	94.6
86-90	1.07	1.07	0	100.0
	1.07	1.11	0.04	96.4
	1.07	1.08	0.01	99.1
96-100	1.62	1.66	0.04	97.6
	1.62	1.75	0.13	92.6
	1.62	1.65	0.03	98.2
106-109	1.63	1.7	0.07	95.9
	1.63	1.67	0.04	97.6
	1.63	1.68	0.05	97.0
66-70	2.16	2.17	0.01	99.5
	2.16	2.11	-0.05	97.7
	2.16	2.06	-0.1	95.4
71-75	2.19	2.16	-0.03	98.6
	2.19	2.11	-0.08	96.3
	2.19	2.13	-0.06	97.3

The experiment was then repeated with the reagent PH-A2. The experimental setup and procedure was similar to the previous experiment with the exception, that the hose box of reagent PH-A2 was now hanged off the pump and pinched off (Figure 16). The first measurement cycle of this experiment is still close to a “normal” development because there is still some reagent left in the system. The frequency curves 2-4 don’t show the characteristic reaction curve. The curve can be described as an almost linear line with a negative slope. After repeating the experiment a decrease of the curves slope was visible until the curve reached an almost horizontal line (Figure 18).

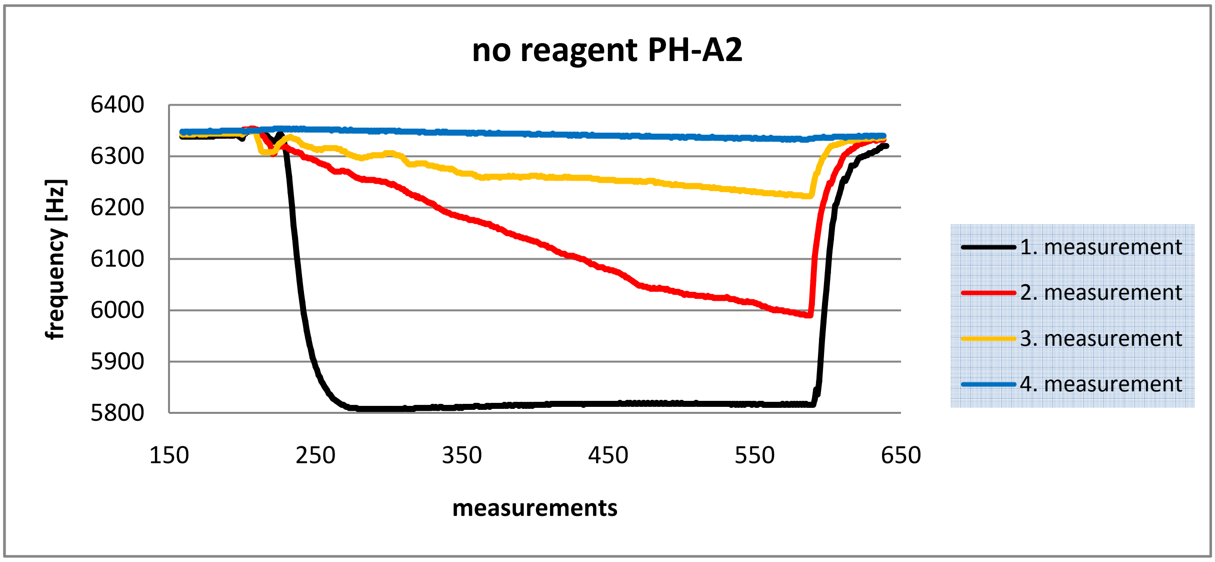


Figure 18: Loss of characteristic reaction curve through pinching off reagent PH-A2

4.5 Air bubbles in the system

Air bubbles can cause inaccuracies during the measurement. To examin the effects of air bubbles and the possibility of detection during the measurement air bubbles were intentionally introduced to the system. The injection of air was done with a medical injection needle. To know exactly when the air bubble passes through the measuring cell the tube right before the measuring cell was chosen to be pierced through (Figure 19).

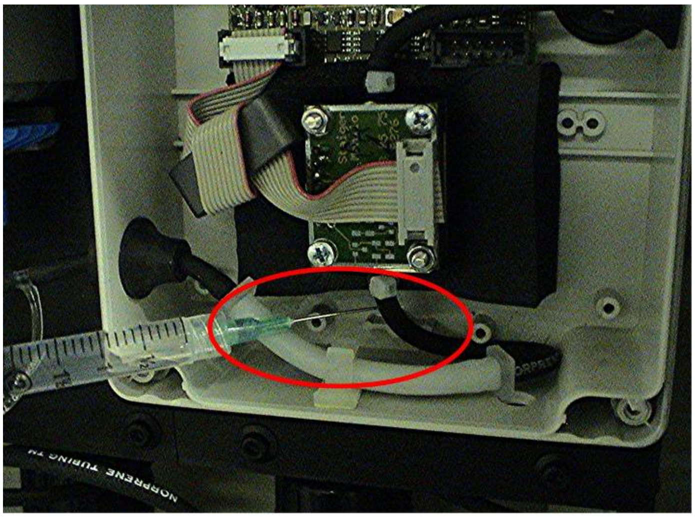


Figure 19: Injection of air bubbles into the analyzers system

Air bubbles in the analyzer’s system cause a specific change of the frequency curve, as soon as the air passes through the measuring cell (Figure 20). The air affects the curve only for a few measurements. As soon as the air passed through the measuring cell, the curve returns to its normal development. The result of this experiment is that air bubbles can be identified by the significant shape of the frequency curve. They only cause negative effects on the measurement when they appear during the measurement of the basis frequency or the plateau frequency. Air bubbles that appear during the reaction time do not affect the measurement. Only in the improbable case that an air bubble get caught in the measuring path a permanent affect on the measurement is likely.

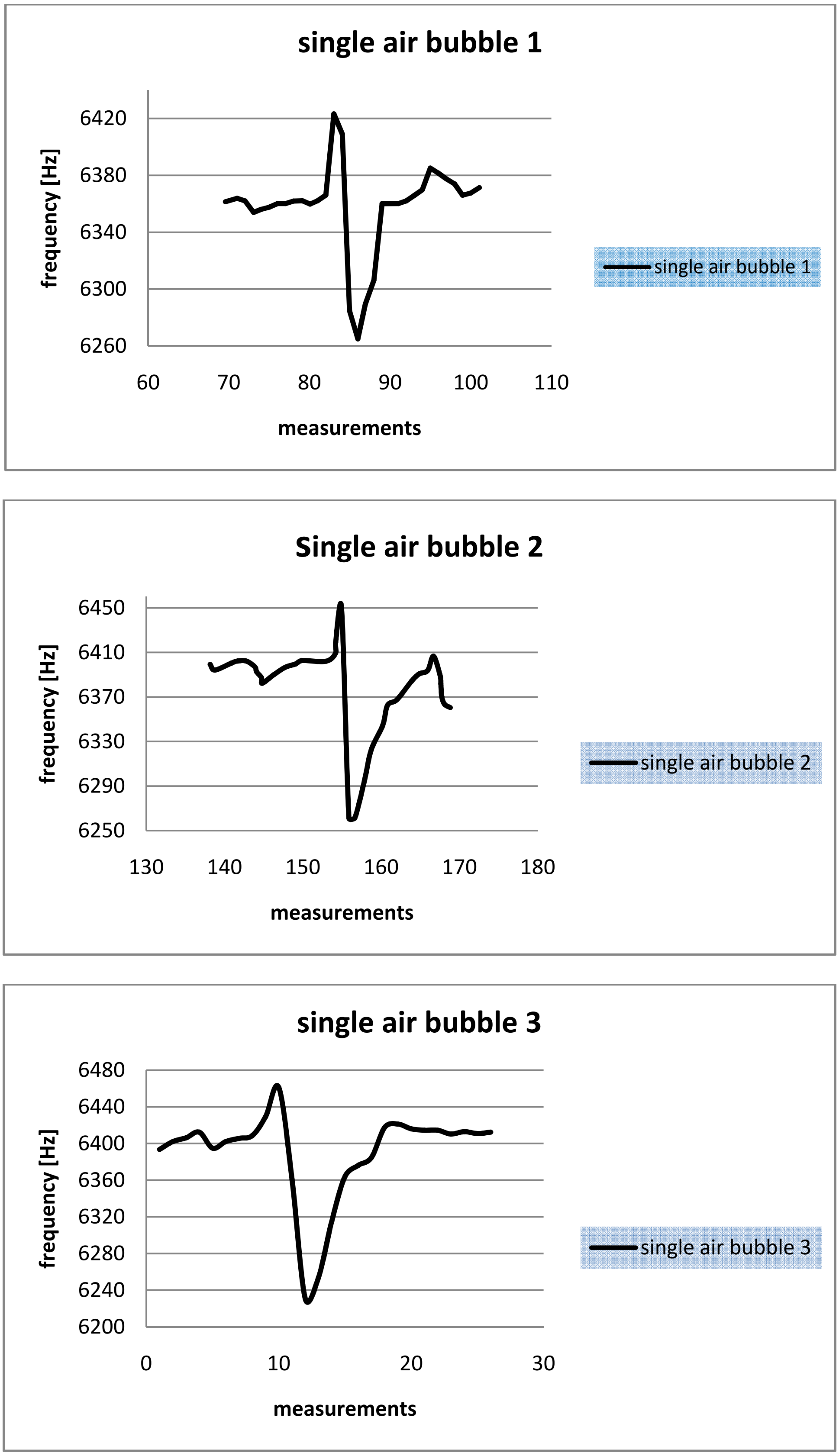


Figure 20: Typical pattern in the frequency curve, caused by air bubbles

4.6 Comparison of “no concentration” and “no sample”

It is possible that two different failures can cause the same behavior in the frequency curve (e.g. a plugged sample tube and a measurement at zero concentration). Since plugging the sample tube caused an almost horizontal development of the frequency curve a second experiment with nano-pure water (0 mg/l PO_4-P) is necessary to find out if there is a measurable difference between those two conditions. Besides the sample, the setup of this experiment does not differ from the “normal measurement”.

Figure 21 compares the results of both experiments. The red curves are the result of the experiments without sample and the blue curves are the result of samples with 0.00 mg/l PO_4-P. Both experiments show similar curves. The differences vary between 0 and 50 Herz.

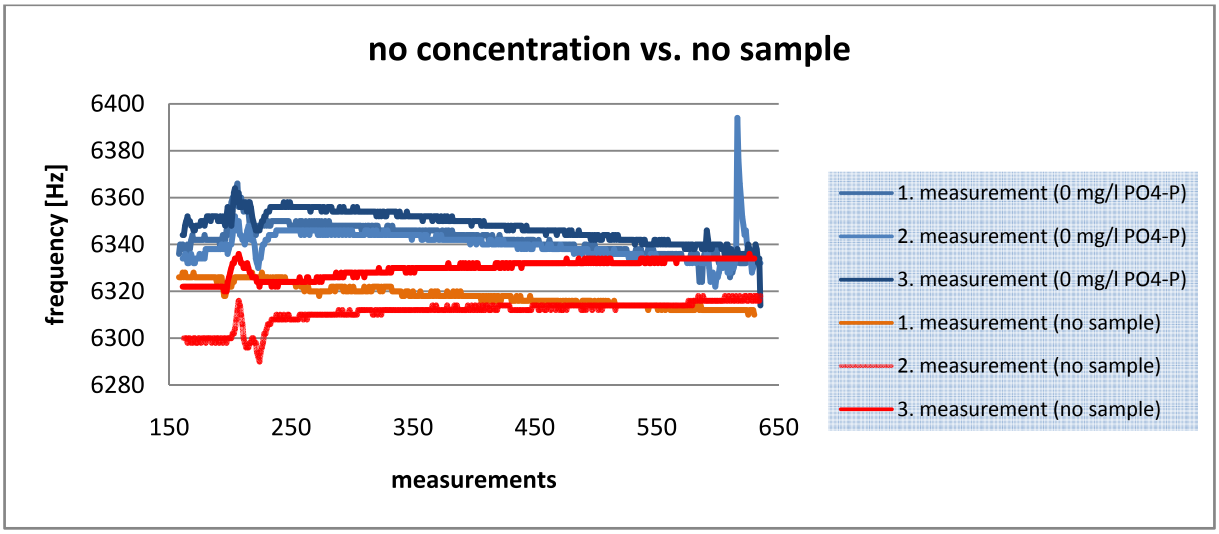


Figure 21: Comparison of measurements with 0 mg/l PO_4-P (blue) and measurements without sample (red)

4.7 Measurement at higher concentration

The calibration of an analyzer is done with a concentration in the middle of the meauring range. Therefore, the closer the samples concentration is to the concentration of the calibration standard the more accurat the measurement will be. The further the concentration to be measured is away from the concentration of the calibration standard the lower the accuracy will be.

To examine the accuracy of the measurement at the limit of the measurable range, sample with a concentration of 2.45 mg/l PO_4-P was created and a testing series was performed. With rising phosphorus concentration the mixture needs more time to reach a steady state. To examine whether an extension of the reaction time increases the accuracy of the measurement, this test was repeated with a reaction time of 360 seconds, 480 seconds and 600 seconds (Figure 22).

The first measurement of this testing campaign was done with the pre-defined reaction time of 360 seconds. The reaction time of 360 seconds did not allow the frequency curve to reach a steady state. This was proven by the experiments with the increased reaction time. After 360 seconds the frequency curve was still in its development and reached the steady state after 480 seconds. An increase of the reaction time gives the mixture more time to reach and stay in the steady state.

Is the concentration after 360 seconds already higher than 2.45 mg/l PO_4-P an increase of the reaction time will not be able to increase the accuracy. In this case the problem lies in the accuracy of the measuring cell and is not caused by an unfinished chemical reaction.

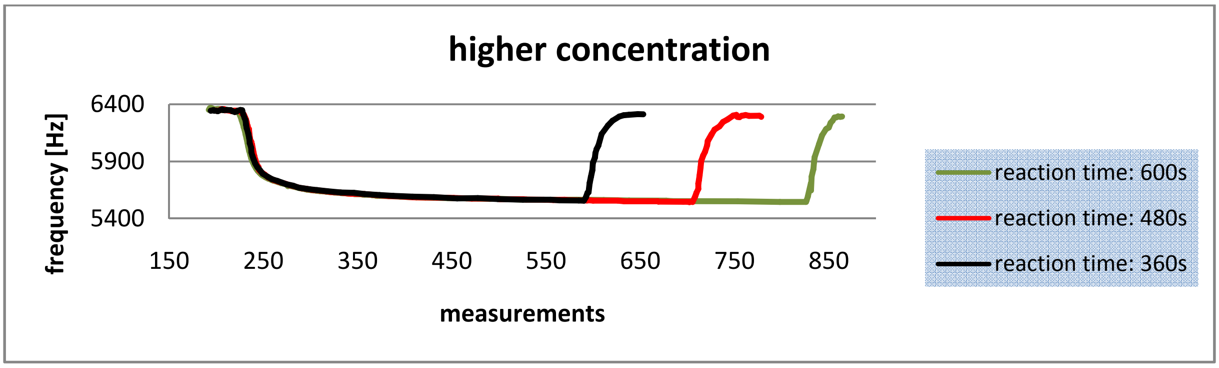


Figure 22: Comparison of three measurements (all with a concentration of 2,45 mg/l PO_4-P) with different reaction times

5 Assessment of steady state trend behavior

The development of a program that computes if the steady state of the frequency curve is reached will be the focus of this chapter. The program is based on the Matlab software (The MathWorks Inc.) and it is created to optimize the duration of measurement cycles. Especially when the concentration to be measured is close to the limit of the measurable range the time until the steady state is reached varies heavily. For low phosphorus concentrations the default reaction time of 360 seconds can be too long because the reaction is completed earlier. For high concentrated samples this reaction time might not provide enough time to reach and stay in the steady state. With this program the reaction time will be adjusted to the condition of the mixture.

The program uses the data of the frequency curve. It takes the measured frequencies during a time frame of 60 seconds and tries to fit two models to the data, a simple constant mean model (one parameter) and a more complex linear trend model (two parameters). For both models the sum of squared residuals will be calculated (Hastie, 2001). The sum of squared residuals is a measure for the deviation of each model from the data set.

$$y = const. + measurements \qquad SSR = \sum_{i=1}^{n} (xpred - y)^2$$

Since one model is more complex than the other it is not possible to decide for the best model on the sum of squared residuals alone. Any method to compare a simple model with a more complex model has to evaluate whether the reduced sum of squared residuals with the more complex model warrants the increased number of parameters, i.e. increased complexity of the model.

To decide which model is appropriate the F-test is used in this work (Johnson, 2002). The F-test requires on the following two assumptions which have been fulfilled:

- Normal distribution of measurement errors
- Independently and identically distributed measurement errors

The F-test is a statistical test in which the test statistic has an F-distribution if the null hypothesis (complex model does not fit significantly fit better than the simple model) is true (Lomax, 2007). In this test the observed F-value and the critical value of F at 95% probability level are compared.

$$F = \frac{\frac{(RSS1 - RSS2)}{p2 - p1}}{\frac{RSS2}{n - p1}}$$

Is F is larger than F_{crit} then the null hypothesis is rejected and the complex model is considered to fit the data significantly better. The reaction of the mixture is considered not to be finished and the regression line of the frequency data is considered linear. Is F smaller or equal to F_{crit}, then the complex model is considered not to fit the data significantly better than the simple one. Therefore the regression line of the data set is considered to be flat and the reaction of the mixture is considered to be finished.

To give an example of how the program works and to express the necessity of this software development, two examples will be given. The first example shows a normal frequency curve (Figure 23). The steady state is reached long before the end of the reaction time. With the default setup of the reaction time the analyzer waits for six minutes until it measures the concentration. In this case only two minutes are needed until the reaction of the mixture is completed.

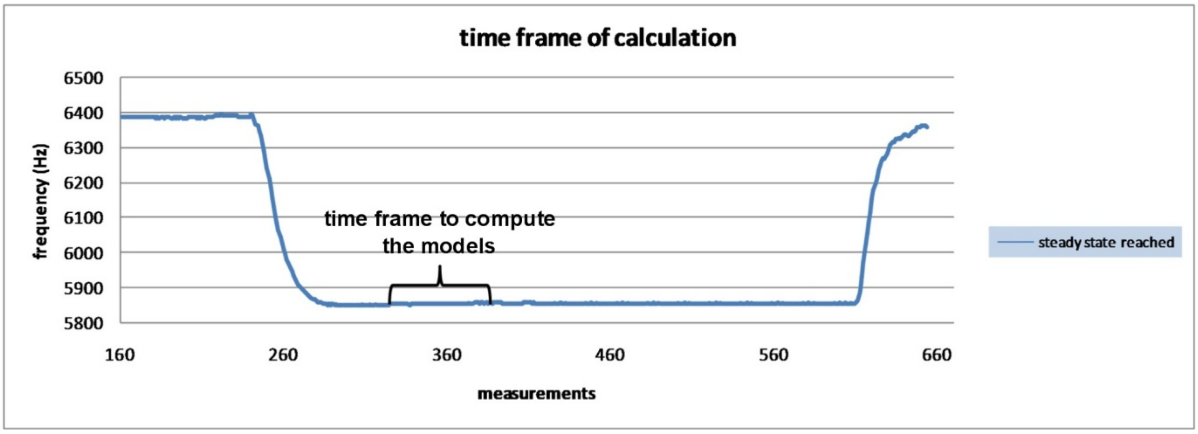


Figure 23: Shows the time frame (on a normal frequency curve) that is used to compute the models. The data that is taken during that time will be implemented in the program and compared to the models

The program follows the frequency curve and uses the data that is taken within the time frame for its calculation. To every set of data it calculates the two models and tries to fit the models to the data. Figure 24 shows the result of the calculation. The red line displays the data that is measured within the time frame. The blue line represents the constant mean model and the green line represents the linear trend model.

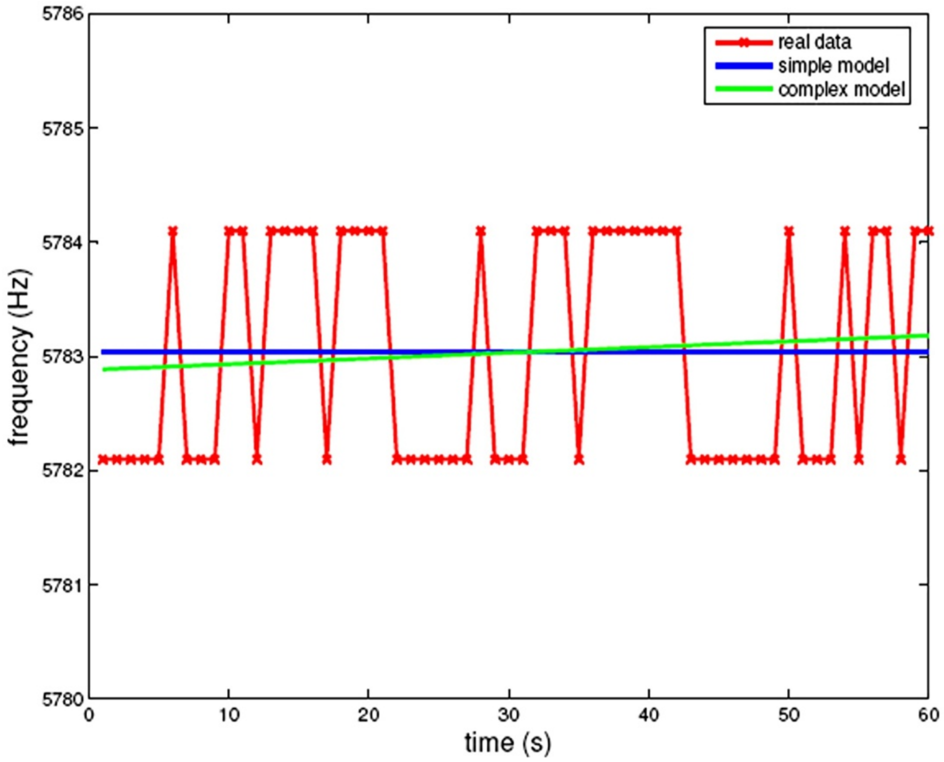


Figure 24: Comparison of the two models with the data of the horizontal frequency curve (red displays the real data; blue displays the simpler model; green displays the more complex model)

By using the F-statistic the matlab based program compares the real data to the two models. It first calculates the sum of squared residuals for both model and then it computes the F-test to detect which model fits significantly better to the real value (Table 5). Here, F is smaller than F_{crit}. This leads to the conclusion that the complex model does not fit significantly better. A horizontal development of the frequency curve is an indicator for a completed reaction of the mixture. Since the complex model does not fit the real data significantly better than the simple model, the regression line of the real data is considered to be horizontal. Therefore, the reaction is considered to be completed.

Table 5: Results of computing the data of a horizontal frequency curve

b=1.0e+003*	5,7829	mean value
	0,0000	
ssr=1,0e+003*	59,7333	
	59,2832	
F	0,4328	
F_{crit}	4,0065	

The following result will be displayed by the program:

use simple model: 1 parameter -> constant -> flat

In the second example the pre-defined reaction time is not sufficient for the mixture to reach the steady state (Figure 25). Due to the default setup of the reaction time the analyzer will measure a concentration, even though the stable state is not reached. The result will therefore be not accurate and worthless.

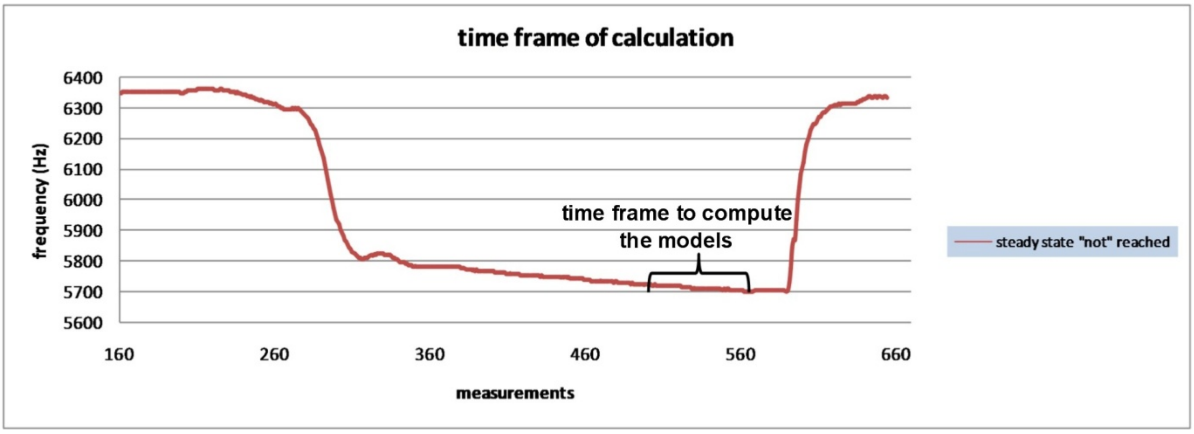


Figure 25: Shows the time frame (on a disturbed frequency curve) that is used to compute the models. The data that is taken during that time will be implemented in the program and compared to the models.

As well as in the previous example the program will compare the measurements of the time frame to the two models. Figure 26 displays a comparison of the models (green line: complex model, blue line: simple model) with the real data (red line).

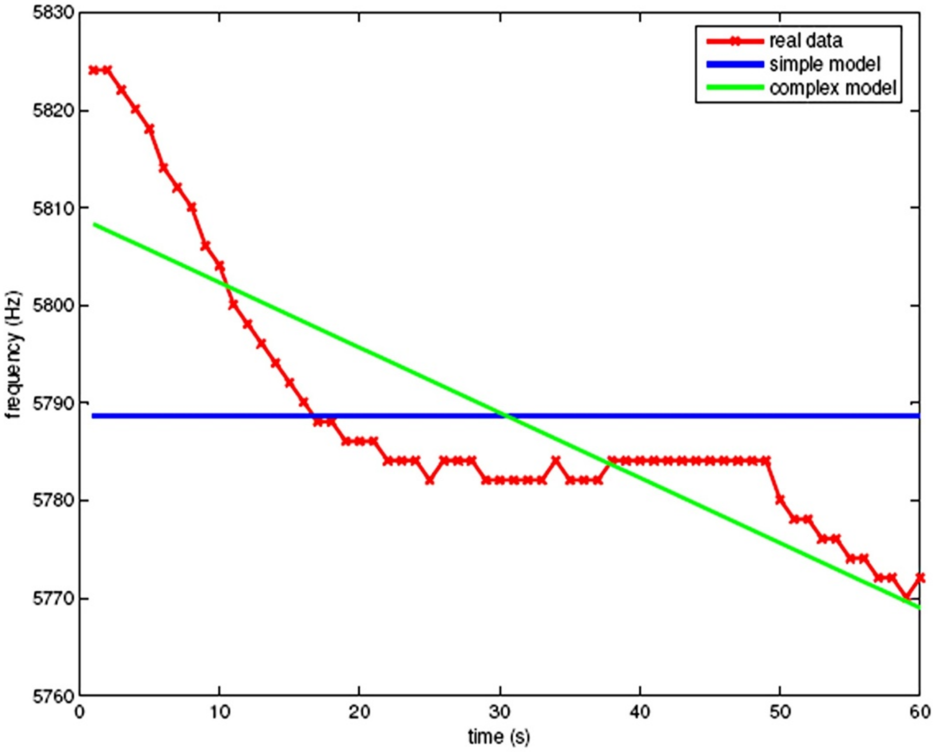


Figure 26: Comparison of the two models with the data of the disturbed frequency curve (red displays the real data; blue displays the simpler model; green displays the more complex model)

The program calculates the sum of squared residuals and uses the F-test to compare which model fits significantly better to the real data again. Since F is greater than F_{crit} (Table 6), the complex model is considered to significantly fit the data better.

Table 6: Results of computing the data of a disturbed frequency curve

b=1.0e+003*	5,8090	intercept
	-0,0007	slope
SSR=1,0e+004*	1,1009	
	0,3011	
F	152,4356	
F_{crit}	4,0065	

The program computed that the data significantly fits better to the linear trend model than to the constant mean model. Therefore the regression line is considered to have slope and not to be horizontal. This is displayed by the program as follows:

use complex model: 2 parameters -> linear trend -> not flat

In this case the program should increase the reaction time to give mixture more time to reach the steady state. Only if the steady state has been reached, the measured concentration is a reliable and worthy piece of information.

After first trials the program seems to work but further development is needed to improve the software. It is for example possible that noise effects measurement and leads to aberrances. Since the program in its current version simply fits the models to the frequency curve it is possible that in this case the complex model does not fit better and the frequency curve is considered to be horizontal, even though it is not. For those cases the program needs further development so that it is able to recognize noise that affects the frequency curve.

6 Discussion

Plugged sample tube

With the detection methods currently used, the first measurement of the plugged sample tube would not have been recognized as a failure. The final result is within the measurable range (concentration: 0.75 mg/l PO_4-P). Only by evaluating the frequency curve this kind of abnormality can be recognized directly. The characteristic that can be recognized is the loss of the charcteristic curve during the flushing process within the first measurement cycle and the horizontal development of the frequency curves of the following measurement cycles. The frequency with the horizontal development rises with every measurement cycle. That is because with every measurement cycle only the reagents are flushed through the system. With every cycle less phosphorus sample that can react with the reagents is left in the system. Step by step it gets pumped out of the system. After the seventh step only reagent is left in the system. With the appropriate analyzing software it should be possible to detect this type of failure.

The measurement cycle is divided into 8 phases. As soon as an abnormality of the frequency curve is detected, software could identify the phase where the problem appeared. Referring to the experiment with the plugged sample tube the software could relate the problem to phase 8 (flushing). This delivers more detailed information for the failure-isolation.

Reagent pump failure

The detection of a reagent pump failure seems to be an easy task because the curve differs strongly from the normal frequency curve. But the experiment with a 0.00 mg/l PO_4-P solution has shown that both curves are very similar. With the information of the frequency curve only it is not possible to make a difference between a 0.00 mg/l PO_4-P solution and a reagent pump failure. For this problem further information is needed. The already available signal from the inlet level meter can give the necessary information to decide between the problems. More precise information about the pump rotation is helpful. At the moment only the set pump rotation can be read out. The possibility to read out the real time pump speed has to be checked (see Outlook).

No reagent PH-A1

The experiment with the blocked reagent PH-A1 is a good example of the importance of evaluating the frequency curve. With the current setup this malfunction would not be recognized. The results can be far off the real concentration but since they are in the measurable range no warning signal will be sent. The evaluation of the frequency curve offers two ways to detect this failure. Firstly the delayed reaction can be detected by comparing the curve with a normal frequency curve. The second indicator is that the steady state is not reached. A small program can be implemented that checks whether the curve reached a steady state (horizontal line). If the steady state is not reached the reaction time can be extended to give the mixture the chance of further reaction.

No reagent PH-A2

The experiments with the clogged PH-A2 tube underline the importance of the frequency curve. As shown in the results the frequency curve did not show the typical behavior but a line with a negative slope. The measured results were significantly lower than the real concentration or were shown as 0.00 mg/l PO_4-P. Under field conditions and by just paying attention to the final results it would be difficult to detect the failure. However, with the additional information of the frequency curve a deviation from the typical frequency curve can be detected. Since the characteristics of the curve can only be caused by this failure the reason for this malfunction can be detected. In this experiment again the steady state of the frequency curve was not reached. Since the reaction was not finished, the result can be judged as not valid.

Air bubbles in the system

Air bubbles in the analyzer’s system are not comparable to the failures of the previous experiments. In terms of the measured concentration air bubbles only cause diverging results when the bubble travels through the measuring cell during the measurement of the basis- or the plateau frequency. If bubbles appear during the reaction time the final result will not be affected. Bubbles can also be an indicator for a leaking tube. Therefore the appearance of bubbles should not be seen as an acceptable status. The basis- and the plateau frequency are the result of the average of five measurements (Figure 27). This reduces the influence of outliers. According to the experiments it should be possible to define a typica automatically detect air bubbles. Another way to detect ai for an increased noise during a limited period of time.

A detection of air in the analyzer’s system should lea measurements during that time are not worthless as l appear during the measurements of the plateau or basis f

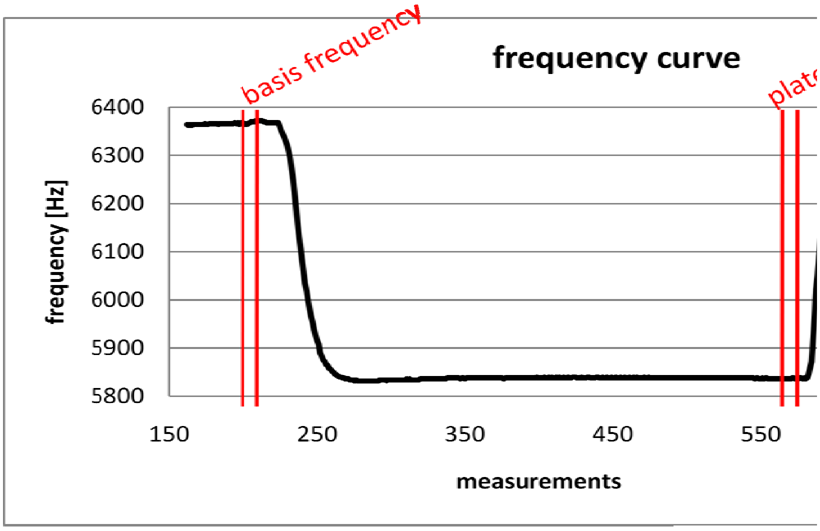


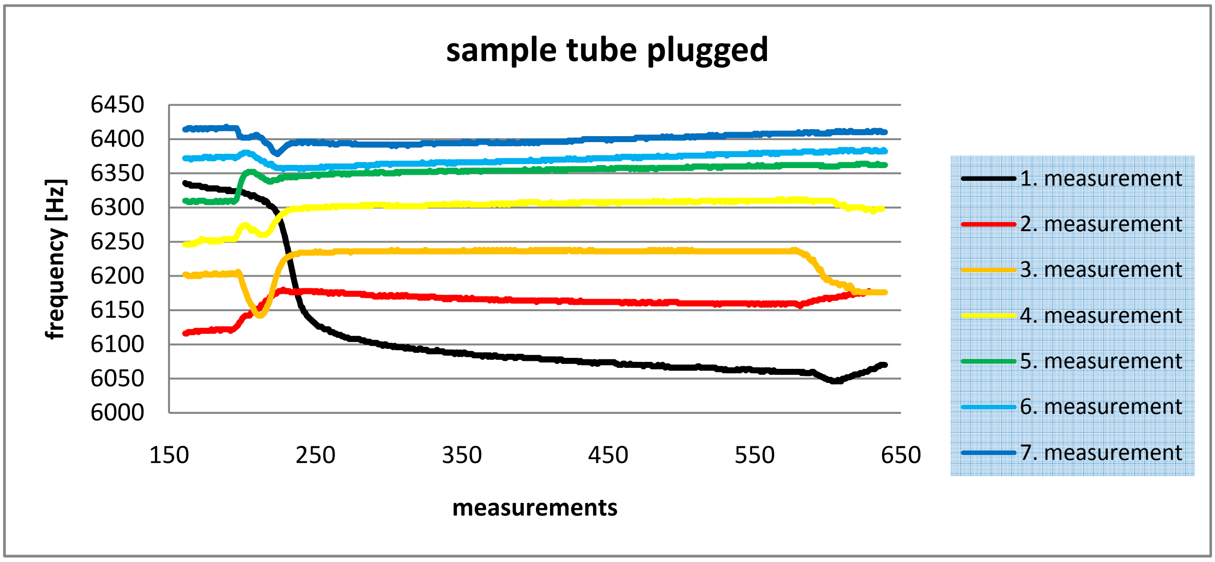
Figure 27: Visualization of the measurements included in the calcul the plateau frequency

Comparison of no concentration and no sample

This experiment shows the limits of the failure identificat curve. In this case the frequency curves of the two fai greatest difference between the both failures varies arou of the failure by using pattern recognition will not be poss be necessary to clearly identify the failure.

Measurement at higher concentration

The experiment with the high phosphorus concentration evaluation of the frequency curve as well. Software n frequency curve. Then the point when the steady state is Especially when the phosphorus concentration is close to range the mixture needs more time until all of the phosph



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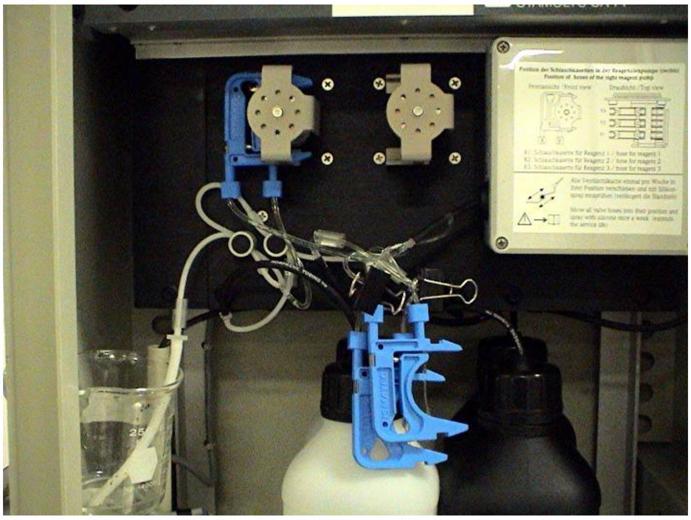

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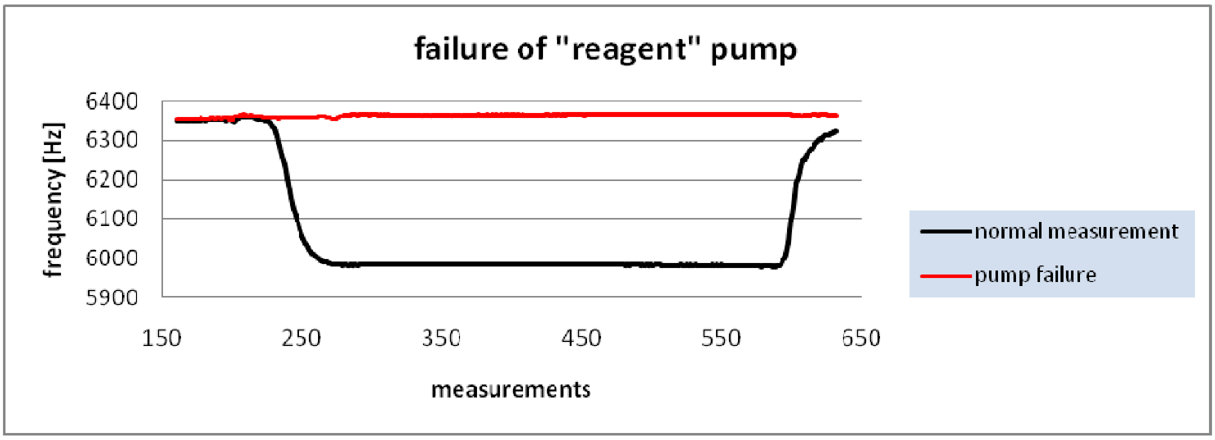

Figure 15: Simulation of a “reagent“-pump break down

4.4 No reagent PH-A1/PH-A2

It is possible that the tube of one reagent is clogged, buckled or bent and subsequently the reagent is not mixed with the sample. To examine this effect the tube of reagent PH-A1 was pinched off and the tube cast was hanged off (Figure 16). Then the measurements were taken. In between the experimental repetitions a normal measurement cycle was performed. The same experimental procedure was repeated with reagent PH-A2.

Figure 16: Simulation of a clogged reagent PH-A1 tube (similar buildup for reagent PH-A2)

A clogged reagent tube, an empty reagent canister or a bent tube can reduce the reagent supply. Hence, the reaction will be disturbed. The frequency curve shows a delayed S-shaped reaction curve (Figure 17). The first measurement is still close to a normal measurement, because there is still some sample left in the tube. The following measurement cycles show a delayed reaction. The delay increases with every measurement cycle because with every cycle fewer reagent is left in the system. Not only is the reaction curve delayed. The further development of the curve is disturbed as well. The curve does not reach the steady state for a sufficient time.

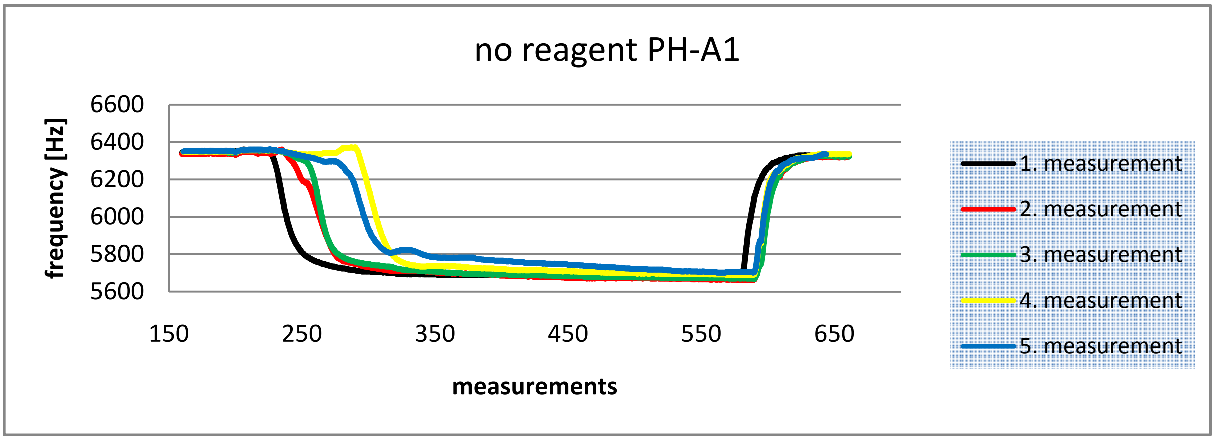

Figure 17: Reduced reactivity through excluding reagent PH-A1 from the mixture

Even though a malfunction is certainly affecting the analyzer, the measured concentrations in this experiment were not far off the real value (Table 4). The reaction with the phosphor takes place but is slowed down.

Table 4: Comparison of the measured concentrations of a normal measurement and a measurement with a clogged PH-A1 tube

experiment	concentration (normal measurement)	concentration (clogged tube PH-A1)	difference	accuracy (%)
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	1.07	1.11	0.04	96.4
	1.07	1.08	0.01	99.1
96-100	1.62	1.66	0.04	97.6
	1.62	1.75	0.13	92.6
	1.62	1.65	0.03	98.2
106-109	1.63	1.7	0.07	95.9
	1.63	1.67	0.04	97.6
	1.63	1.68	0.05	97.0
66-70	2.16	2.17	0.01	99.5
	2.16	2.11	-0.05	97.7
	2.16	2.06	-0.1	95.4
71-75	2.19	2.16	-0.03	98.6
	2.19	2.11	-0.08	96.3
	2.19	2.13	-0.06	97.3

The experiment was then repeated with the reagent PH-A2. The experimental setup and procedure was similar to the previous experiment with the exception, that the hose box of reagent PH-A2 was now hanged off the pump and pinched off (Figure 16). The first measurement cycle of this experiment is still close to a “normal” development because there is still some reagent left in the system. The frequency curves 2-4 don’t show the characteristic reaction curve. The curve can be described as an almost linear line with a negative slope. After repeating the experiment a decrease of the curves slope was visible until the curve reached an almost horizontal line (Figure 18).

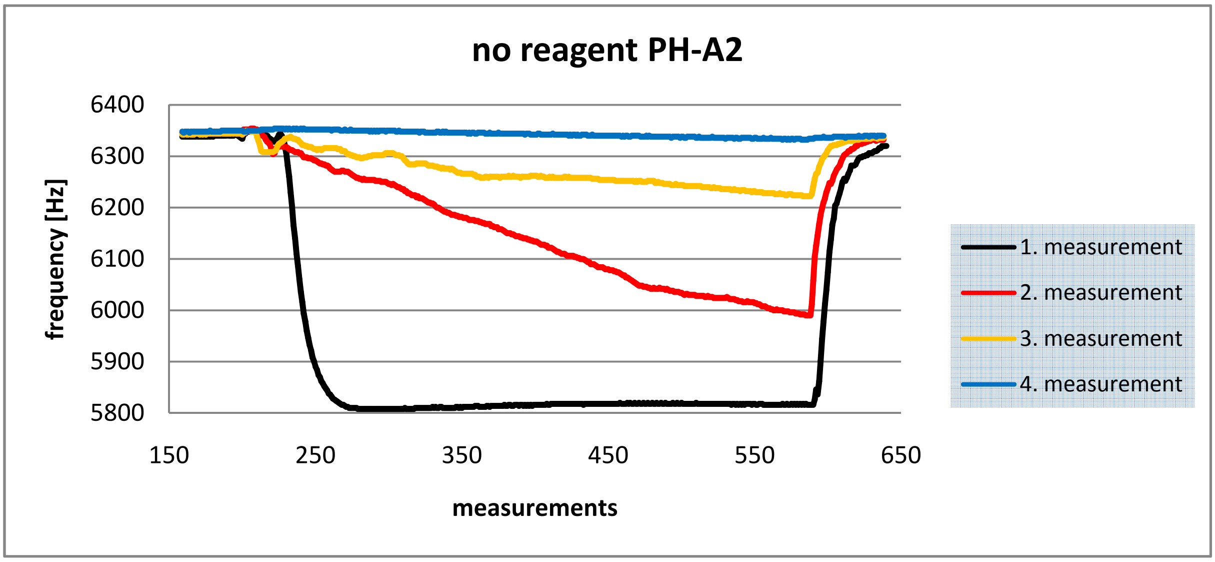

Figure 18: Loss of characteristic reaction curve through pinching off reagent PH-A2

4.5 Air bubbles in the system

Air bubbles can cause inaccuracies during the measurement. To examin the effects of air bubbles and the possibility of detection during the measurement air bubbles were intentionally introduced to the system. The injection of air was done with a medical injection needle. To know exactly when the air bubble passes through the measuring cell the tube right before the measuring cell was chosen to be pierced through (Figure 19).

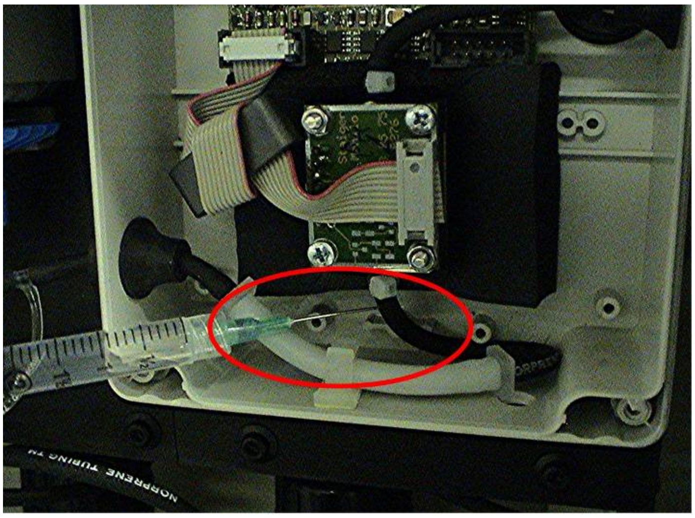

Figure 19: Injection of air bubbles into the analyzers system

Air bubbles in the analyzer’s system cause a specific change of the frequency curve, as soon as the air passes through the measuring cell (Figure 20). The air affects the curve only for a few measurements. As soon as the air passed through the measuring cell, the curve returns to its normal development. The result of this experiment is that air bubbles can be identified by the significant shape of the frequency curve. They only cause negative effects on the measurement when they appear during the measurement of the basis frequency or the plateau frequency. Air bubbles that appear during the reaction time do not affect the measurement. Only in the improbable case that an air bubble get caught in the measuring path a permanent affect on the measurement is likely.

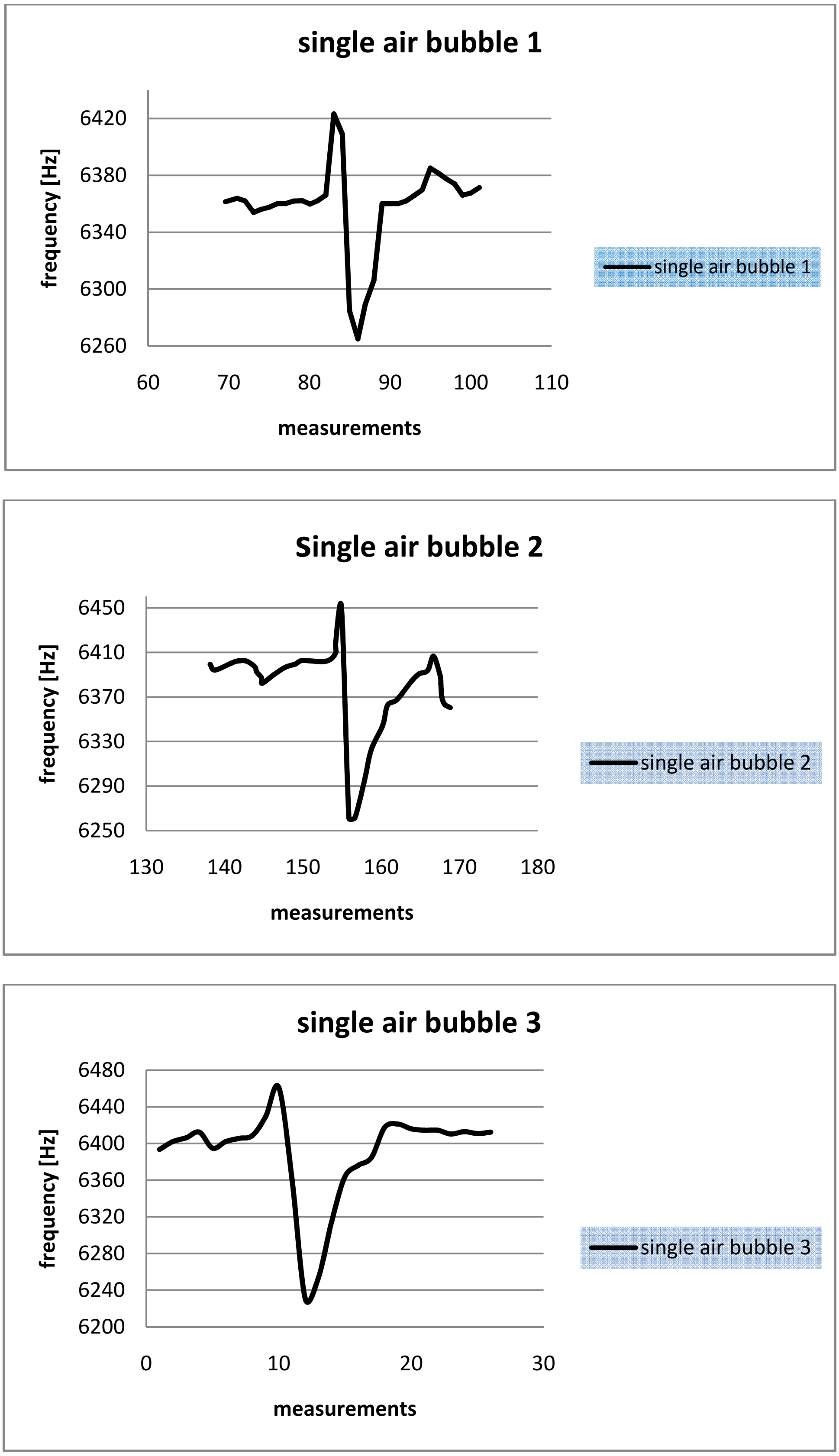

Figure 20: Typical pattern in the frequency curve, caused by air bubbles

4.6 Comparison of “no concentration” and “no sample”

It is possible that two different failures can cause the same behavior in the frequency curve (e.g. a plugged sample tube and a measurement at zero concentration). Since plugging the sample tube caused an almost horizontal development of the frequency curve a second experiment with nano-pure water (0 mg/l PO_4-P) is necessary to find out if there is a measurable difference between those two conditions. Besides the sample, the setup of this experiment does not differ from the “normal measurement”.

Figure 21 compares the results of both experiments. The red curves are the result of the experiments without sample and the blue curves are the result of samples with 0.00 mg/l PO_4-P. Both experiments show similar curves. The differences vary between 0 and 50 Herz.

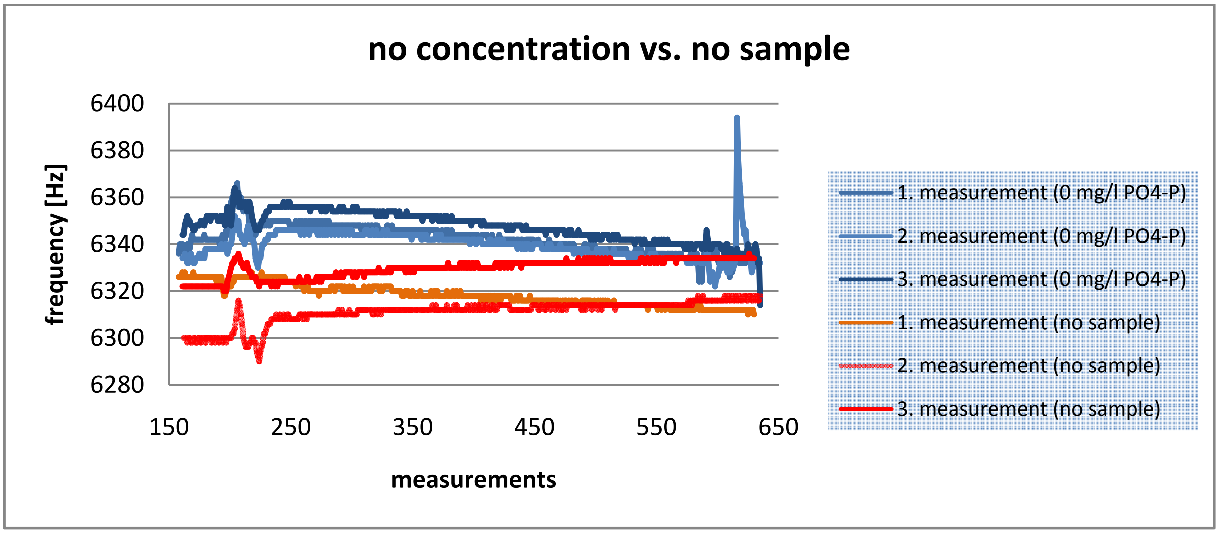

Figure 21: Comparison of measurements with 0 mg/l PO_4-P (blue) and measurements without sample (red)

4.7 Measurement at higher concentration

The calibration of an analyzer is done with a concentration in the middle of the meauring range. Therefore, the closer the samples concentration is to the concentration of the calibration standard the more accurat the measurement will be. The further the concentration to be measured is away from the concentration of the calibration standard the lower the accuracy will be.

To examine the accuracy of the measurement at the limit of the measurable range, sample with a concentration of 2.45 mg/l PO_4-P was created and a testing series was performed. With rising phosphorus concentration the mixture needs more time to reach a steady state. To examine whether an extension of the reaction time increases the accuracy of the measurement, this test was repeated with a reaction time of 360 seconds, 480 seconds and 600 seconds (Figure 22).

The first measurement of this testing campaign was done with the pre-defined reaction time of 360 seconds. The reaction time of 360 seconds did not allow the frequency curve to reach a steady state. This was proven by the experiments with the increased reaction time. After 360 seconds the frequency curve was still in its development and reached the steady state after 480 seconds. An increase of the reaction time gives the mixture more time to reach and stay in the steady state.

Is the concentration after 360 seconds already higher than 2.45 mg/l PO_4-P an increase of the reaction time will not be able to increase the accuracy. In this case the problem lies in the accuracy of the measuring cell and is not caused by an unfinished chemical reaction.

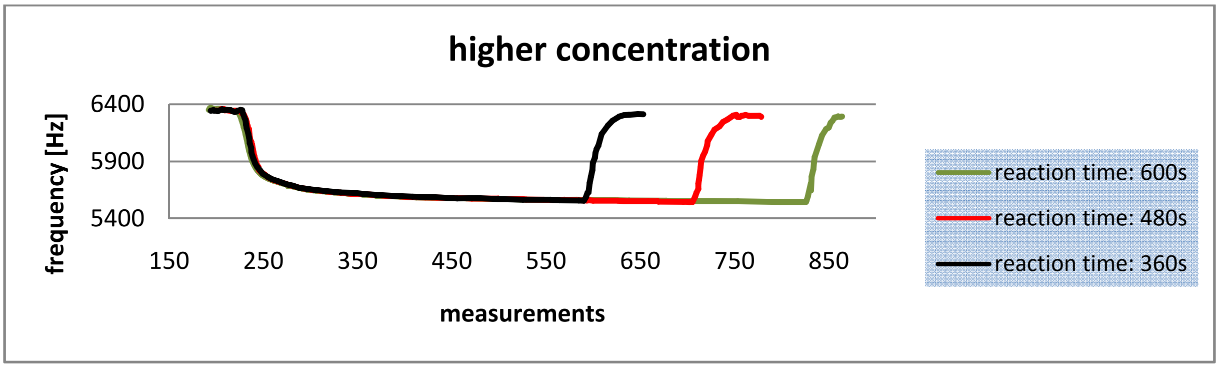

Figure 22: Comparison of three measurements (all with a concentration of 2,45 mg/l PO_4-P) with different reaction times

5 Assessment of steady state trend behavior

The development of a program that computes if the steady state of the frequency curve is reached will be the focus of this chapter. The program is based on the Matlab software (The MathWorks Inc.) and it is created to optimize the duration of measurement cycles. Especially when the concentration to be measured is close to the limit of the measurable range the time until the steady state is reached varies heavily. For low phosphorus concentrations the default reaction time of 360 seconds can be too long because the reaction is completed earlier. For high concentrated samples this reaction time might not provide enough time to reach and stay in the steady state. With this program the reaction time will be adjusted to the condition of the mixture.

The program uses the data of the frequency curve. It takes the measured frequencies during a time frame of 60 seconds and tries to fit two models to the data, a simple constant mean model (one parameter) and a more complex linear trend model (two parameters). For both models the sum of squared residuals will be calculated (Hastie, 2001). The sum of squared residuals is a measure for the deviation of each model from the data set.

$$y = const. + measurements \qquad SSR = \sum_{i=1}^{n} (xpred - y)^2$$

Since one model is more complex than the other it is not possible to decide for the best model on the sum of squared residuals alone. Any method to compare a simple model with a more complex model has to evaluate whether the reduced sum of squared residuals with the more complex model warrants the increased number of parameters, i.e. increased complexity of the model.

To decide which model is appropriate the F-test is used in this work (Johnson, 2002). The F-test requires on the following two assumptions which have been fulfilled:

- Normal distribution of measurement errors
- Independently and identically distributed measurement errors

The F-test is a statistical test in which the test statistic has an F-distribution if the null hypothesis (complex model does not fit significantly fit better than the simple model) is true (Lomax, 2007). In this test the observed F-value and the critical value of F at 95% probability level are compared.

$$F = \frac{\frac{(RSS1 - RSS2)}{p2 - p1}}{\frac{RSS2}{n - p1}}$$

Is F is larger than F_{crit} then the null hypothesis is rejected and the complex model is considered to fit the data significantly better. The reaction of the mixture is considered not to be finished and the regression line of the frequency data is considered linear. Is F smaller or equal to F_{crit}, then the complex model is considered not to fit the data significantly better than the simple one. Therefore the regression line of the data set is considered to be flat and the reaction of the mixture is considered to be finished.

To give an example of how the program works and to express the necessity of this software development, two examples will be given. The first example shows a normal frequency curve (Figure 23). The steady state is reached long before the end of the reaction time. With the default setup of the reaction time the analyzer waits for six minutes until it measures the concentration. In this case only two minutes are needed until the reaction of the mixture is completed.

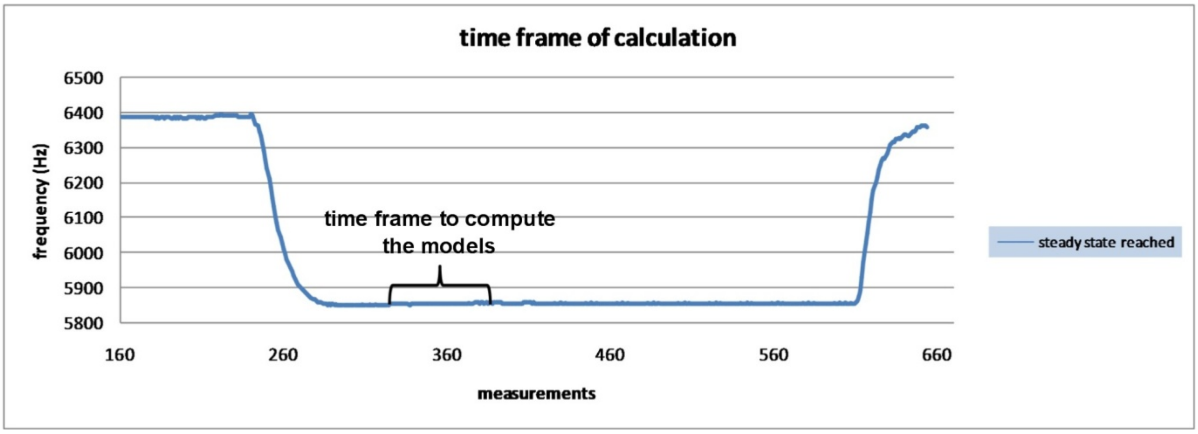

Figure 23: Shows the time frame (on a normal frequency curve) that is used to compute the models. The data that is taken during that time will be implemented in the program and compared to the models

The program follows the frequency curve and uses the data that is taken within the time frame for its calculation. To every set of data it calculates the two models and tries to fit the models to the data. Figure 24 shows the result of the calculation. The red line displays the data that is measured within the time frame. The blue line represents the constant mean model and the green line represents the linear trend model.

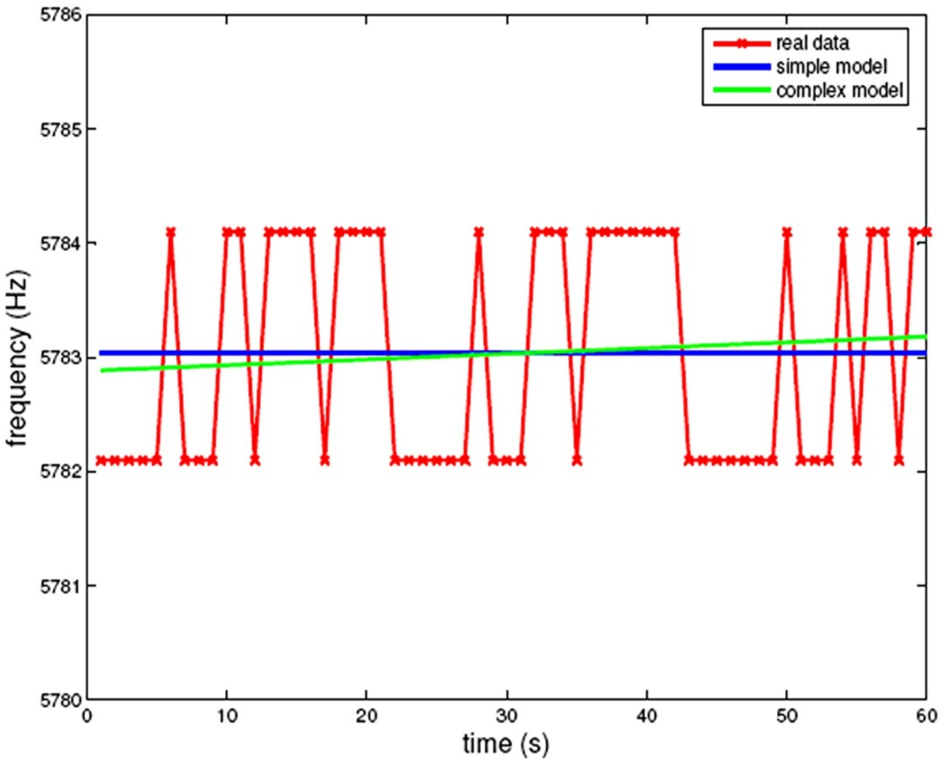

Figure 24: Comparison of the two models with the data of the horizontal frequency curve (red displays the real data; blue displays the simpler model; green displays the more complex model)

By using the F-statistic the matlab based program compares the real data to the two models. It first calculates the sum of squared residuals for both model and then it computes the F-test to detect which model fits significantly better to the real value (Table 5). Here, F is smaller than F_{crit}. This leads to the conclusion that the complex model does not fit significantly better. A horizontal development of the frequency curve is an indicator for a completed reaction of the mixture. Since the complex model does not fit the real data significantly better than the simple model, the regression line of the real data is considered to be horizontal. Therefore, the reaction is considered to be completed.

Table 5: Results of computing the data of a horizontal frequency curve

b=1.0e+003*	5,7829	mean value
	0,0000	
ssr=1,0e+003*	59,7333	
	59,2832	
F	0,4328	
F_{crit}	4,0065	

The following result will be displayed by the program:

use simple model: 1 parameter -> constant -> flat

In the second example the pre-defined reaction time is not sufficient for the mixture to reach the steady state (Figure 25). Due to the default setup of the reaction time the analyzer will measure a concentration, even though the stable state is not reached. The result will therefore be not accurate and worthless.

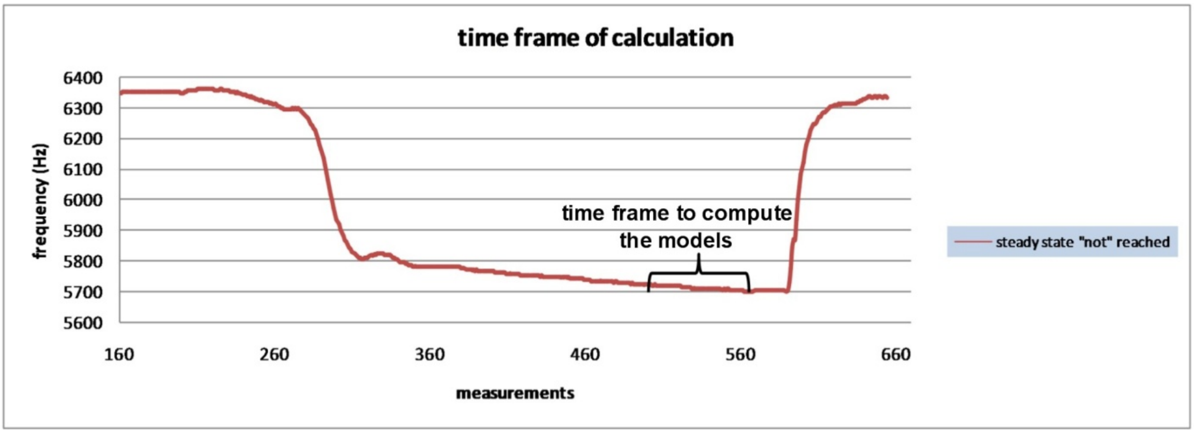

Figure 25: Shows the time frame (on a disturbed frequency curve) that is used to compute the models. The data that is taken during that time will be implemented in the program and compared to the models.

As well as in the previous example the program will compare the measurements of the time frame to the two models. Figure 26 displays a comparison of the models (green line: complex model, blue line: simple model) with the real data (red line).

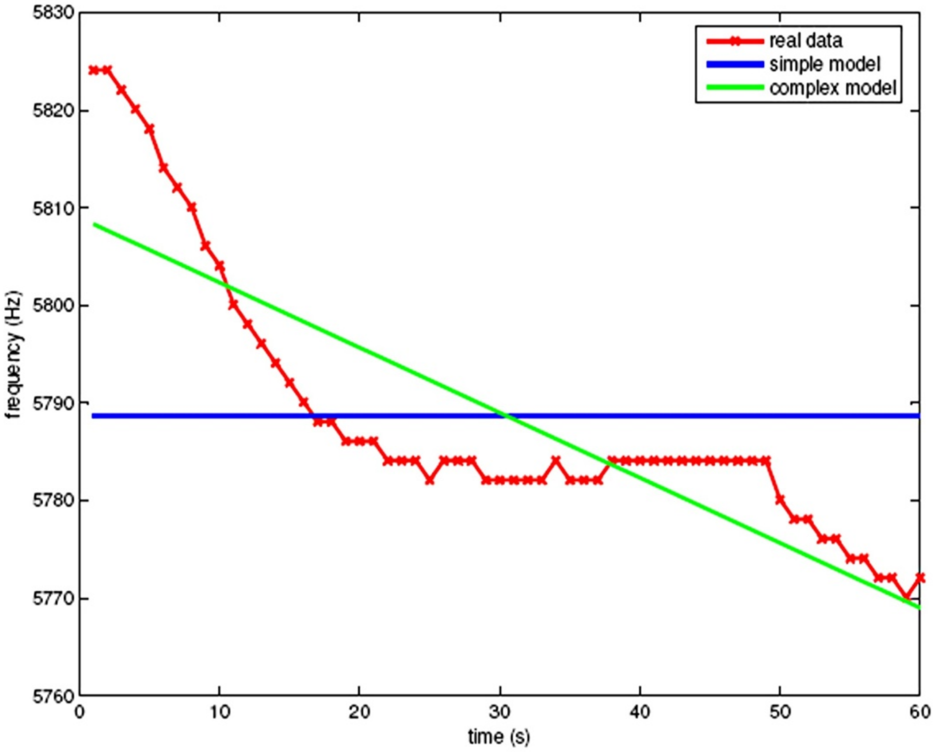

Figure 26: Comparison of the two models with the data of the disturbed frequency curve (red displays the real data; blue displays the simpler model; green displays the more complex model)

The program calculates the sum of squared residuals and uses the F-test to compare which model fits significantly better to the real data again. Since F is greater than F_{crit} (Table 6), the complex model is considered to significantly fit the data better.

Table 6: Results of computing the data of a disturbed frequency curve

b=1.0e+003*	5,8090	intercept
	-0,0007	slope
SSR=1,0e+004*	1,1009	
	0,3011	
F	152,4356	
F_{crit}	4,0065	

The program computed that the data significantly fits better to the linear trend model than to the constant mean model. Therefore the regression line is considered to have slope and not to be horizontal. This is displayed by the program as follows:

use complex model: 2 parameters -> linear trend -> not flat

In this case the program should increase the reaction time to give mixture more time to reach the steady state. Only if the steady state has been reached, the measured concentration is a reliable and worthy piece of information.

After first trials the program seems to work but further development is needed to improve the software. It is for example possible that noise effects measurement and leads to aberrances. Since the program in its current version simply fits the models to the frequency curve it is possible that in this case the complex model does not fit better and the frequency curve is considered to be horizontal, even though it is not. For those cases the program needs further development so that it is able to recognize noise that affects the frequency curve.

6 Discussion

Plugged sample tube

With the detection methods currently used, the first measurement of the plugged sample tube would not have been recognized as a failure. The final result is within the measurable range (concentration: 0.75 mg/l PO_4-P). Only by evaluating the frequency curve this kind of abnormality can be recognized directly. The characteristic that can be recognized is the loss of the charcteristic curve during the flushing process within the first measurement cycle and the horizontal development of the frequency curves of the following measurement cycles. The frequency with the horizontal development rises with every measurement cycle. That is because with every measurement cycle only the reagents are flushed through the system. With every cycle less phosphorus sample that can react with the reagents is left in the system. Step by step it gets pumped out of the system. After the seventh step only reagent is left in the system. With the appropriate analyzing software it should be possible to detect this type of failure.

The measurement cycle is divided into 8 phases. As soon as an abnormality of the frequency curve is detected, software could identify the phase where the problem appeared. Referring to the experiment with the plugged sample tube the software could relate the problem to phase 8 (flushing). This delivers more detailed information for the failure-isolation.

Reagent pump failure

The detection of a reagent pump failure seems to be an easy task because the curve differs strongly from the normal frequency curve. But the experiment with a 0.00 mg/l PO_4-P solution has shown that both curves are very similar. With the information of the frequency curve only it is not possible to make a difference between a 0.00 mg/l PO_4-P solution and a reagent pump failure. For this problem further information is needed. The already available signal from the inlet level meter can give the necessary information to decide between the problems. More precise information about the pump rotation is helpful. At the moment only the set pump rotation can be read out. The possibility to read out the real time pump speed has to be checked (see Outlook).

No reagent PH-A1

The experiment with the blocked reagent PH-A1 is a good example of the importance of evaluating the frequency curve. With the current setup this malfunction would not be recognized. The results can be far off the real concentration but since they are in the measurable range no warning signal will be sent. The evaluation of the frequency curve offers two ways to detect this failure. Firstly the delayed reaction can be detected by comparing the curve with a normal frequency curve. The second indicator is that the steady state is not reached. A small program can be implemented that checks whether the curve reached a steady state (horizontal line). If the steady state is not reached the reaction time can be extended to give the mixture the chance of further reaction.

No reagent PH-A2

The experiments with the clogged PH-A2 tube underline the importance of the frequency curve. As shown in the results the frequency curve did not show the typical behavior but a line with a negative slope. The measured results were significantly lower than the real concentration or were shown as 0.00 mg/l PO_4-P. Under field conditions and by just paying attention to the final results it would be difficult to detect the failure. However, with the additional information of the frequency curve a deviation from the typical frequency curve can be detected. Since the characteristics of the curve can only be caused by this failure the reason for this malfunction can be detected. In this experiment again the steady state of the frequency curve was not reached. Since the reaction was not finished, the result can be judged as not valid.

Air bubbles in the system

Air bubbles in the analyzer’s system are not comparable to the failures of the previous experiments. In terms of the measured concentration air bubbles only cause diverging results when the bubble travels through the measuring cell during the measurement of the basis- or the plateau frequency. If bubbles appear during the reaction time the final result will not be affected. Bubbles can also be an indicator for a leaking tube. Therefore the appearance of bubbles should not be seen as an acceptable status. The basis- and the plateau frequency are the result of the average of five measurements (Figure 27). This reduces the influence of outliers. According to the experiments it should be possible to define a typical pattern and subsequently automatically detect air bubbles. Another way to detect air bubbles could be to check for an increased noise during a limited period of time.

A detection of air in the analyzer’s system should lead to maintenance but the measurements during that time are not worthless as long as air bubbles do not appear during the measurements of the plateau or basis frequency.

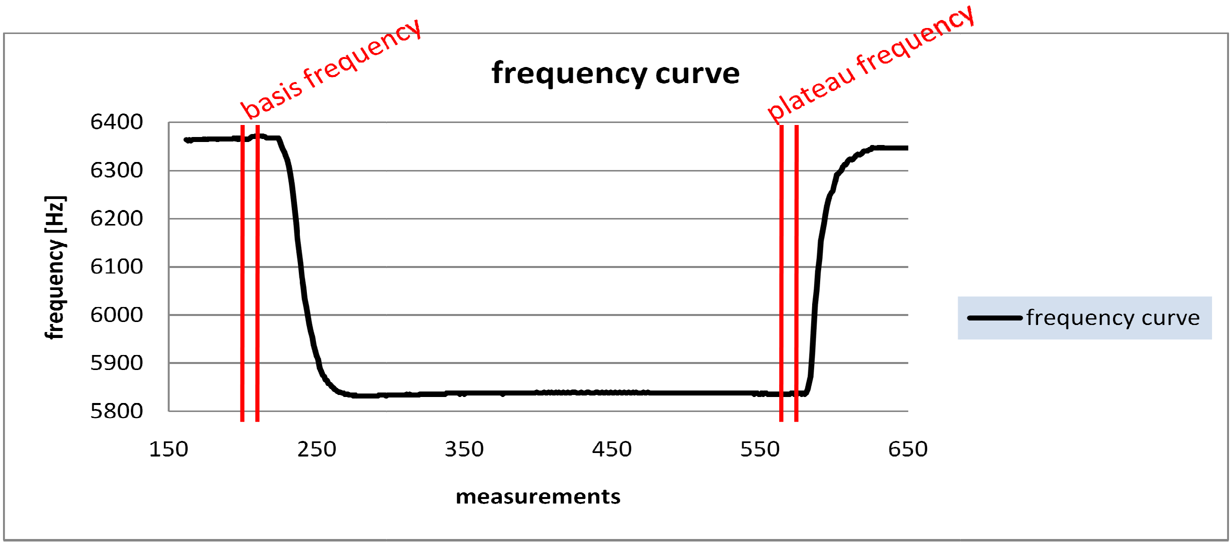

Figure 27: Visualization of the measurements included in the calculation of the basis frequency and the plateau frequency

Comparison of no concentration and no sample

This experiment shows the limits of the failure identification based on the frequency curve. In this case the frequency curves of the two failures are very similar. The greatest difference between the both failures varies around 50 Hz. The identification of the failure by using pattern recognition will not be possible. Further information will be necessary to clearly identify the failure.

Measurement at higher concentration

The experiment with the high phosphorus concentration shows the necessity of the evaluation of the frequency curve as well. Software needs to keep track of the frequency curve. Then the point when the steady state is reached can be identified. Especially when the phosphorus concentration is close to the limit of the measurable range the mixture needs more time until all of the phosphor reacts with the reagents.

7 Concept

7.1 Sensor self-diagnosis

Sensor self-diagnosis is the ability of a technical device to check its current state. The momentary state of the phosphorus analyzer (Stamolys PH 71 CA) in terms of its ability to run a self-diagnosis is very limited. It is able to detect some basic malfunctions like being out of the measuring range or if a pre-set value is crossed. The liquid sensor can cause the analyzer to completely shut down if liquids are leaking into the analyzer. These already available signals are the first step to an automated sensor self-diagnosis but this information delivers not enough data to get a reliable impression of the analyzer’s current state.

The analyzer in combination with sufficient readout software is able to deliver more information. Reading out the frequency curve can be used to detect abnormalities from the “normal” course of the curve. Pattern recognition can be used to detect typical patterns of a malfunction. Through a logical comparison of the measurement mode, the calibration mode and the cleaning mode single parts of the analyzer can be isolated and finally identified as the cause of the malfunction.

With the validation of the frequency curve information can be gathered that give hints whether the reaction curve took a normal development or if there were some abnormalities during the measurement. In some cases the final measurement can accidently be right, but by taking a closer look at the frequency curve it becomes clear that there must be a malfunction in the system. One example is air bubbles in the tube system. When air bubbles pass through the measuring cell the course of the frequency curve turns into a significant zigzag pattern. The appearance of this specific pattern during the reaction time would not affect the measured concentration. It would be a sign that there is air in the system that could cause problems.

The second signal that could be used to develop the sensor self-diagnosis is pattern recognition. Some malfunctions cause a specific pattern in the frequency curve. With pattern recognition, those curve developments can be recognized and the failure can be diagnosed directly.

The comparison of the three modes (measurement mode, calibration mode, cleaning mode) and any additional signals of the phosphorus analyzer can also deliver valuable information about the current state. Therefore a matrix was developed which lists up the modes with the phases on the y-axis and the spare parts on the x-axis (Table 7). An X marks in which phase a certain part is used. This matrix is the basis of the concept for fault isolation.

Table 7: Matrix describing which part is used in the single phases

			inflow	flowmeter	Valve V1	Valve V2	sample pump (P1)	cleaning solution	cleaner canister	standard 1 solution 1,5 mg/l	standard 1 canister	123-a, C-Flex hose, 1,5 mm	123-b, C-Flex hose, 1,5 mm	123-c, C-Flex hose, 1,5 mm	123-d, C-Flex hose, 1,5 mm	123-e, C-Flex hose, 1,5 mm	123-f, C-Flex hose, 1,5 mm	123-g, C-Flex hose, 1,5 mm	123-h, C-Flex hose, 1,5 mm
Measurement	**Phase 1** Flushing (Sample)	**3x15**	×		×	×	×						×	×		×			×
	Phase 2 Delay to sample	**20 - 999**	×		×	×	×					×		×					×
	Phase 3 Stabilization	**8**																	
	Phase 4 1. Measurement (basis)																		
	Phase 5 Fill mixture	**30**	×		×	×	×					×		×			×	×	×
	Phase 6 Reaction	**360**																	×
	Phase 7 2. Measurement (plateau)																		
	Phase 8 Flushing (Sample)	**30**	×		×	×	×					×		×					×
Calibration	**Phase 1** Flushing (Standard)	**3x15**			×	×	×			×			×	×		×			×
	Phase 2 Delay to standard	**20 - 999**			×	×	×			×			×	×		×			×
	Phase 3 Stabilization	**8**																	
	Phase 4 1. Measurement (basis)																		
	Phase 5 Fill mixture	**30**			×	×	×			×			×	×		×	×	×	×
	Phase 6 Reaction	**360**								×									×
	Phase 7 2. Measurement (plateau)																		
	Phase 8 Flushing (Sample)	**20**	×		×	×	×					×		×					×
Flushing (Cleaning)	**Phase 1** Pump cleaning solution	**1/2 flushing duration**			×	×	×	×					×	×	×				×
	Phase 2 Allow to react	**5**			×	×	×	×					×	×	×				×
	Phase 3 Pump cleaning solution	**1/2 flushing duration**			×	×	×	×					×	×	×				×

			120-1, neopren hose, 1,6 mm	120-2, neopren hose, 1,6 mm	120-3, neopren hose, 1,6 mm	120-4, neopren hose, 1,6 mm	120-5, neopren hose, 1,6 mm	hose connector	T-hose connector	reagent pump (P2)	static mixer	reagent 1 solution	reagent 1 canister	reagent 2 solution	reagent 2 canister	photometric cell	outlet	143, leak sensor for collecting tank
Measurement	**Phase 1** Flushing (Sample)	**3x15**	×			×		×	×							×	×	
	Phase 2 Delay to sample	**20 - 999**	×					×	×							×	×	
	Phase 3 Stabilization	**8**																
	Phase 4 1. Measurement (basis)															×		
	Phase 5 Fill mixture	**30**	×	×	×			×	×	×	×	×		×			×	
	Phase 6 Reaction	**360**										×		×				
	Phase 7 2. Measurement (plateau)															×		
	Phase 8 Flushing (Sample)	**30**	×					×	×							×	×	
Calibration	**Phase 1** Flushing (Standard)	**3x15**	×			×		×	×							×	×	
	Phase 2 Delay to standard	**20 - 999**	×			×		×	×							×	×	
	Phase 3 Stabilization	**8**																
	Phase 4 1. Measurement (basis)															×		
	Phase 5 Fill mixture	**30**	×	×	×	×		×	×	×	×	×		×		×	×	
	Phase 6 Reaction	**360**										×		×				
	Phase 7 2. Measurement (plateau)															×		
	Phase 8 Flushing (Sample)	**20**	×					×	×							×	×	
Flushing (Cleaning)	**Phase 1** Pump cleaning solution	**1/2 flushing duration**	×				×	×	×							×	×	
	Phase 2 Allow to react	**5**	×				×	×	×							×	×	
	Phase 3 Pump cleaning solution	**1/2 flushing duration**	×				×	×	×							×	×	

If the result of a measurement seems not to be reliable the calibration mode or the cleaning mode could be started to test the functionality of the modes. Is the functionality of the cleaning mode or the calibration mode sufficient but the measurement is not the number of parts that could cause this malfunction will be limited.

Is the sample tube clogged, no sample can be pumped into the measuring cell. The frequency curve would narrow its course through several steps to a flat line. The final concentration will then always be 0.00 mg/l PO_4-P. If this happens, the analyzer detects that something is wrong. For this case, with the strategy of logical comparison of the modes the analyzer can point out the spare part that causes the malfunction. After the detection of a malfunction during the measurement mode the analyzer runs the calibration mode. The calibration and the measurement are very similar processes. Most parts that are used during measurement will also be used during calibration. Only two parts are used for the measurement but not for the calibration (Table 8).

Table 8: Comparison of used parts during measurement mode and calibration mode

	inflow	Valve V1	Valve V2	sample pump (P1)	cleaning solution	cleaner canister	standard 1 solution 1,5 mg/l	standard 1 canister	123-a, C-Flex hose, 1,5 mm	123-b, C-Flex hose, 1,5 mm	123-c, C-Flex hose, 1,5 mm	123-d, C-Flex hose, 1,5 mm	123-e, C-Flex hose, 1,5 mm	123-f, C-Flex hose, 1,5 mm	123-g, C-Flex hose, 1,5 mm	123-h, C-Flex hose, 1,5 mm	120-1, neopren hose, 1,6 mm	120-2, neopren hose, 1,6 mm	120-3, neopren hose, 1,6 mm	120-4, neopren hose, 1,6 mm	120-5, neopren hose, 1,6 mm	hose connector	T-hose connector	reagent pump (P2)	static mixer
mesurement	x	x	x	x					x	x	x		x	x	x	x	x	x	x	x		x	x	x	
calibration		x	x	x			x			x	x		x	x	x	x	x	x	x	x		x	x	x	

Since the problem lies in the sample tube, the calibration will not be affected. The calibration will therefore measure the right concentration of the standard solution (Figure 28).

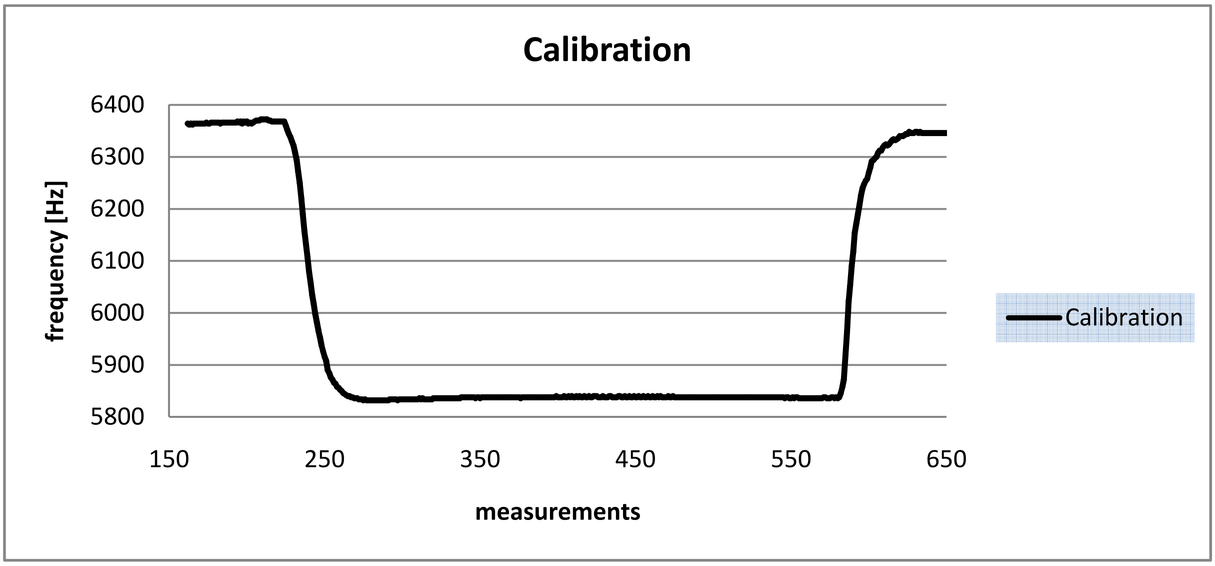

Figure 28: Calibration curve with normal development

When the calibration delivers the expected result all the parts that are used for both modes (calibration and measurement) can be ruled out of the list of parts that could cause the problem. In this case, there are only two spare parts left that could cause the malfunction (Table 8). One possibility is that no sample is available. The second possibility is that the sample tube is clogged. The analyzer is equipped with an inlet level meter. This inlet level meter collects the sample in a funnel shaped vessel and signalizes the analyzer when enough sample is available. In this experiment the level meter signalized that there is enough sample available to run a measurement. This leads to the conclusion that only one spare part could have caused the malfunction, the sample tube.

The comparison of the modes does not always lead to the broken part. For example, if the malfunctioning part is used for all three modes the comparison of the modes will not automatically lead to the broken spare part. For those cases additional signals a necessary.

With the knowledge of all available signals and all potential signals a concept needs to be developed that structures the procedure of fault detection, fault isolation and fault identification (Figure 29).

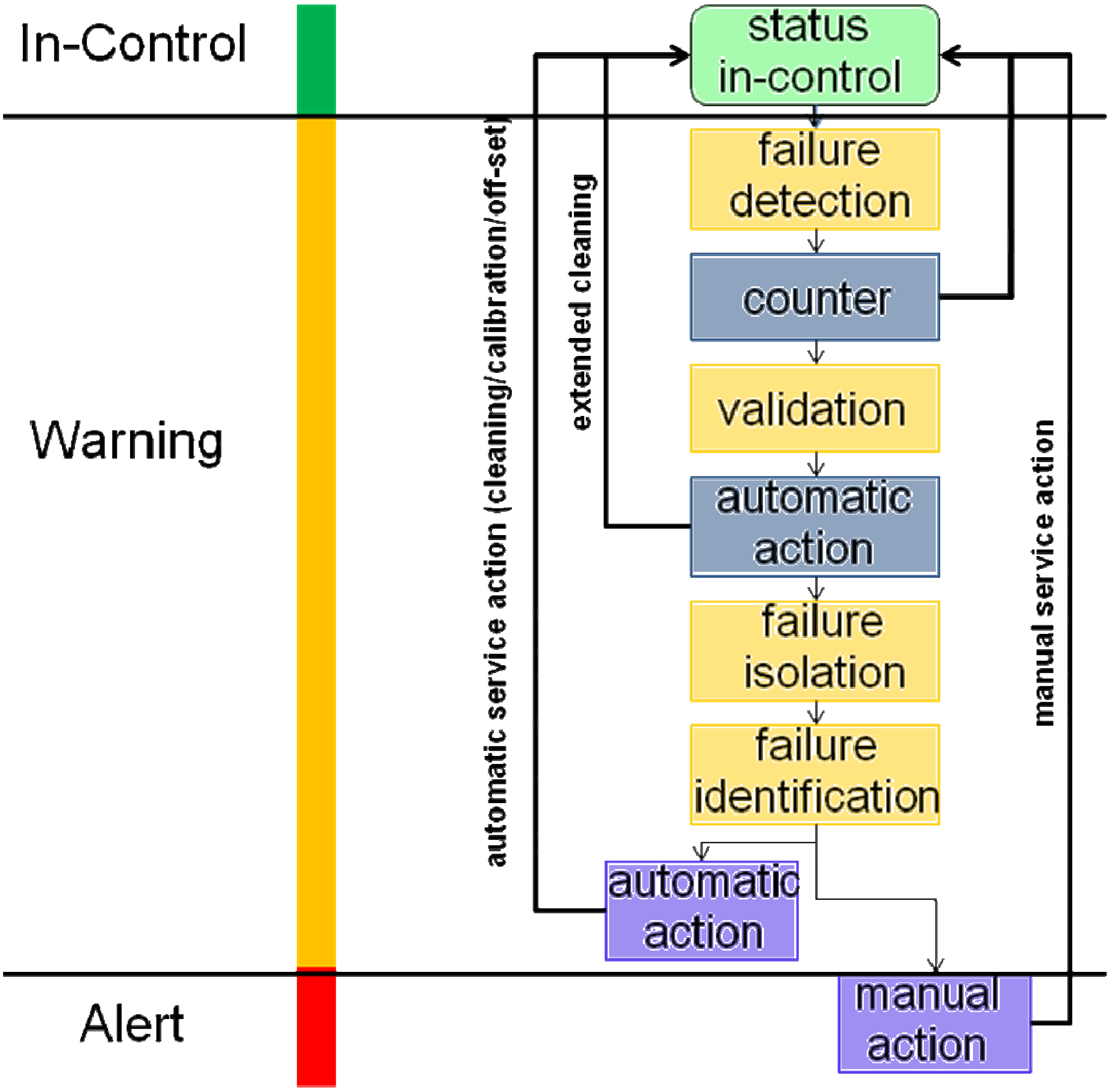

Figure 29: Concept of sensor self-diagnosis, including warning messages

As long as no problem occurs the analyzer runs the In-control status. The system is running smoothly and no maintenance is needed.

When the analyzer detects an abnormality during one measurement it automatically repeats the measurement cycle to check whether the abnormality was a single incident (outlier) or if there is a real problem. Once a failure is detected the analyzer leaves the In-control status and switches to the warning status. The change from In-control to warning is visible for the maintenance staff but it does not automatically lead to a manual service action. The failure has to be identified first. To prevent that the concept gets stuck in a loop between failure detection and the In-control status a counter was implemented. If the analyzer gets caught in a loop the analyzer recognizes this and judges a repetition of two times as a failure. Is the analyzer certain that there is a malfunction the failure is deemed to be validated.

An extended cleaning cycle will be run to try to flush the failure out of the system. If the failure is still present, the next step will be the isolation. The concept uses the comparison of the functionality of the modes (logic), pattern recognition and the evaluation of the frequency curve to isolate the malfunctioning part.

The next step will then be the failure identification. Here, the system searches for the reason why the failure occurred. For this, all spare parts, used in the analyzer were separated into classes (tubes, pumps, etc). Then a matrix for each class was created, which lists up all possible reasons why a spare part of this group could break down (Table 9). With the matrices the concept tries to rule out failures that could not appear. For example, when the leakage sensor does not detect liquids within the analyzer then the concept can rule out a broken/leaking tube as the cause of the malfunction. With the process of elimination and by considering all available signals the concept tries to identify the actual cause of the failure.

Table 9: Example of a list of possible failures (Possible tube failures)

C-Flex hose	broken/leaking	wrong hose (diameter/consistancy)	plugged	polluted	change of consistance
123-a, C-Flex hose, 1.5 mm					
123-b, C-Flex hose, 1.5 mm					
123-c, C-Flex hose, 1.5 mm					
123-d, C-Flex hose, 1.5 mm					
123-e, C-Flex hose, 1.5 mm					
123-f, C-Flex hose, 1.5 mm					
123-g, C-Flex hose, 1.5 mm					
123-h, C-Flex hose, 1.5 mm					

If the failure can be identified and if it is possible to remove it automatically the analyzer will remove the failure with an automatic service action (e.g.: re-calibration, off-set, etc.). If an identification of the failure is not possible or if the failure is identified but impossible to remove automatically the system will change to the alert status and a manual service action should be carried out. The system will be reset to the In-control status after the service action is finished.

7.2 Maintenance

The field of maintenance can be subdivided into two types of maintenance work (WEF, 2007). There is the repetitive (preventive) maintenance and the non-repetitive (corrective) maintenance (Table 10).

Table 10: Comparison of preventive and corrective maintenance (WEF, 2007)

Preventive	Corrective
• extends the lifespan and the efficiency of equipment • retards equipments deterioration via: o regular inspections o routine maintenance o parts replacements o calibration o statistical performance monitoring techniques	• fixes broken component

Corrective maintenance is still a common maintenance strategy. This strategy contains a reactive action (simply fix the broken parts after a malfunction). A second commonly used maintenance strategy is the “blindly proactive” action (exchange spare parts in a certain cycle before breakdowns are expected) (Lee et al., 2006). Both strategies have severe weaknesses. When using the reactive maintenance strategy a high frequency of breakdowns and high labor costs must be considered. Also, since most spare parts do not suddenly break down, but slowly affect the measurements while their state decreases, the negative effects on the measurement will probably not be detected. Hence, the measurements have an unknown accuracy and loose their value for the costumer.

The main disadvantages of the “blindly proactive” maintenance strategy are the high costs for the spare parts (also well functioning spare parts are replaced) and the labor costs.

Initially as much as 80 % of a maintenance program’s labor hours are spent on corrective maintenance. With an optimization of the equipment use, the labor hours can be dropped to 50 % (WEF, 2007). Sensor maintenance is not just a matter of keeping the device functioning but also of periodically validating its readings. Appropriate instrument calibration and verification depends on statistical quality control techniques. The statistical data must be collected, stored and evaluated.

The drawback conclusion is that neither corrective nor preventive maintenance is a choice for an effective maintenance concept.

7.3 Pro-active Maintenance

In this chapter a new maintenance concept is introduced combining sensor self-diagnosis and a dynamic maintenance concept allowing an effective and reliable use of sensors in monitoring concepts. Figure 30 shows the different sections of the dynamic maintenance concept.

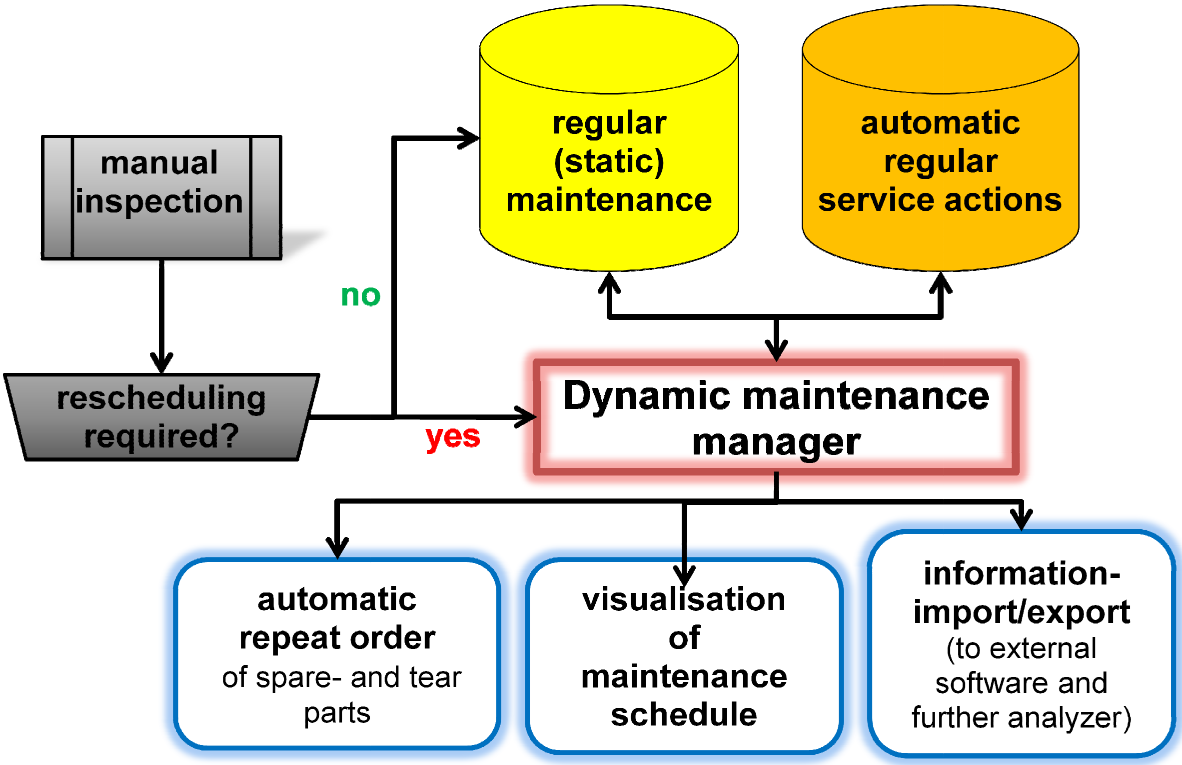

Figure 30: The dynamic maintenance concept

A maintenance concept consists of the equipment to be maintained, the maintenance instructions and tools, the replacement parts and a comprehensive schedule of maintenance tasks (WEF, 2007).

Even though one goal of a pro-active maintenance concept is to get away from static maintenance cycles, they are still an inherent part of it. These cycles are important for those spare parts in the sensor that have a known lifetime. For instance phosphorus analyzers, using the molybdateblue method, need two reagents. One of those reagents has a lifetime of approximately 12 weeks, before it ages and becomes useless. The following list (Table 11) gives an impression on how a static maintenance cycle for a phosphorus analyzer can look like.

Table 11: Static maintenance schedule for a phosphorus analyzer (Endress+Hauser)

Period:	Tasks:
monthly	flush sample line hose system with pressurized water, check and replace reagents if necessary
	spray pump hoses and roller heads with silicon spray
	check sample collector for fouling and clean it if necessary
every 3 month	clean drain lines: Flush all hoses with 10% ammonia solution and then rinse with sample for 30 minutes at least
	rotate pump hoses
	check reagents
every 6 month	replace pump hoses
	replace valve hoses

The time schedule can vary, depending on the type of analyzer/sensor and depending on the environmental influences. For example the surrounding temperature can extend (<20° C) or reduce (>20° C) the lifetime of the reagents.

To achieve a reduction of the labor costs the analyzer should be able to run automatic service actions. It should be able to fix basic problems (e.g. pollution of the tubes, clogging, settlements …). The cleaning mode of the Stamolys CA71PH is one of those automatic service actions.

Although the reduction of the manual service action such as inspection, spare part replacement or cleaning is one of the main tasks of the pro-active maintenance concept, it is still urgently needed. For those cases in which the automatic service action fails to solve a malfunction a trained technician has to do an on-site inspection. Because of the cost intensity of the manual service actions, this should always be the last option.

For the optimization and synchronization of the service actions a dynamic maintenance manager (dmm) should be implemented. It has the task to schedule and optimize the automatic- and manual service actions. If a manual service action out of the normal maintenance cycle is needed, it has to automatically re-schedule the maintenance schedules. Further, the dynamic maintenance manager should be able to combine maintenance actions. For instance, if a problem occurs and manual service actions are necessary and few days later the reagents have to be changed, the dynamic maintenance manager should combine these two maintenance actions.

Successful maintenance programs also require an effective inventory management system. A well-stocked inventory of replacement instruments, parts, and materials can keep a facility run smoothly. An overstocked warehouse is a misuse of resources (WEF, 2007) and a leak of spare parts can lead to unnecessary breakdowns. To avoid those incidents a history of actual parts usage should be established in the dynamic maintenance manager. Then a realistic list of parts to keep on hand should be implemented into the dynamic maintenance manager. Every time the quantity of a spare part reaches a critical minimum, the dmm automatically restocks the inventory by ordering new spare parts.

Further optimization can be achieved when the dmm communicates with several analyzers. For example, when monitoring a river section it is important that the dmm receives and treats the data from all analyzing devices.

To inform the maintenance staff a maintenance schedule is needed. The maintenance schedule is provided by the dynamic maintenance manager. It is a graphical interface (time schedule) that informs the maintenance staff about necessary service actions for the day.

An essential part of a well functioning pro-active maintenance concept is the earlier described sensor self-diagnosis. It makes the difference between a maintenance concept and a pro-active maintenance concept. Only with the knowledge of the current state of the analyzer, needed service actions can be demanded before the quality of the measurements goes down. Therefore, the information of the sensor self-diagnosis and the maintenance concept must be bundled (Figure 31).

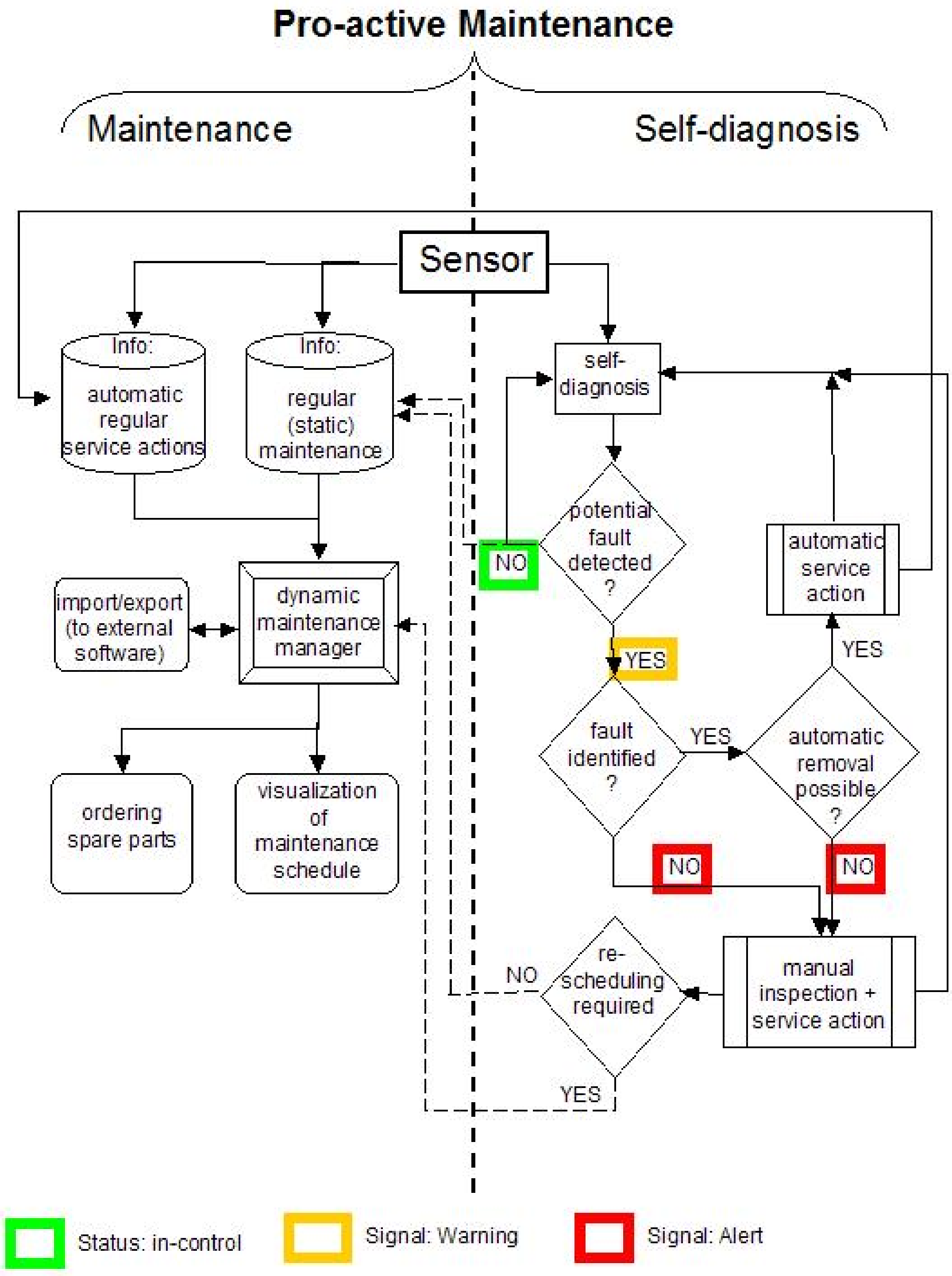

Figure 31: Pro-active Maintenance Concept for Water Quality monitoring

Figure 31 shows the links between the maintenance concept and the sensor self-diagnosis concept. As long as the sensor is in the In-control status it sends an “In-control” signal to the dynamic maintenance concept. In this situation the concept runs the regular (static) maintenance cycles. If the sensor detects a failure it switches to the warning status and tries to identify the failure. If the failure is identified and removable through an automatic service action the analyzer will start this service and go back to the In-control status after removing the malfunction. If the failure is unidentifiable or if it is not possible to remove it by an automatic service action the sensor switches to the alert status and demands for manual maintenance. After the manual maintenance the question is whether a rescheduling of the maintenance schedule is necessary or not. Is a rescheduling necessary, the sensor will send information to the dynamic maintenance manager to reschedule the maintenance plan. If no rescheduling is necessary, the sensor will demand the maintenance concept to run the regular (static) maintenance cycle. The combination of both concepts is the basis of the “pro-active” maintenance concept.

8 Conclusion

The enhancement of the available signals and the development of the sensor self-diagnosis concept allow the analyzer to detect more failures and to give more precise information about malfunctions. During the experimental period the frequency curve was examined and its reaction on intentionally triggered failures was observed. The experiments showed the great potential of the frequency curve. State of the art still is a warning that signalizes the appearance of a failure somewhere within the system. Through the evaluation of the curve the analyzer has the ability to gather valuable information about the current measurement cycle and its current state. Further, the testing series has shown that an automation of the failure identification is realizable. With the development of a concept for the logical evaluation of the available signals (the sensor self-diagnosis concept) a step towards detection, isolation and finally identification of a failure was made. For the sensor self-diagnosis concept, matrices for systematic failure detection were developed. With the developed procedure the concept collects all available information and tries to identify the malfunctioning part through the evaluation of the frequency curve, pattern recognition or logical comparison of the modes. With the concept some malfunctioning parts were detected but more information is needed to further increase the number of detectable errors.

A program that recognizes when a steady state of the frequency curve has been reached can optimize the duration of a measurement cycle. The time that is needed for one measurement cycle should not be pre-set by a constant time interval. Therefore, the program could compute the necessary reaction time to reach the steady state (or give an error message if the reaction needs too much time). The development of the software was started and first tests were performed. The program showed that a software based observation of the frequency curve is possible but it needs further development to be implemented in an online sensor. It has been tested for some faults but has not been tested for other and also not for overlapping faults.

With the development of the dynamic maintenance concept the aimed step away from the static maintenance cycles was performed. The static components were reduced to a minimum. The concept foresees the dynamic maintenance manager (dmm) as the basic component. It is the dmm that takes care about the inventory of spare parts, the visualization of the maintenance schedule and the organization and optimization of the manual and automatic maintenance actions. The dmm communicates with a series of analyzing devices to achieve an optimized and smooth running maintenance.

Both concepts by themselves would already be an improvement of the current state but by combining both concepts to a “pro-active” maintenance concept the standards of operating analyzing devices are brought to the next level. The analyzer does not communicate directly with the maintenance staff anymore. The communication will be between the analyzer and the dmm. Only in cases where manual maintenance is needed the dmm will demand for manual maintenance.

9 Outlook

There is still a great potential of further optimization of the sensor self-diagnosis. The goal is to receive as much information about the processes as possible. Integration of additional signals could improve the ability to detect faults. A major improvement would be to have information on the liquid level of the reagent containers. This could be done by pressure sensors or level meters. Other analyzers on the market use this information already to know when the reagents need to be changed. Flow meter can give more information about the volume that is pumped through the system. With this additional information missing reagents or samples could be detected.

The experiment with the simulated reagent pump failure showed the importance of real time monitoring of the pump speed. Changes of the pump performance or a total pump breakdown can easily be detected if this information is available.

Within the development of the “pro-active” maintenance concept the identification of further malfunctions and the automated statistical failure detection should be an inherent part. To use all available signals for the diagnosis adequate software needs to be developed and appropriate hardware needs to be implemented.

The concept of the sensor self diagnosis and the “pro-active” maintenance concept were tested in the laboratory. However, tests under field conditions need to be carried out to proof the reliability of the results and the functionality of the concept under field condition.

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