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NITRITE PREDICTOR COMPLEMENTARY TESTS

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1 INTRODUCTION

The nitrifying compartment has been upgraded with two new on-line analysers to determine the ammonium and nitrate concentration in the outflow of the third compartment of the MELISSA Pilot Plant. This implementation together with the characterisation of the main parameters affecting the measuring performance have been already described and discussed in previous technical notes (TN 52.22). Both analysers use selective electrodes, avoiding main interference compounds, and providing satisfactory accuracy in the measurement of these two nitrogen compounds, both of which are of high importance for the proper operation and control of the nitrification process carried out in the fixed-bed compartment. In TN 52.22, the description of the analysers and their technical features (measuring range, precision and accuracy), as well as the optimisation of the main operational parameters (conditioning reagents, injection volume, injection time, etc) were widely discussed.

On the other hand, the necessity of controlling the nitrifying process and the whole MELISSA Loop stability, demands an increase in reactor automation. A set of mathematical models has been developed in Blaise Pascal University (France) for this compartment, regarding main engineering aspects: flow, biological degradation and production of nitrogen compounds, and side metabolites (depending on the particular pH, temperature and dissolved oxygen conditions of reactor operation), as well as biomass growth. Mathematical modeling has been calibrated and validated with some experiments performed in the MELISSA pilot plant bioreactor, at UAB, and already discussed in previous technical notes, in terms of RTD (residence time distribution) and nitrifying activity regarding several key operating conditions (temperature, dissolved oxygen, recirculation flow-rate, residence time, ammonium load, etc). These experiments have been also complemented regarding particular aspects as oxygen mass transfer and RTD in similar reactors with several sets of experiments carried out in Blaise Pascal University.

After this long campaign of experiments and mathematical modeling all the obtained information was used by ADERSA (France) to design a control strategy for compartment III.

One of the main objectives of the control strategy is to maintain low ammonium concentration in the outflow of compartment III and avoid accumulation of nitrite in the outlet of this compartment, due mainly to the toxic effects of this compound in humans.

As a key tool to achieve these goals in terms of the nitrifying compartment control, a Nitrite Predictor was developed in ADERSA (France). This mathematical modeling consisted of using a simplified approach of the more complex mathematical model developed by Blaise Pascal University, due to the high time requirements of the control strategy itself (Leclercq, 2000). This simplification was necessary because of the excessive computing time of the full model. The main goal of the Nitrite Predictor is to estimate the nitrite concentration in the outflow of compartment III using ammonium and nitrate values coming from the on-line analysers. This calculation is directly affected by the sampling frequency, and experimental transient states were carefully studied to finally provide precise nitrite estimation.

The set of parameters should be optimized in the Nitrite Predictor in order to obtain good results in control purposes by using experimental data of the nitrifying pilot reactor. These particular experiments specially designed for this particular purpose are the so-called “Nitrite Predictor Complementary Tests”.

In the tests that are described in this technical note, a set of different disturbances in process variables is carried out. On-line analysers are used to determine the ammonium and nitrate concentrations in the outflow of the pilot reactor. Two main operating conditions are changed in the set of tests: the ammonium input concentration and the residence time used in the reactor.

The current period of operation of the nitrifying pilot reactor is as long as 3.5 years and thus some limitations in the operation have appeared, the main of which is found at high aeration flow rates.

2 SYSTEM SET-UP DESCRIPTION

In order to attain a correct performance of the MELISSA loop, it is necessary to ensure the correct performance of all the compartments separately, so that any accumulation or deficiency can be corrected and have the minimum effect on the other compartments.

The nitrogen cycle in the MELISSA loop is governed by the ammonium generated in the crew compartment, which is subsequently oxidised to nitrate in compartment III. The pilot reactor of compartment III was sized in such a way that it fulfils the nitrate requirements of compartment IVa, colonised by Spirulina platensis, and IVb (the higher plant compartment), of the MELISSA loop, both of which use nitrate as their nitrogen source.

The biological nitrification that takes place in compartment III is carried out in two stages: first the ammonium is oxidised to nitrite by *Nitrosomonas europaea* and after this, a conversion of nitrite to nitrate is carried out by *Nitrobacter winogradskyi*.

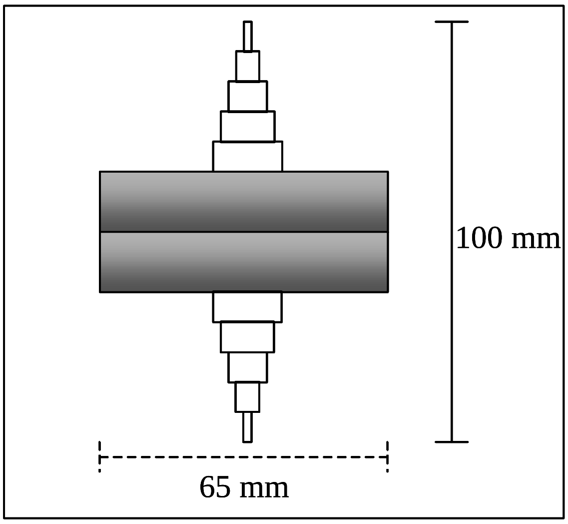
Nitrite must be avoided in the MELISSA loop due to its toxicity to humans and to bacteria in compartment IVa. Therefore the production of nitrite must be controlled locally in compartment III. To this effect, it is necessary to monitor the concentration of the nitrogen species in the outlet of the nitrifying compartment in order to provide the control law with reliable data.

Monitoring of the concentration of a certain chemical compound at the outlet of a bioreactor requires an optimal configuration of the sampling loop that allows a high sampling frequency, i.e. the dead time with which the data are obtained is minimised. This is essential for the correct implementation of the control system, as it will base its actions on the data supplied by the analysers. A diagram containing the main features of the sampling loop is presented in figure 2.1.

Due to the outlet flow of the nitrifying reactor containing an important fraction of gas, a gas-liquid separation step is required before the sample enters the analysis loop. To this effect, a small buffer tank was installed at the outlet of the pilot reactor, in which the liquid phase was separated from the gas phase. The design volume of the buffer tank has been eventually reduced from an initial value of 75 mL to a smaller volume of only 25 mL. The reduction of this dead volume contributed to keep the value of the overall dead time low enough to ensure that, at the sampling frequency fixed by control requirements, the delay between the sampling time and the analysis time is minimised. The dead time due to the buffer tank used as a gas separator was reduced from 30 minutes to 10 minutes by this change in the dead volume when the reactor was operating at a high residence time (25 hours). Minimising the delay in the concentration measurements is important in order to ensure that the control actions are based on reliable, real-time data. Installation of the gas separator improved the performance of the analysis loop as much as permitted by the restrictions in the present hardware of the pilot reactor of compartment III.

A redefinition of the sampling loop will be included as one of the main issues to be solved when the hardware of the pilot reactor of compartment III is updated. The set-up used in this technical note was meant to simulate the conditions provided by the foreseen sampling system, as it was not possible to implement any improvements that required to stop and start up the reactor again due to the long period of time this operation requires.

To obtain a sample free of biomass, once the gas phase has been separated, a filtration step is required before the sample is pumped to the analysers. The filtration step assures the axenic conditions are kept in the reactor and, at the same time, avoids biomass growth in the tubing of the analysis loop. Initially an Opticap® (Millipore) filter with a pore size of 0.22 µm was used, however, the high liquid retention in this filter (approximately 75 mL) originated a very high dead time in the filtration step. Therefore, the 0.22µm filter was replaced with a filtration unit that consists of an autoclavable filter holder (Nalgene, UK), which has a volume of only 5 mL, coupled with a 0.22 µm filter (Millipore) that had to be replaced periodically in order to avoid clogging.



To avoid that any new sample used for measurement by the analysers is polluted by the previous sample, the so-called initial time is increased so that the volume that was retained in the filter (5 mL) is completely replaced. Taking into account the average flow rate going through the filter (1.12 mL/min), the initial time was fixed at 5 minutes. The filtration cell was duplicated to allow its replacement when necessary without the need to stop the analysis process.

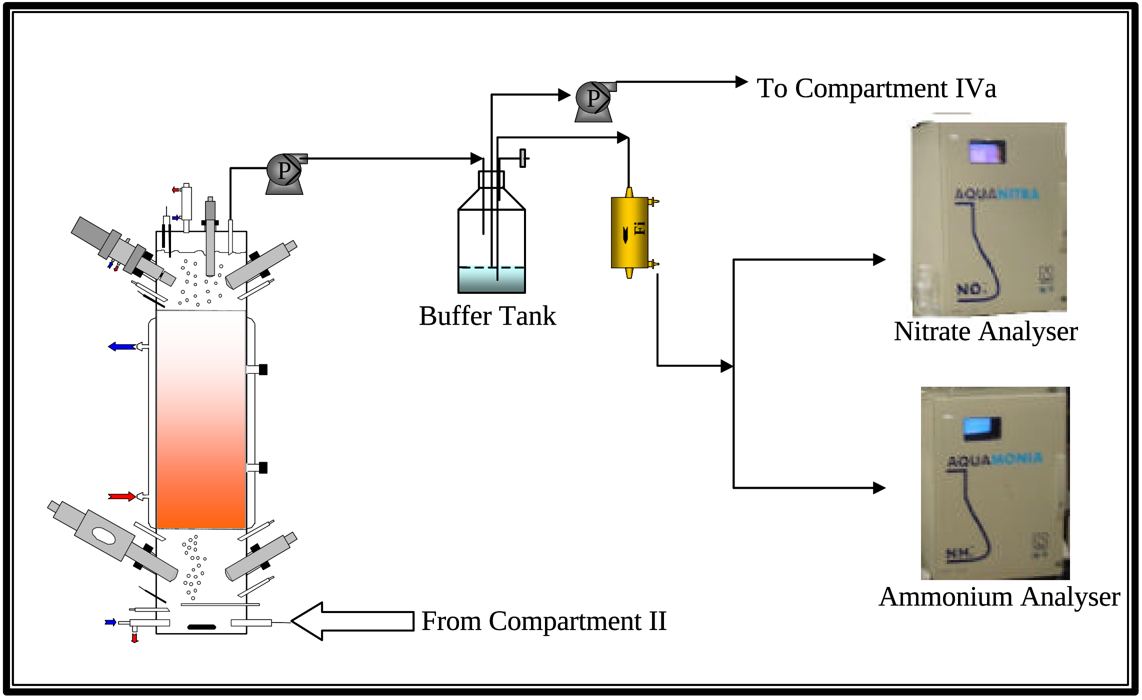


Figure 2.1: Configuration of the sample extraction system and analysis loop in compartment III

Biofilm growth in compartment III is regulated by detachment, which increases suspended biomass concentration in the outlet flow of the reactor, leading to interferences in the online analysis of ammonium and nitrate.

The described system set-up for the analysis loop is able to provide on-line sampling free of biomass. Nevertheless, this configuration requires the inclusion of vessels, as well as a certain length of tubing connections, which all contribute to introduce a delay in the ammonium and nitrate monitoring. It is important to take into account that this configuration is only a provisional one that was adopted to fit the current hardware of compartment III without stopping the operation of the reactor, which had been in continuous operation for over three years when this experiments were carried out. Therefore, the sampling loop will be improved when the hardware of compartment III is updated and the reactor is started up again.

The main problem introduced by the buffer tank and the tubing is the delay in concentration measurements. The distance between the analysers and the outlet of the reactor was shortened as much as possible and the width of the tubing in the analysis loop, where the flow rate is low, was reduced to capillary tubes so that its effect on the total dead time was negligible when compared to the dead time in the buffer tank. Therefore, the main contribution to the dead time in the measurements is reduced to the contributions by the filter and the buffer. Concrete estimations for the values of the dead time in the buffer tank and in the filter are presented further on in this document.

Taking into account all mass flows, it becomes clear that the main contribution to the delay, once the volume of the buffer tank has been minimised, is due to the big liquid residence time in the filter (see table 2.2). The high residence time of the sample in the filter can only be minimised by reducing the volume of the filter unit itself, as the flow going through the filter is given by the sample requirements of the analyser and cannot be altered.

2.1 Estimation and reduction of the dead time

As stated before, the main contribution to the overall dead time in the sampling is due to the filtration step used to obtain a biomass free liquid sample to be processed by the on-line analysers.

In order to quantify the total delay in the ammonium and nitrate data acquisition, it is necessary to calculate the mass flows both in the buffer tank and the filter, taking into account the dilution rate of the bioreactor as well as the sample flow rate consumed by the analysers.

Each analysis is carried out in several stages, as described below, during which the sample and the reagents are switched to the detection system. The length of each one of these time intervals can be set in order to fulfil the requirements of the process to be monitored. Both the ammonium and the nitrate analysers are based on the principle of potentiometry, and thus their response times are very similar.

Each analysis cycle comprises the following stages:

- *Initial time*: Before the actual analysis cycle starts, sample flows through the system so that any remaining sample from previous cycles is removed. During this period of time the detection system is not active.

- *Stabilising time:* Distilled water is flushed through the system as described in TN52.21 for the nitrate analyser, in order to stabilise the electrode before the analysis starts.
- *Injection time:* A given volume of sample is switched to the system by means of an electrovalve and is subsequently mixed with the continuous flow of distilled water and conditioning solution. When the mixture reaches the detection system, a peak in the value of the potential measured by the Ion Selective Electrode (ISE) is compared to the base line and the concentration is computed by means of the calibration curve.

These steps contribute to the total delay of the measurements. The optimisation of all the above parameters leads to the correct performance of the analysis loop. The values set for these parameters during the experiments presented in this technical note are summarised in table 2.1.

AQUANITRA		AQUAMONIA	
Total analysis time	16 min	**Total analysis time**	16 min
Initial time	5 min	**Initial time**	5 min
Stabilisation time	4 min	**Stabilisation time**	4 min
Injection time	11s	**Injection time**	11s
Time between samples	4 min	**Time between samples**	4 min
Sample	6 mL/analysis	**Sample**	9.5 mL/analysis
Na_2SO_4	7mL/analysis 21 mL/calibration cycle	**Tris**	4 mL/analysis 16 mL/calibration cycle
Water	7mL/analysis 21 mL/calibration cycle	**Water**	8mL/analysis 32mL/calibration cycle
Nitrate Standards	0.5 mL/calibration cycle	**NaOH**	2mL/analysis 8mL/calibration cycle
		Ammonium Standards	7.5 mL/calibration cycle

Table 2.1: Configuration of the analysers. Reagent and sample requirements.

In order to estimate the delay in the data obtained by the analysers, the volumes of the buffer tank and the filter, as well as the analysis times presented in table 2.1 have been used. For this set of experiments the volume of the buffer tank was 75 mL, and the filter had a total volume of approximately 5 mL. In addition to these dead volumes, the volume due to the tubing between the outlet of the reactor and the analysers was taken into account. When referring to tubing we are mainly taking into account the connections between the outlet of the reactor and the buffer tank, as the tubing in the analysis loop was composed of capillary tubes that had very low effect on the total dead time (3-6% of the total dead time) as can be observed in table 2.2. With all these data the mass flow balances were solved and an estimation of the total dead time between sampling and the final value of concentration was calculated.

The balances were solved assuming that both the ammonium and the nitrate analysers are synchronized in their analysis cycles and using the total sample requirements of each of the analysers during a complete analysis cycle, which can be found in table 2.1. The total amount of sample used by the nitrate analyser over a full analysis cycle is 6 mL, while the ammonium analyser consumes 9.5 mL of sample, including flushing of the analyser. The length of an analysis cycle was 16 minutes for both analysers, which lead to an average sample requirement of 1 mL/min.

The dead times caused by the gas separator and the filter are presented in table 2.2 for the usual range of operation of the nitrifying pilot reactor.

Table 2.2: Estimation of the different contributions to the dead time

Range of flow rate (L/h)	Dead time in gas separator (min)	Dead time in filter (min)	Dead time analysis loop + tubing (min)
0.15	10	5	0.5
0.60	2.5	5	0.5

Although the use of a filter whose volume is 5 mL reduced the delay to a high extent, further improvements will be introduced when the hardware of the pilot reactor of compartment III is upgraded in the near future. Optimisation of dead times is important because the data generated have to be used for control purposes. Therefore, not only a high precision and repeatability in the analyses is necessary, but the data must be obtained with a high frequency as well and the configuration must be such that the delay is minimised.

3 OPERATING CONDITIONS IN COMPARTMENT III

The experiments described in this technical note have been carried out using a culture medium with a constant composition, only altering the concentration of ammonium when the disturbance was based on a nitrogen concentration step in the input flow.

The composition of the culture medium used at compartment III is specified in table 3.1.

Table 3.1:
Composition of the culture medium used in compartment III
pH is set to 8.1-8.2 with Na_2CO_3.
$MgSO_4 \cdot 7H_2O$ and $CaCl_2 \cdot 2H_2O$ are sterilized separately and subsequently added to the main solution

Compound	Concentration (g/L)
$(NH_4)_2SO_4$	1.32
$FeSO_4 \cdot 7H_2O$	0.0025
$CuSO_4 \cdot 5H_2O$	$4 \cdot 10^{-6}$
Na_2HPO_4	0.71
KH_2PO_4	0.68
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.177
$ZnSO_4 \cdot 7H_2O$	$4.3 \cdot 10^{-6}$
$MgSO_4 \cdot 7H_2O$	0.052
$CaCl_2 \cdot 2H_2O$	$7.4 \cdot 10^{-4}$
$NaHCO_3$	0.8

The conditions used in compartment III during this set of experiments were similar to those used in previous tests performed in phase 4 (TN 47.2), in which the continuous operation of the reactor was followed for a long period of time.

The experiments described in this document were performed keeping the operating conditions of the reactor constant, only altering the liquid flow-rate and input ammonium concentration when required by the test.

During the performance of preliminary tests with the ammonium and nitrate analysers connected on-line to the pilot reactor of compartment III, a problem was detected due to the high dead time of the configuration that led to a high variability in the measurements when the reactor was going through a transitory state. When the reactor is operating at a steady state, the ammonium and nitrate concentrations are constant and the effect of the dead time on the measurements cannot be clearly observed. However, even in steady state there is a certain noise in the measurements, which is higher for nitrate and is a consequence of the performance of the analyzer, as the nitrate ISE has a lower repeatability than the ammonium ISE.

The effect of the dead time is best noticed during a transient state, when in addition to the noise in the measurements the possibility exists that some degradation occurs in the dead volumes of the buffer tank and the filtration cell, which would lead to erroneous concentration values. Therefore, the decision was made to introduce some improvements on the configuration of the analysis loop before carrying on with the on-line tests. To this effect the volume of the buffer vessel and the filter were reduced as described in section 2 of the present document, and a new design for the sampling and analysis loop is foreseen in the near future, when the hardware of the pilot reactor of compartment III will be updated.

The conditions for this set of experiments had been fixed in TN 48.3 (Leclercq, 2002), and were redefined later on in order to adapt the tests to the limitations that have been previously described for the nitrifying pilot reactor. While the original number of steps to perform was maintained, the actual values of ammonium inflow concentration and the liquid flow rate were modified in order to make the tests feasible in these new operating conditions.

The operating conditions finally used in this set of experiments were as follow:

Three steps up in flow-rate were performed (the first one from 0.15 L/h to 0.25 L/h, the second one from 0.25 L/h to 0.40 L/h and the third one from 0.4 L/h to 0.6 L/h) and one step down (from 0.6 L/h back to 0.15 L/h), using an ammonium inflow concentration of 300 mg/L NH_4^+-N/L in all cases. Following the steps in flow rate, and keeping the input flow rate constant to 0.15 L/h, a step in input ammonium concentration was subsequently performed from the initial concentration of 300 mg NH_4^+-N /L to 600 mg NH_4^+-N /L. A summary of all the steps described above is presented in figure 3.1.

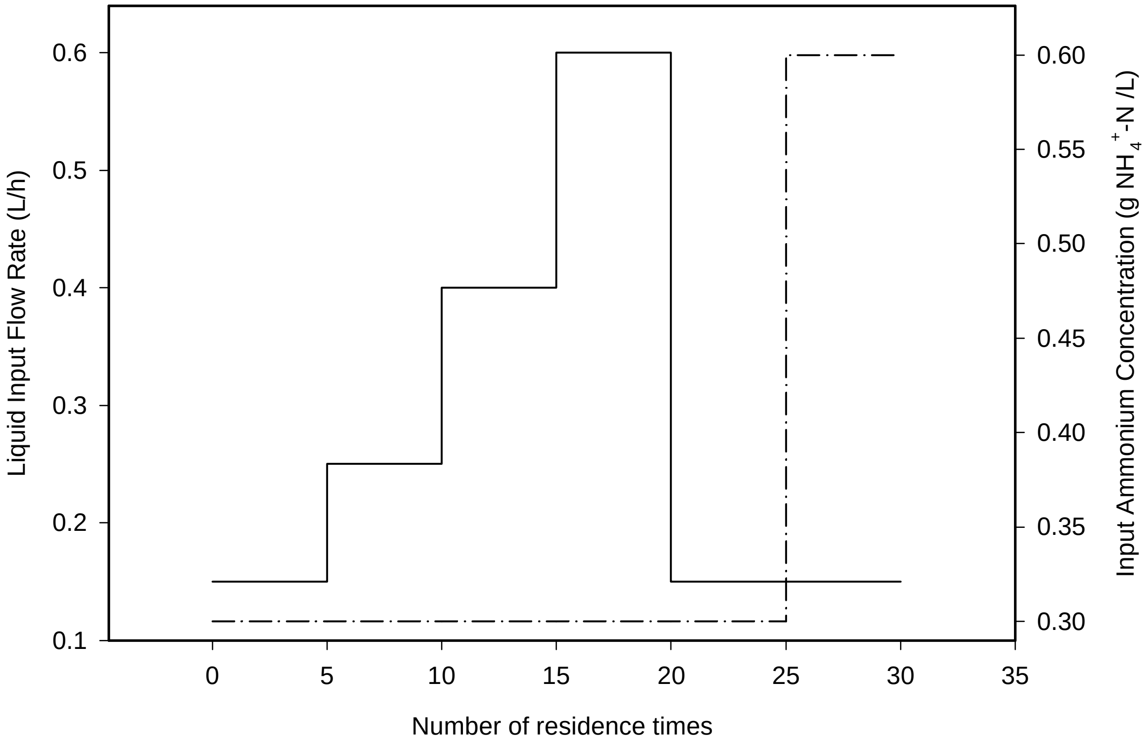


Figure 3.1: Steady states required for the validation of the nitrite predictor.
The straight line indicates the steps of flow rate and the dashed line applies to the step in ammonium concentration.

The aeration conditions in the reactor were kept constant around 1.5 L/min, which ensures that the oxygen is not limiting at any stage during the tests. With this flow-rate, an average dissolved oxygen concentration of approximately 50% of saturation was attained in the fixed bed, with some fluctuations during the transient states.

The pH was kept to 7.8-8.2 by using $NaHCO_3$ as base and CO_2 as acid, and the temperature was of 28ºC during all the experiments.

The main operating parameters of the analysers (frequency of analysis, injection volume, injection time, reagents concentration) used during these experiments were set to the values obtained in TN 52.22 after optimisation, which can be found in table 3.2

Table 3.2: Optimised operating conditions for the ammonium and nitrate on-line analysers

AMMONIUM ANALYSER		**NITRATE ANALYSER**	
Frequency of analysis	16 min	**Frequency of analysis**	16 min
Injection Volume	3 mL	**Injection Volume**	200 μL
Injection Time	100 s	**Injection Time**	11 s
pH conditioning reagent (TRIS)	7.48	**pH conditioning reagent (Na_2SO_4)**	2.3
Concentration TRIS	0.01 mol/L	**Concentration Na_2SO_4**	0.75 mol/L

4 RESULTS OBTAINED IN THE EXPERIMENTS

Due to the long period of continuous operation the nitrifying reactor was experiencing some problems at the time the experiments presented below were performed. In order to carry out the nitrite predictor complementary tests it was important that the air flow rate in the reactor was at least of 1.5 L/min. Due to clogging of the packed bed after a long period of continuous operation it was becoming very difficult to keep the oxygen levels in the reactor high, and thus the reactor flow needed to be periodically reversed in order to allow excess biomass to wash out and reduce the effect that the long time submission to pressure had had on the packed bed.

After this maintenance operation, the nitrifying reactor was operated at a low flow-rate, so that any remaining nitrite, which had accumulated due to oxygen limiting conditions, could be removed. The flow-rate was fixed to the required 0.15 L/h, and this step was followed by a long transient state in which an important nitrite accumulation was detected due to biomass limiting the process. After enough biomass had developed, the normal activity of the biofilm was recovered and a high conversion was achieved, making it possible to start the tests described in figure 3.1.

The analysers were operated in the conditions described above in table 3.2, while the operating conditions of the reactor were as defined above in figure 3.1. The analysers provide ammonium and nitrate measurements every 16 minutes, and in order to verify their correct performance, these results are compared to those obtained with an off-line reference method (LCK305/LCK341/LCK339, Dr Lange, Germany). Both the on-line measurements and the results obtained off-line with the reference method are presented in figures 4.1-4.4 for each of the steps in figure 3.1.

The frequency of analysis was fixed at the beginning of this set of experiments and was kept constant throughout it. The analysers were both operated with a frequency of analysis of 16 minutes including sample analysis plus time between analyses.

Concentration data generated by the analysers were registered by the GPS and their values were refreshed every 60 seconds. The files generated contained all data concerning the operation of the reactor and were used to obtain the graphs presented in this technical note.

4.1 Step in flow rate from 0.15 L/h to 0.25 L/h

The first of the perturbations consists on increasing the liquid flow rate from 0.15 L/h to 0.25 L/h. In these conditions the nitrite accumulation was close to the lower detection limit, and only a slight increase of approximately 0.4 mg/L NO_2^- -N was found during the transient state.

The on-line analyser measured the nitrate concentration with an estimated repeatability of around 16%, which at this low level of nitrite is not enough to estimate the nitrite concentration with an acceptable reliability. On the other hand, the ammonium measurements were performed with a higher precision and repeatability, as indicated in figure 4.1 by the similarity between the data obtained on-line and the off-line measurements using the reference method based on colorimetry (LCK305/341/339, Dr Lange, Germany).

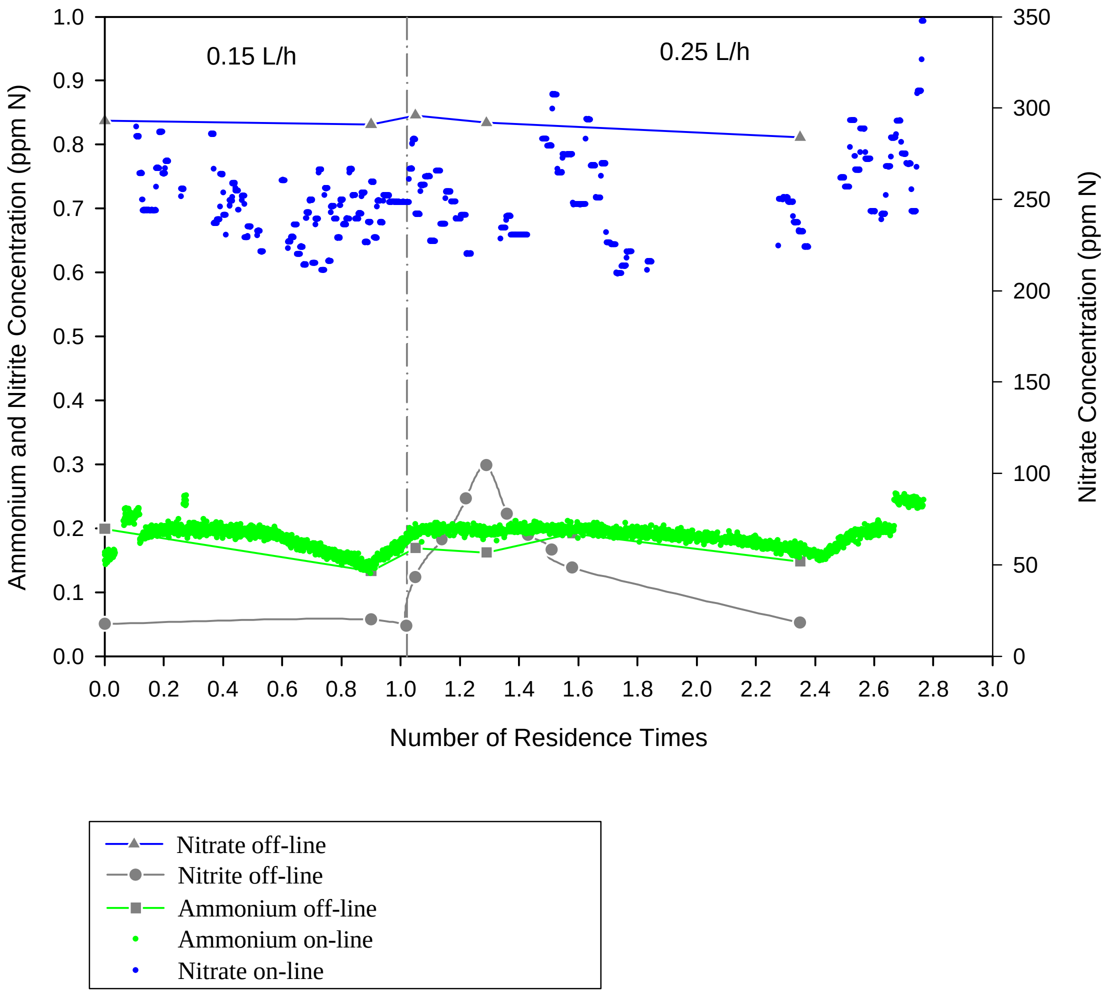


Figure 4.1: Flow rate step 0.15-0.25 L/h

4.2 Step in flow rate from 0.25 L/h to 0.40 L/h

In figures 4.2 and 4.3 the results from the remaining flow rate steps foreseen in figure 3.1 are presented. The results are similar in terms of precision and repeatability to those obtained in figure 4.1, with only a slightly higher deviation in the ammonium data during some stages of the experiments. The deviation between off-line measurements and data obtained by means of the on-line analysers was found to range from 5% for the ammonium data, and up to around 15% for the nitrate data. Regarding accuracy, the values of around 16% obtained in the experiments of figure 4.1 for the nitrate analyser are verified in figure 4.2.

Although no nitrite accumulation was detected during this transient state, there was a clear decrease of the nitrate concentration that can be observed in figure 4.2. However, no increase in the nitrite or ammonium concentration is detected after the step. This fact could only be explained by a change in the input medium concentration, as the decrease of the nitrate concentration due oxygen limitation would go together with an increase of the nitrite concentration, and eventually a certain accumulation of ammonium. A decrease in the input ammonium concentration would explain the fact that there is not any nitrite accumulation at any stage of this transient state.

Because the concentration of the input medium was always checked before it was fed to compartment III, we consider that it is more likely that a certain denitrification was occurring at the moment in the reactor, or that the dilution effect observed in the data was consequence of the addition of a higher than usual volume of the Na_2CO_3 solution used for pH control.

The flow rate at which the pilot reactor was operated was kept at 0.40 L/h until the steady state was achieved and after and then the flow rate was increased from 0.40 L/h to 0.60 L/h. The results obtained during this new transient state will shown in figure 4.3 and discussed in the following section of this document.

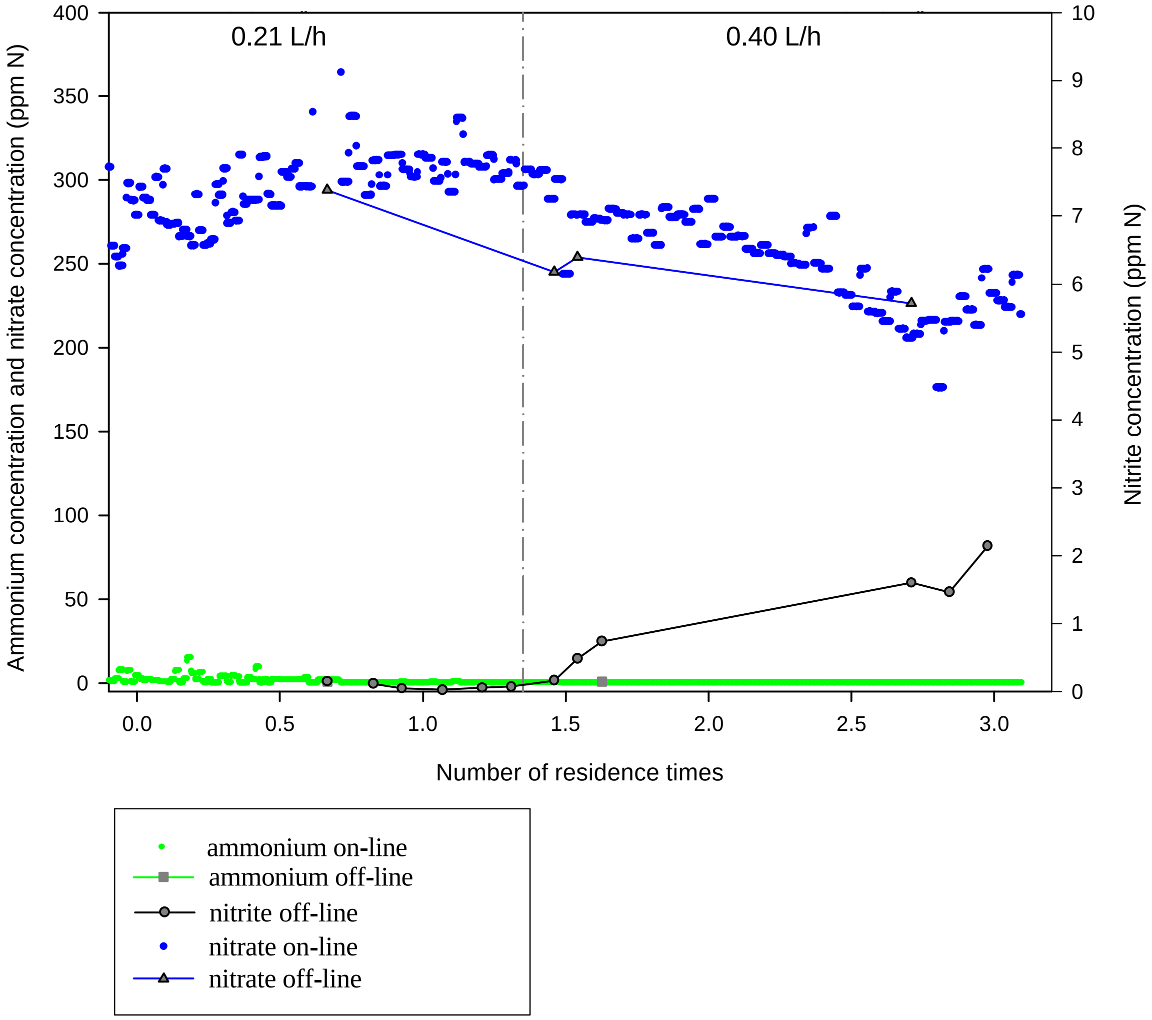


Figure 4.2: Flow-rate step 0.21-0.40 L/h

4.3 Step in flow rate from 0.40 L/h to 0.60 L/h

During the experiment presented in figure 4.3, air flow-rate was kept around 0.75 L/min, which led to an average dissolved oxygen concentration of approximately 50% of saturation during the first transient state. When the liquid flow rate was set to 0.15L/h after the end of the step, the dissolved oxygen concentration at the bottom of the fixed bed increased and thus the average oxygen level was of 70-80% relative to saturation.

The nitrite accumulation in this transient state was slightly higher than in the previous disturbances, the maximum value of the nitrite concentration attained being around 4 mg/L NO_2^- -N.

Taking into account the known limitations of the used ion selective electrodes at low nitrite concentrations, correlation between on-line and off-line measurements can still be observed. The noise in the measurements in figure 4.3 was slightly higher than that calculated for the data in figures 4.1 and 4.2, most probably because of a reduction in the efficiency of the ion selective electrode after a long period of continuous operation. Ion selective electrodes experience a gradual decrease of its efficiency along their lifetime that gives as a consequence a lack of repeatability in the concentration measurements. Evolution of the efficiency throughout the lifetime of an ISE can be checked observing the slope of the calibration curve. A decrease in the slope leads to a higher error when the potential measurement is translated to concentration by means of this calibration curve, and this leads to a decrease in the repeatability of the concentration measurements. The replacement of an electrode is decided according to this parameter.

The nitrite measurements performed off-line with the reference method show how there was some nitrite accumulation after the flow rate was increased from 0.4 L/h to 0.6 L/h. The nitrite accumulation in this transient state was slightly higher than in the previous disturbances, the maximum value of the nitrite concentration attained being around 4 mg/L $N\text{-}NO_2^-$, however, the low repeatability on nitrate determination makes it impossible to detect such low a nitrite concentration.

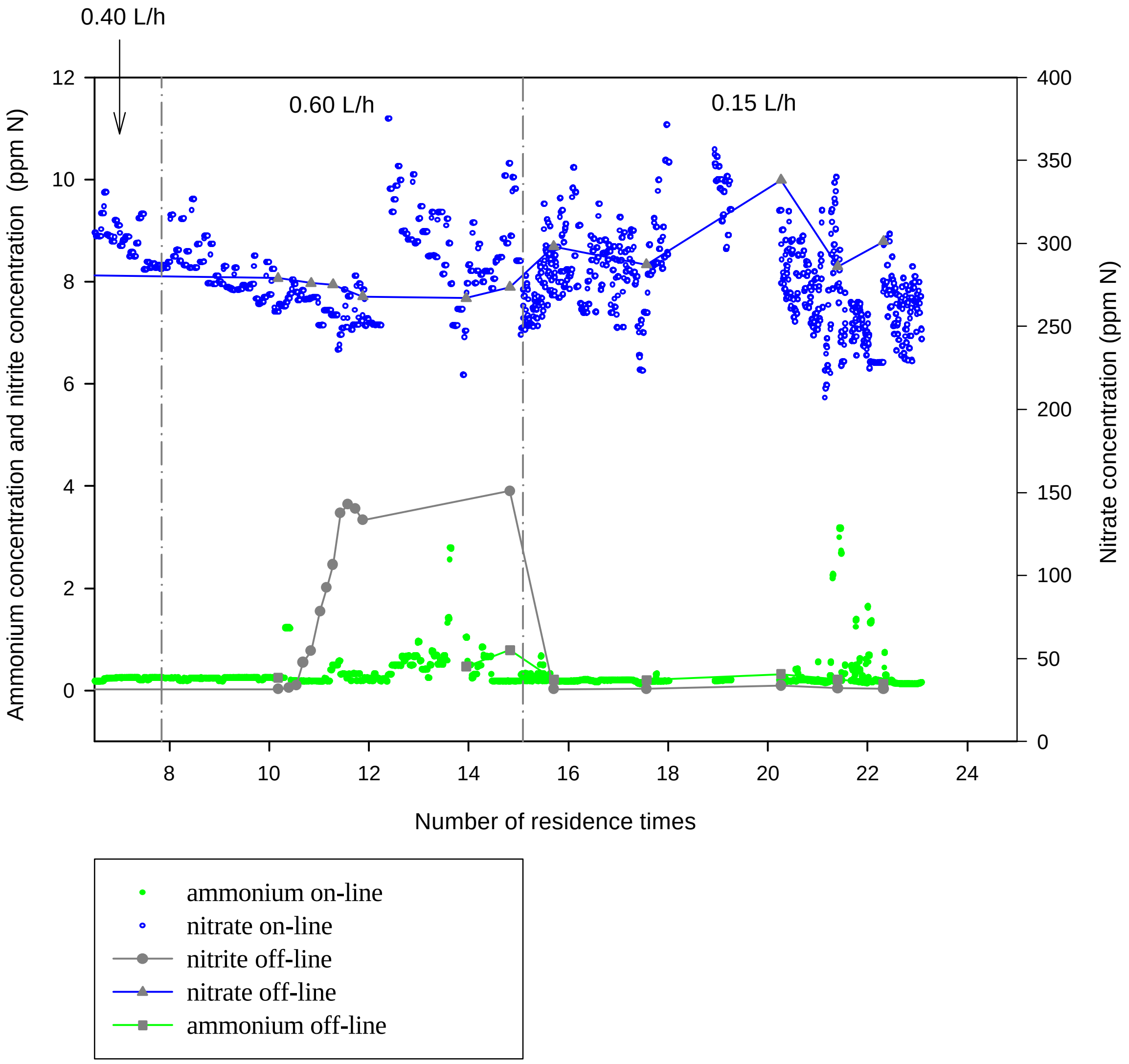


Figure 4.3: Flow-rate step 0.40-0.60 L/h

4.4 Step in the input ammonium concentration

The main operating scheme suggested by ADERSA included an experiment in which the input ammonium concentration had to be increased from 300 mg NH_4^+-N/L to 600 mg NH_4^+-N /L. Nitrate concentration in the nitrifying reactor during this test ranges from 300 to 600 mg/L NO_3^--N. With a relative standard deviation of approximately 10%, it can be concluded that a nitrite concentration lower than 30 mg/L NO_2^--N cannot be calculated by using the data provided by the analysers in combination with the mass balances.

The nitrite accumulation attained in this test was higher than in the previous transient states in which it had been induced by a step in the flow-rate, but the peak obtained in the latter was very brief and the maximum concentration attained was of 16 mg NO_2^--N /L. After this brief nitrite accumulation, the operation of the reactor reached another steady state in which the nitrate concentration became constant and the ammonium and nitrite concentrations were negligible. In figure 4.4 a good correlation between on-line data and off-line data can be observed during the transient state.

After sixteen residence times, the presence of support beads in the outlet of the reactor partially obstructed the tubing, reducing the amount of liquid sample in the buffer tank for a few minutes. As a consequence, air entered the analysis loop leading to incorrect on-line measurements. Like in the case of the filter used in the analysis loop, actions will be taken in the design of the new pilot reactor of compartment III to avoid any loss of support beads from the reactor. This work is included in the description of work package 78.6 in phase 10: “Re-design of compartment III pilot reactor”.

In order to follow the operation of the reactor off-line measurements were performed periodically until residence time 17, when all the nitrogen concentrations became stable and it was clear that a steady state had been attained. Off-line data of ammonium, nitrite and nitrate after residence time 16 have been included that show the accomplishment of the steady state.

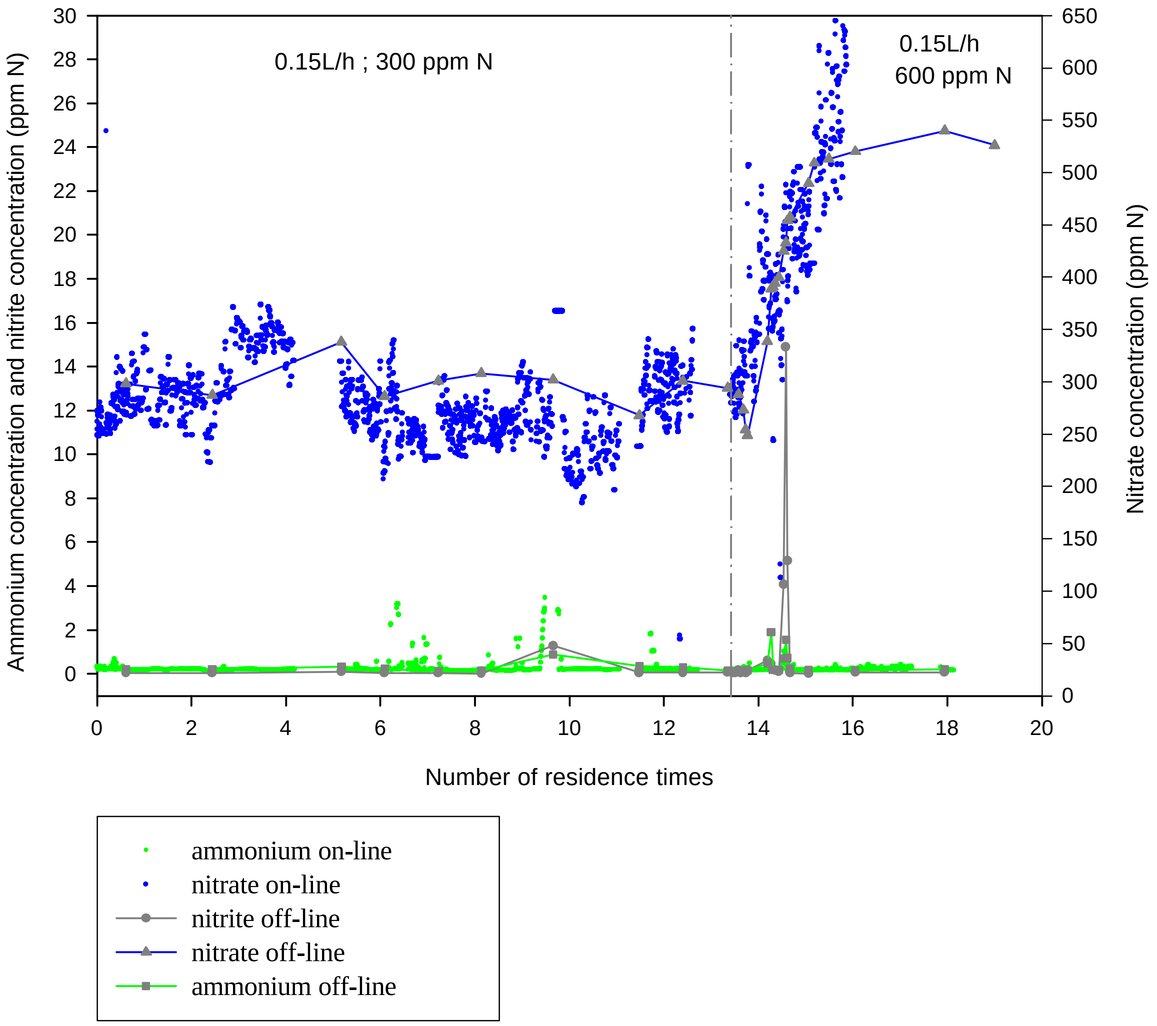


Figure 4.4: Concentration step 300 mg/L N - 600 mg/L N

5 CONCLUSIONS

The experiments suggested in TN 48.3 for the first validation of the nitrite predictor have been performed using two on-line analysers for the measurements of ammonium and nitrate concentration in the outflow of the nitrifying pilot reactor.

Some limitations in the operation of the reactor have been encountered during this long set of experiments, the main difficulty being the supply of a constant aeration flow rate in the nitrifying reactor. It was necessary to perform maintenance operations in the pilot reactor of compartment III in between experiments that made it possible to fulfil the aeration requirements of the nitrification process. On the other hand, the design of a sampling system that would satisfy the demands of the analysis loop was a critical subject that had to be solved. A specific study for the quantification of the delay associated to the on-line measurement of ammonium and nitrate was carried out.

The main drawback of the current design of the analysis loop was found to be the long dead time, as a result of the low sample demands of the analysers combined with the volumes of the buffer tank and the filter unit. A second handicap, which is to some extent a consequence of the high retention time in both the buffer tank and the filter unit, is the presence of bacteria in the sampling loop. The latter led to inaccurate measurements of the ammonium and nitrate analysers and was solved by replacing the buffer tank and part of the sampling loop more frequently. The presence of the buffer tank before the filtration unit cannot be avoided with the current hardware configuration, because of the biphasic flow at the outlet of the reactor. However, the high values of the dead time could be improved to some extent by reducing the volume of both the buffer tank and the filter as much as possible. The overall delay in the measurements induced by these dead times has been quantified in this technical note, and needs to be taken into account, together with the frequency and length of each analysis performed by the analysers. A solution to all these drawbacks will be considered during the upgrade of the hardware of compartment III in the near future.

In all the experiments described above, the nitrite accumulation is very low, its maximum value being 16 mg/L NO_2^-- N, and the accuracy in the measurements, in terms of relative standard deviation, fluctuates from 5% to around 20%. It was agreed by the MELISSA partners that the estimator was not efficient at low concentrations of nitrite (0.02 to 10 mg/L NO_2^--N) because it is too sensitive to the noise of the ammonium and nitrate measurements (Leclercq, 2004, personal communication). The nitrite accumulation obtained in the experiments described in this technical note is too low to endure values of repeatability as high as the average 15% with which the nitrate data are obtained

Due to this difficulty to validate the nitrite predictor at low nitrite concentrations, further discussion with ESA and SHERPA-Engineering has been initiated to finally design and validate the control law for compartment III.

In the meantime, it was agreed that it is necessary to measure the nitrite concentration on-line in the outflow of compartment III in order to obtain an accurate and reliable value that can be used for control purposes. In this way, work is currently being done in order to select an on-line nitrite analyser (WP 66.1).

6 REFERENCES

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