On-Line titrator for bacterial activity monitoring in activated sludge processes

- ✓ **Laboratory scale experimentation pH/DOstat technique with titrator**
  MARTINA (Multiple Analyte pRogrammable TitratioN Analyzer)
- ✓ **On-Line titrator prototype for activated sludge process monitoring on the plant (TITAAN:** TITrimetric Automated ANalyzer**)**

Modes of operation for the On-Line titrator

1. **Acute toxicity on autotrophic biomasses assessment**
2. **Nitrifiable nitrogen influent's content assessment**
3. **Maximum nitrifying activity assessment**
4. **Detection of the end of nitrification process (SBR)**
5. **Residual nitrates assessment at end of anoxic/aerobic phase (SBR)**

TITAAN TITrimetric Automated ANalyzer

On-Line titrator prototype

Titrator operations:

- Sludge and sewage sampling
- performs titration test at controlled temperature
- samples discharge
- on-line data elaboration in real time
- on-line data are available for monitoring
- and control systems

User interface:

- touch-screen

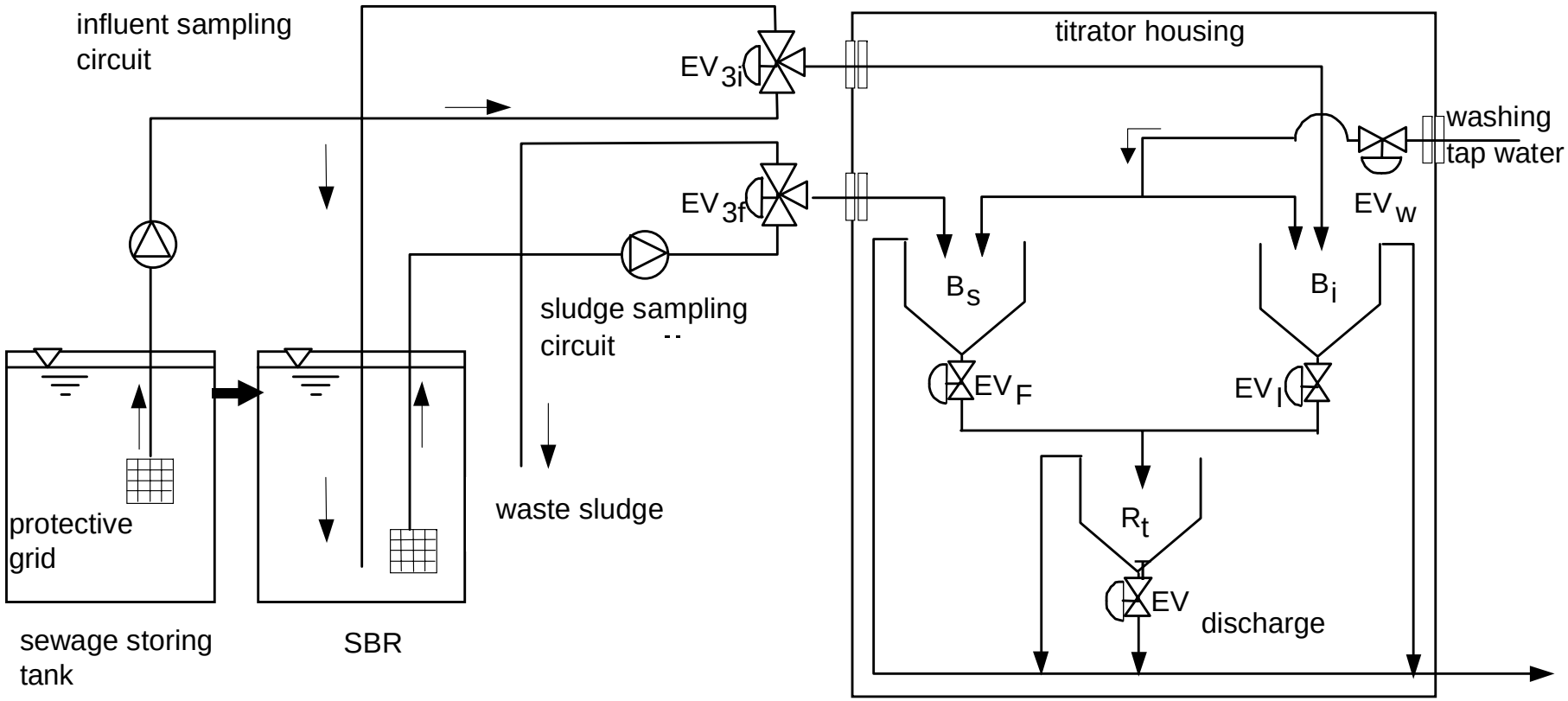
Connections:

- RS232 serial port for PC e PLC
- RF (DECT standard) wireless link
- PSTN modem link

Data storage: Compact Flash Card

TITAAN - On-Line titrator prototype
Hydraulic connections with ENEA SBR pilot plant

TITAAN, **TIT**rimetric **A**utomatic **AN**alyzer



sludge and sewage sampling circuits

Titrator

Mode 1 - Influent toxicity assessment

Purpose:

Evaluate the presence in the sewage of inhibiting/toxic compounds with acute effects on autotrophic biomasses (AOB and NOB) and estimate the consequence on substrate removal capacity

Sampling procedure

- ✓ ***sludge****:* endogenous conditions
  - sludge can be aerated inside the titrator
  - in SBR sludge withdrawal at the end of aerobic phase
- ✓ ***sewage:*** can be withdrawn in every moment

field calibration is necessary

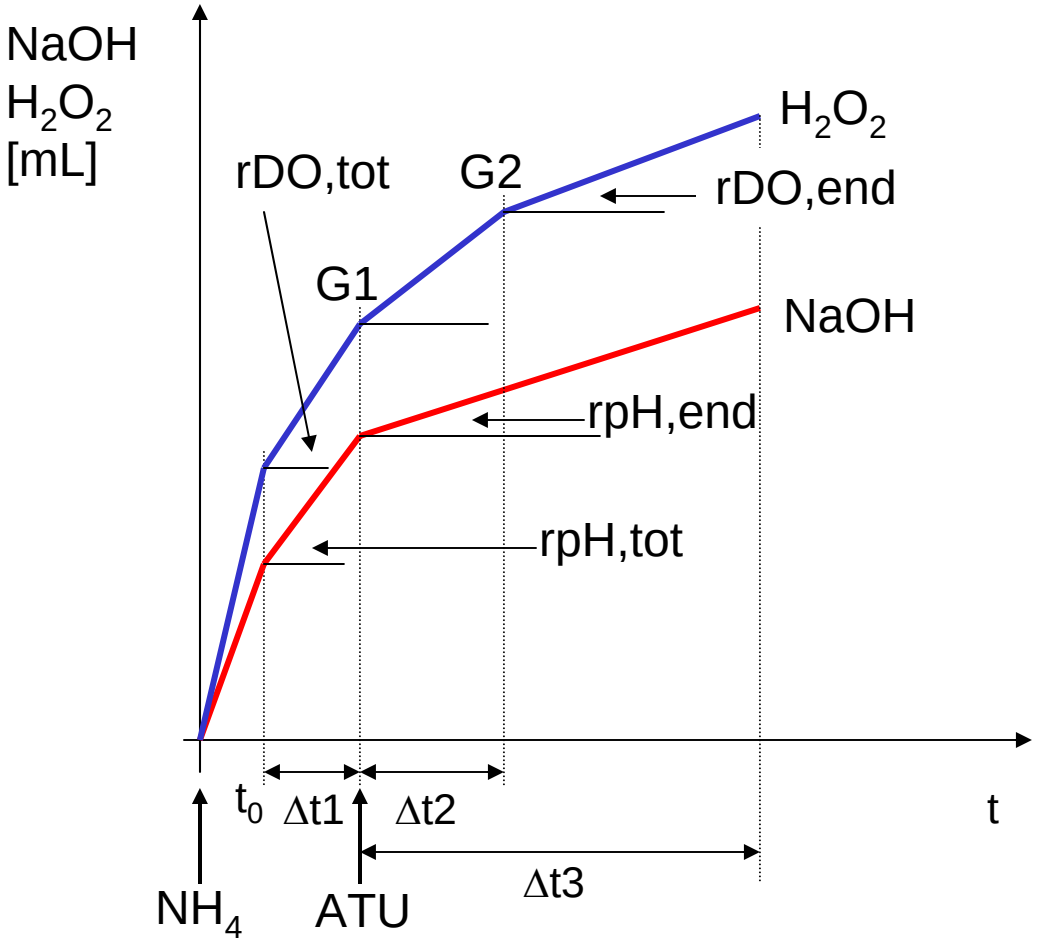
Titration reactor loading procedure

1. *sewage*
2. *sludge*

Mode 1 - Influent toxicity assessment

Test pH/DOstat

set points: pH=8.3 - DO=8 mgO_2/L



protocol for nitrification inhibition test with pH-stat titration as alternative to method UNI ISO9509

- **method validated with inter-laboratory tests**
- **confidence intervals similar to existing methods**

Operating procedure

- ✓ **set point routine**
- ✓ **NH_4Cl dosage**
- ✓ **nitrifying reaction titration**
- ✓ **allylthiourea dosage (ATU)**
- ✓ **on-line slopes determination for titration curves**

Mode 1 - Influent toxicity assessment

AOB and NOB activity rates determination

$$ACT(AOB) = \frac{(rpH,tot - rpH,end)\cdot M_{NaOH}\cdot f_{stNaOH}\cdot 60\,min}{\theta^{(T°C-20°)}\cdot V_{sludge}}$$

$$ACT(NOB) = \left[\frac{(r_{DO,tot} - r_{DO,end})\cdot 32\,mgO_2/mmol\cdot M_{O2}\cdot 60\,min/h}{\theta^{(T-20)}\cdot V_{sludge}} - ACT(AOB)\cdot f1_{stO2}\right]\cdot\frac{1}{f2_{stO2}}$$

Influent toxicity evaluation

AOB and NOB activity rates determined during last test are compared with historical activity data measured in previous tests (tests that didn't mark toxicity)

$$\left[\frac{(ACT_{mean} - ACT_{measured}}{ACT_{mean}}\right]\cdot 100$$

if TOX (%) > 1,2 CV(%) then $ACT_{measured}$ marks influent toxicity

warning advice is displayed on the control panel

Mode 2 - Nitrifiable nitrogen influent's content assessment

Purpose:

Rapidly obtain nitrifiable nitrogen influent's content assessment

- Concentrated sludge
- High ratio sludge/influent

✓ ***sludge****:* endogenous conditions

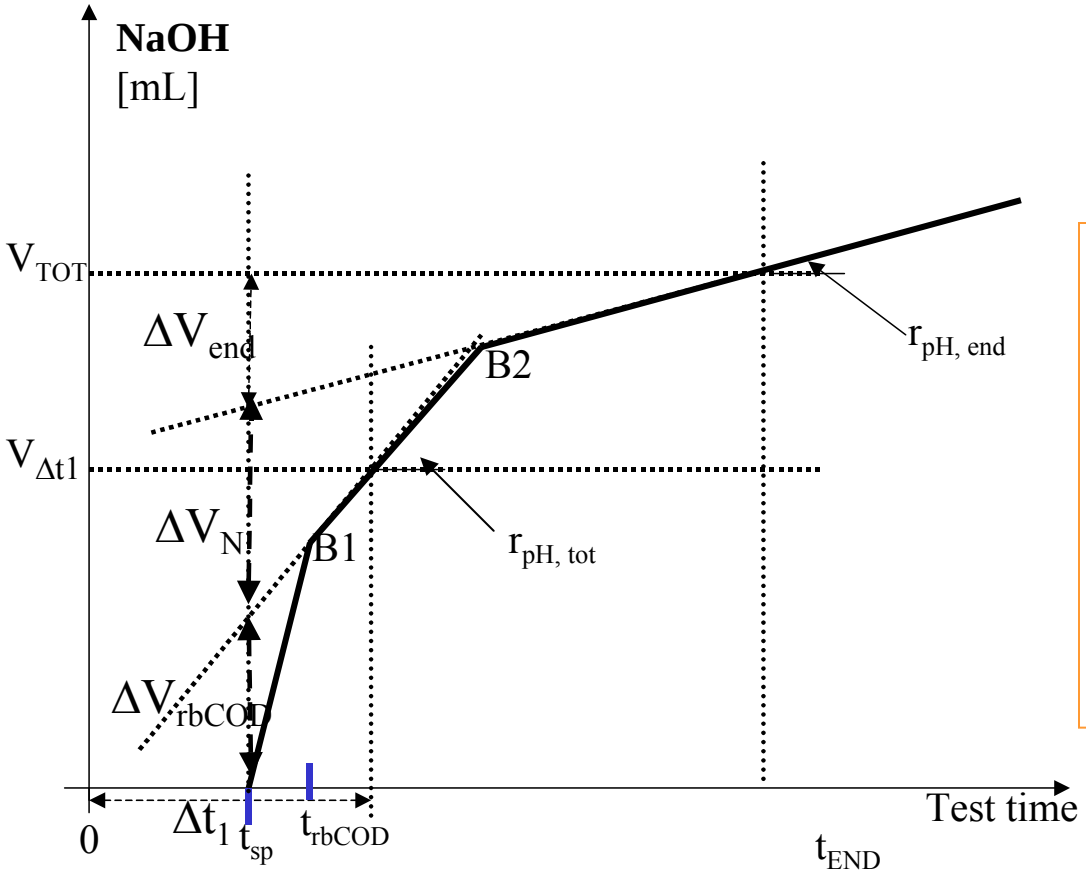
✓ ***influent:*** it can be withdrawn at every moment

field calibration is necessary

Titration reactor loading procedure

1. *influent*
2. *sludge*

Mode 2 - Nitrifiable nitrogen influent's content assessment



Test pH stat:

set point pH=8.3

Operating procedure

- ✓ **Oxygen furnished by H_2O_2**
- ✓ **set point routine**
- ✓ **nitrification reaction titration**
- ✓ **on-line slope determination for NaOH titration curve**

$$V_{NIT} = V_{TOT} - r_{pH,end} \cdot (t_{END} - t_{sp}) - [V_{\Delta t1} - r_{pH,TOT} \cdot (\Delta t_1 - t_{sp})] + (r_{pH,TOT} - r_{pH,end}) \cdot t_{sp}$$

$$[N] = \frac{V_{NIT} \cdot f_{st\,NaOH} \cdot M_{NaOH}}{V_{influent}}$$

Mode 3 – Maximum nitrification activity assessment

Purpose:

Estimate maximum specific activity for ammonia-oxidizer and nitrite-oxidizer biomasses (AOB and NOB)

- test is totally independent from influent characteristics
- substrate is furnished as NH_4CL

Operating conditions

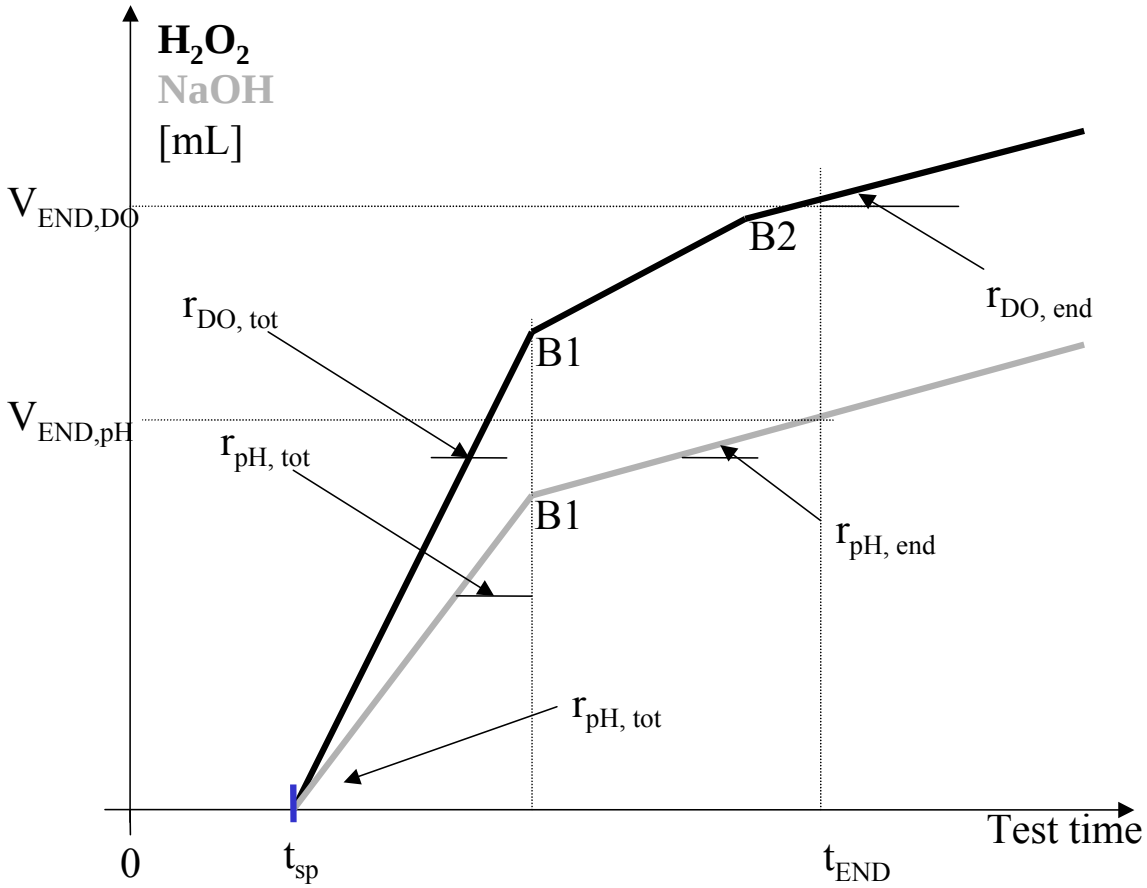
✓ ***sludge****: endogenous conditions*

field calibration is necessary

Mode 3 – Maximum nitrification activity assessment

Test pH/DOstat

Set points: pH=8.3 - DO=8 mgO_2/L



Operating procedure

- ✓ **set point routine**
- ✓ **NH_4Cl dosage**
- ✓ **Nitrification reaction titration**
- ✓ **on-line slopes determination for titration curves**

Mode 3 – Maximum nitrification activity assessment

AOB and NOB activity assessment

$$ACT(AOB) = \frac{(r_{pH,tot} - r_{pH,end}) \cdot M_{NaOH} \cdot f_{stNaOH} \cdot 60 min/h}{\theta^{(T-20)} \cdot V_{sludge}}$$

$$ACT(NOB) = \left[\frac{(r_{DO,tot} - r_{DO,end}) \cdot 32\, mgO_2/mmol \cdot M_{O2} \cdot 60\, min/h}{\theta^{(T-20)} \cdot V_{sludge}} - ACT(AOB) \cdot f1_{stO2} \right] \cdot \frac{1}{f2_{stO2}}$$

pH/DOstat titration assessments accuracy evaluation

Comparison between initial NH_4^+ concentration evaluated by titration and the real initial concentration (furnished as NH_4CL solution)

pHstat

$$V_{NIT,NaOH} = V_{END,pH} - r_{pH,end} \cdot (t_{END} - t_{sp})$$

$$[N]_{calculated,\,pH} = \frac{V_{NIT,NaOH} \cdot f_{st\,NaOH} \cdot M_{NaOH}}{V_{sludge}}$$

$$err,\,pH = \left| \frac{[N]_{calculated,pH} - [N]_{dosed}}{[N]_{dosed}} \right| \cdot 100$$

DOstat

$$V_{NIT,H2O2} = V_{END,DO} - r_{DO,end} \cdot (t_{END} - t_{sp})$$

$$[N]_{calculated,DO} = \frac{V_{NIT,H2O2} \cdot f1_{st\,O2} \cdot M_{O2}}{V_{sludge}}$$

$$err,\,DO = \left| \frac{[N]_{calculated,DO} - [N]_{dosed}}{[N]_{dosed}} \right| \cdot 100$$

Confidence interval for the assessments: ±20% of real value

- ✓ Threshold overcoming
- ⇓
- ✓ ***Warning message***

on the control panel

Mode 4 - Detection of the end of nitrification process

End of aerobic phase for SBR plants

On-line monitoring of ammonium oxidation process with detection of the end of the process

- ***Useful information for strategic management of the process***
  - nitrogen under-load and/or high nitrification activity
    - *aerobic phase stopped in advance*
  - nitrogen over-load and/or limited nitrification activity
    - *aerobic phase prolonged*

AOB and NOB activity assessment

Availability to detect nitrite accumulation (if limited NOB activity is reported)

operating strategies*:*

- ✓ *aerobic phase prolonged*
- ✓ *new inoculum of nitrifying biomass*

Mode 5 - Residual nitrates assessment at end of anoxic/aerobic phase (SBR)

Residual nitrate concentration assessment at the end of aerobic phase (a) or at the end of anoxic phase (b)

Purposes:

- Foresee the efficiency and the duration of denitrification process and of the following anoxic phase (a)
- detect progressive nitrate accumulation (a/b)
- evaluate the opportunity to dose an external carbon source to cope with complete denitrification (a)

Method:

Neutralization with acid solution (HCL) of the alkalinity produced by denitrification process in presence of acetate

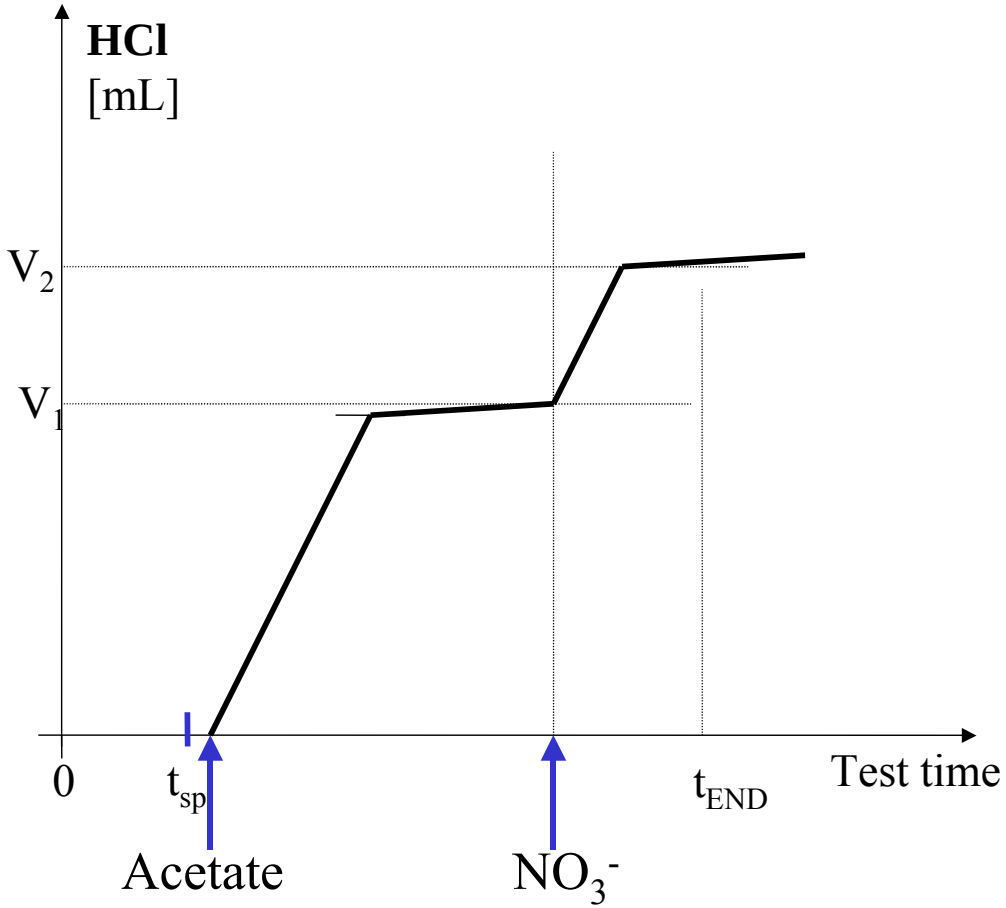
Hypothesis:

Denitrification kinetic independent from nitrate and acetate concentration

Mode 5 - Residual nitrates assessment at end of anoxic/aerobic phase (SBR)

Test pHstat (pH set point value established in calibration)

- Denitrification with simple substrate
- Reaction stoichiometry is known



Operating procedure

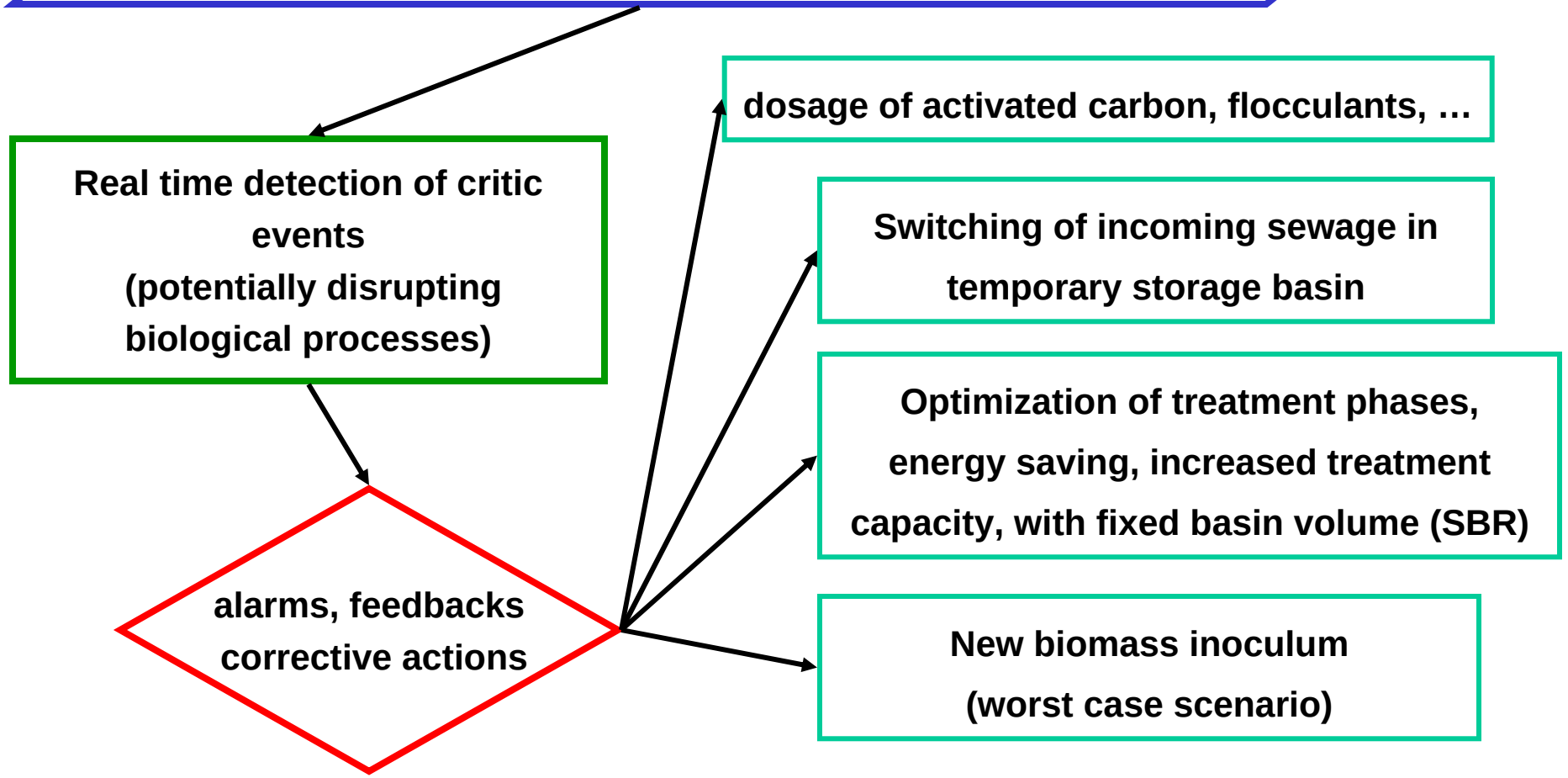
- **Sludge withdrawn at the end of anoxic/aerobic phase**
- **set point routine**
- **Acetate dosage (not limiting) → titration of the produced alkalinity (V_1)**
- **After nitrate reduction, nitrate is added (known amount) → titration of the produced alkalinity (V_2)**

Assessment of initial nitrate concentration in the sludge

$$N\text{-}NO_3^-{}_{fango} = N\text{-}NO_3^-{}_{dosati} \cdot V_1/V_2$$

On-Line titrator usefulness

- On-line bacterial activity monitoring
- Influent toxicity estimate
- Nitrifiable nitrogen influent's content assessment
- End of nitrification and residual nitrate assessment (SBR)



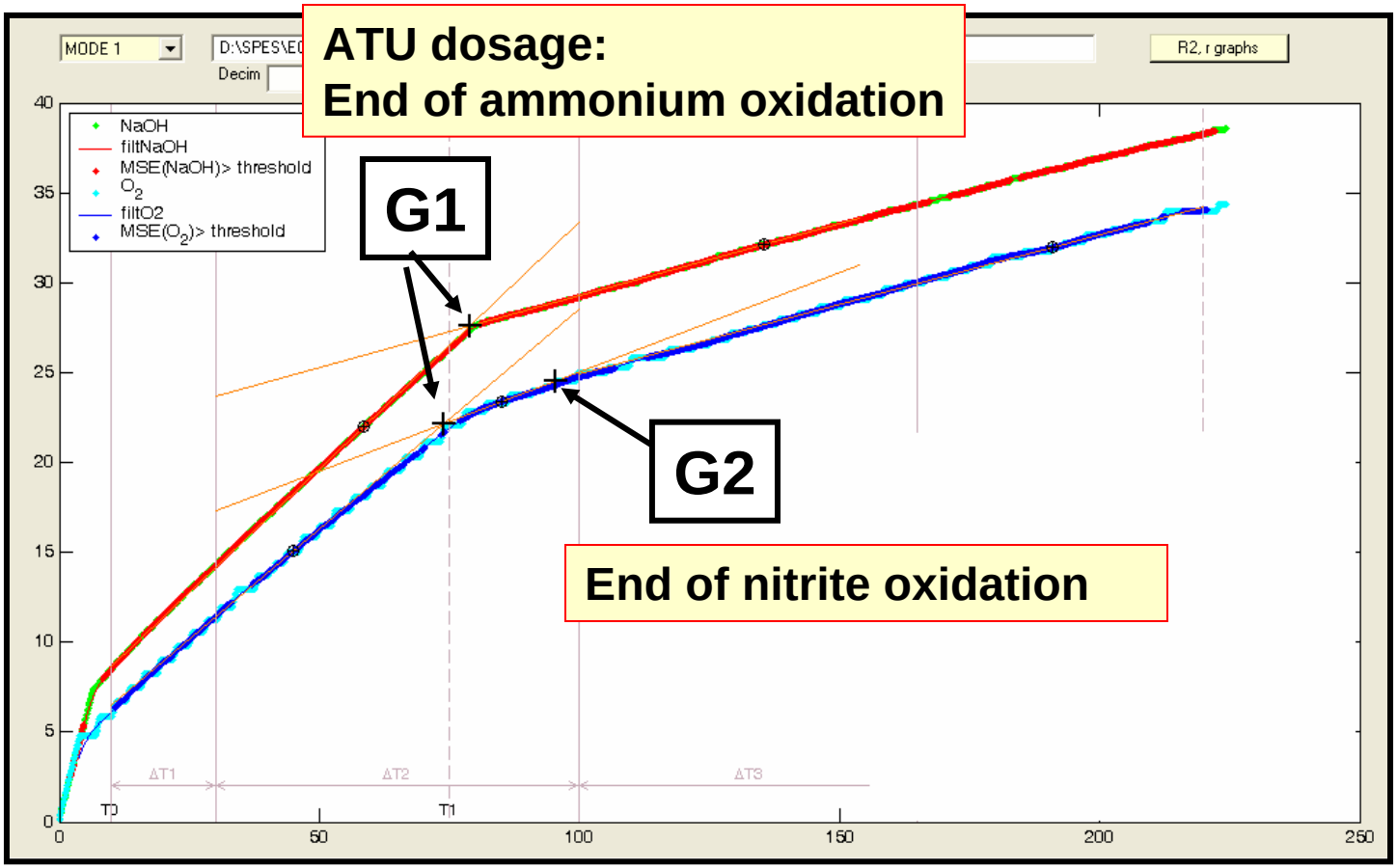
pH/DOstat titration tests on sludge and sewage samples from a full scale WWTP

- A series of tests were held before on sludge from a full scale continuous flow WWTP then on pilot plant SBR sludge
- Real sewage was used to test ph/DOstat technique
- Operation modes 1, 2 and 3 of the On-Line titrator prototype were tested with lab-scale titrator MARTINA

Mode 1 - Influent toxicity assessment

First experimental results: AOB and NOB activities measured on real sewage in absence of toxic compounds

- On-line data processing of data previously recorded with real time acquisition simulation



Mode 1 - Influent toxicity assessment

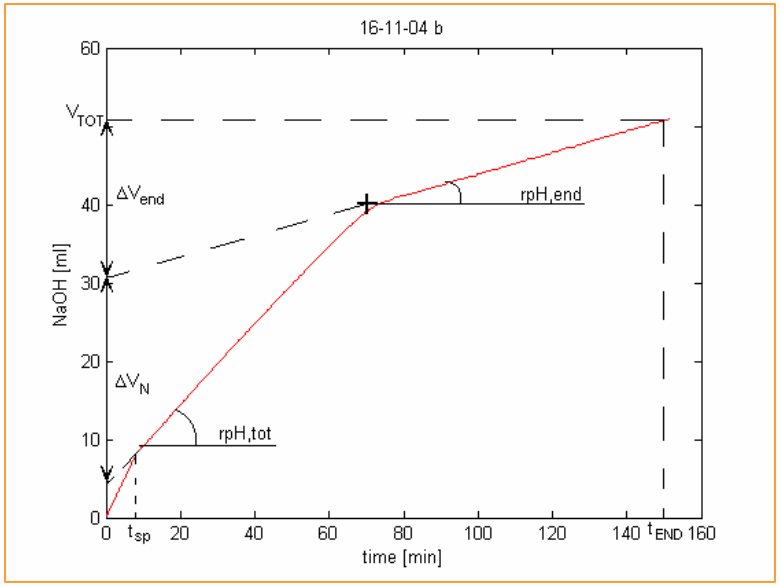
First experimental results:

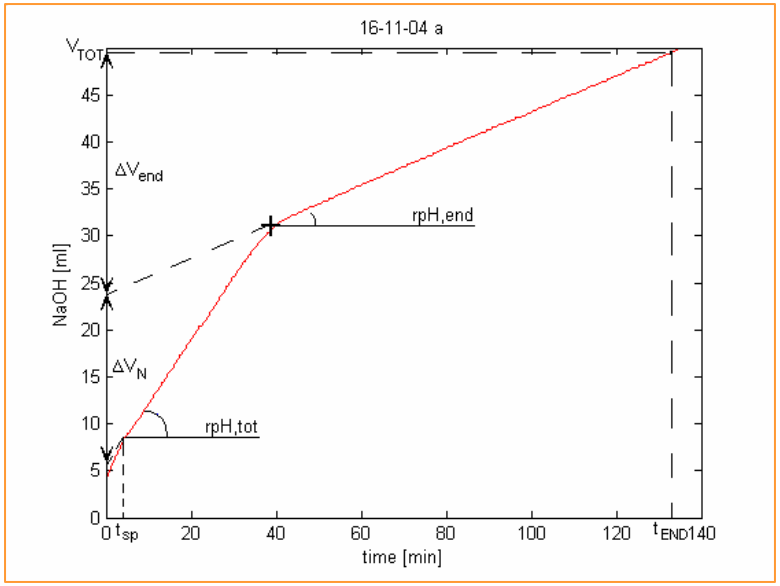
AOB and NOB activities measured on SBR sludge with real sewage in absence of toxic compounds

test	AOB pHstat mgN/(gVSS*h)	AOB+NOB DOstat mgN/(gVSS*h)	pHstat/DOstat discrepancy	NOB activity mgN/(gVSS*h)
17/8/04	1.06	0.93	12%	0.53
2/9/04	1.67	1.69	-1%	2.38
7/9/04	2.10	1.73	18%	1.76
8/9/04	3.20	2.80	13%	0.65
9/9/04	3.09	3.02	2%	1.63
14/9/04	2.74	2.55	7%	2.85
24/9/04	1.65	1.64	1%	2.01
28/9/04	1.10	0.89	19%	1.62
1/10/04	1.09	1.37	-26%	0.27
5/10/04	3.23	3.41	-6%	2.24
11/10/04	1.52	1.49	2%	3.98
average			**10%**	

Mode 2 - Nitrifiable nitrogen influent's content assessment

First experimental results

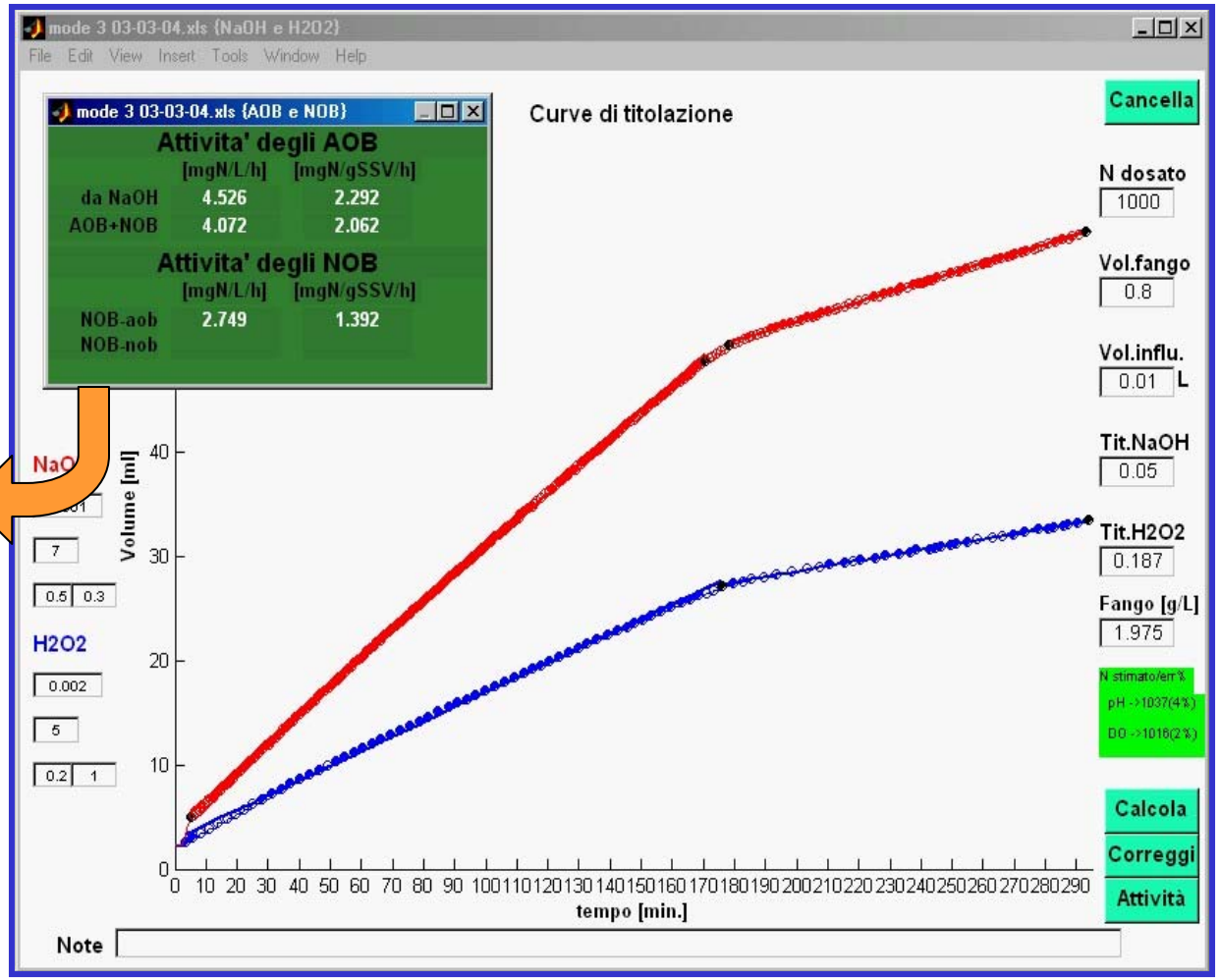




test	titration assessment	analytical result	difference (as percentage)	volumetric sludge/influent ratio
	mgN-NH_4/L	mgN-NH_4/L		
28-05-04	33.60	28.85	-16%	5
04-06-04	75.60	65.38	-16%	8
22-06-04	55.40	50.98	-9%	8
08-07-04	38.17	33.90	-13%	10
16-11-04	27.00	36.00	-25%	2.8
16-11-04	29.00	36.00	-19%	1.7
17-11-04	48.89	45.50	+7%	2.5
19-11-04	35.32	45.50	-22%	20
19-11-04	39.13	45.50	-14%	12.6
19-11-04	41.90	45.50	-8%	9.7
		average value	**-12%**	

Mode 3 – Maximum nitrification activity assessment

Graphical Matlab interface for real time titration curves, slope detection and activity rates calculations



input data: sludge volume and VSS concentration

input data: titrants concentrations

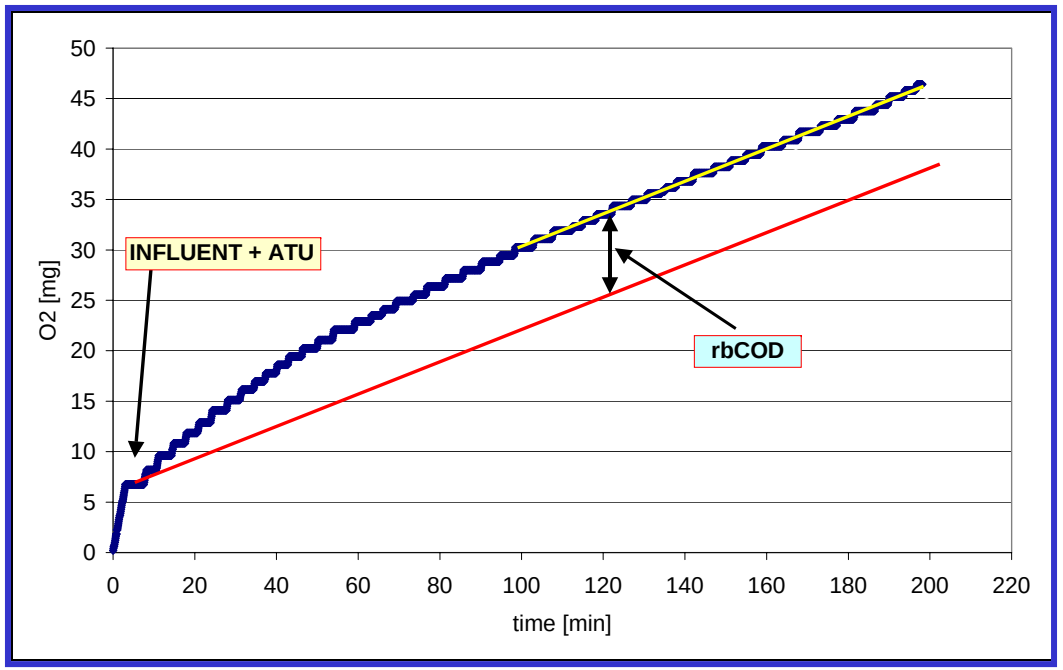
output data: specific activities for AOB and NOB

Evaluation of influent rbCOD by titration tests with MARTINA

DOstat tests performed to:

- evaluate the interference of heterotrophic respiration rate with nitrification respiration rate due to autotrophic biomass (set up of mode 1 implementation)
- estimate the rbCOD

test performed on 24/09/04



Procedure (see Mode 1) allylthiourea dosed at the very beginning of the test to evaluate heterotrophic respiration only

oxygen mass balance allows computation of COD removed until the hydrogen peroxide titration rate reaches a pseudo-constant slope (about 2 h of reaction)