EOLI Contract Number ICA4-CT-2002-10012
Efficient Operation of Urban Wastewater Treatment Plant

SIMPLIFIED LOW-COST ON-LINE UV SPECTROPHOTOMETER SENSOR

Deliverable 3.3

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Task WP3.2

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Abstract:
The objective is to adapt an existing UV spectrophotometer for the on-line monitoring of nitrate, nitrite and COD during cycles of SBRs. The SECOMAM company was asked to do some changes to an existing spectrophotometer sensor based a detailed schedule of conditions. A filtering system was also developed in order to provide particle-free fluids to the sensor. The modified UV-pectrophotometer sensor (STAC) was implemented into the bioreactor at INRA-Narbonne. First results have shown that the on-line spectrophotometer sensor was able to monitor on-line and quite efficiently nitrate, nitrite and COD in SBR effluent.

Keyword List: SBR, wastewater treatment, UV, spectrophotometry, on-line sensor

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I– Introduction

Gradient, whose contribution started on November 2002, is concerned with WP3.2 (Development of a simplified low-cost on-line UV-spectrophotometric sensor) and WP3.3 (Pilot plant implementation).

Ultra-violet (UV) spectral analysis can be used to quantitatively monitor several compounds in water. The main objective is to develop a low-cost on-line UV spectrophotometric sensor to monitor on-line specific compounds (such as nitrate, biomass and organic nitrogen) during the operation of a Sequential Biological Reactor (SBR). The global methodology consists in:

- Evaluating the applicability of UV spectrophotometric existing sensors to quantitatively monitor target compounds water.
- Developing a simplified low-cost UV spectrophotometric sensor to monitor on-line target compounds during the operation of a SBR.
- Evaluating the performance of the developed spectrophotometric sensor on a pilot-scale SBR bioreactor; it has been decided at the meeting of Mexico to install the sensor on the INRA-LBE bioreactor.

This deliverable focuses on the development of a low-cost on-line spectrophotometer and on its implementation at the pilot-scale bioreactor in Narbonne (LBE-INRA).

II– Description of the on-line spectrophotometer

The company SECOMAM developed an on-line spectrophotometer, called STAC. The STAC instrument exists in a standard version but it was modified to manage the behaviour of SBR with different wastewaters and finally with the INRA-LBE wastewater where the system will be finally installed.

The development of the STAC consists of adapting the standard analyser STAC to a resolution of 0.5 nm with 256 measurement points, from 190 to 240nm , and latter from 190 to 360, to make possible discrimination between nitrate (205 nm) and nitrite (211 nm) peaks. This adaptation was done in two steps:

- Adaptation of the monochromatic system with, in particular, a CCD detector of 256 pixels and a an adaptation of a new diffraction system,
- Development of the UV-Pro software to manage pumps, lamps, diode captor, for data storage and UV spectrum management and for the interface man-machine.

The measuring range is:

Nitrate: $\mathbf{NO_3^-}$: 1 to 50 mg/L
Nitrite: $\mathbf{NO_2^-}$: 1 to 50 mg/L
Organic matter: **COD**: 5 to 350 ng/L

The STAC instrument was implemented in the INRA-LBE bioreactor in May and has been operated continuously thereafter.

To know more about STAC instrument:
STAC (Compact Alarm System) measures the sample absorbance in the specific area of the UV spectrum, the STAC records the spectral profile of the sample, a true numerical photograph of the water quality (www.SECOMAM.com). It is composed of 3 connected modules.

Advantages

- Physical method with almost no consumable
- Very fast reading
- Easy and low maintenance
- Both quantitative and qualitative reading
- Built in separates enclosures with aqueous sample separated from electronics

- Fitting with most of tele-transmitable systems
- Fully automatic

Sampling
- Cuvette cleaning and sampling circuit rinsing automatic and sequential
- Automatic sampling programmable from 5 to 30 minutes
- Pinching valves and 8 mm tubing for TSS reading and filtration free

Data transfert
- 4 current loops
- RS 232
- UV PRO software for data storage and UV spectrum management

The STAC spectrophotometer sensor is illustrated in Figure 1 and 2.

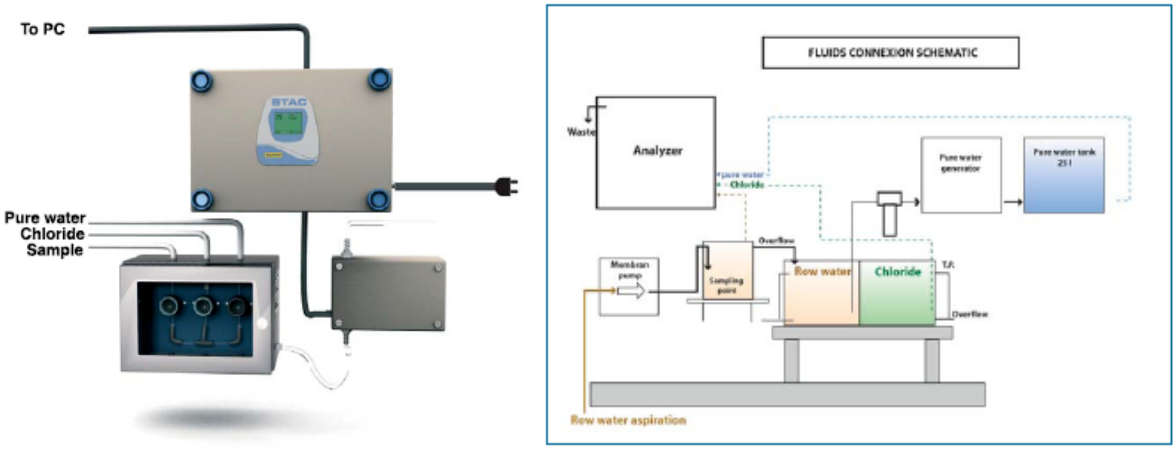
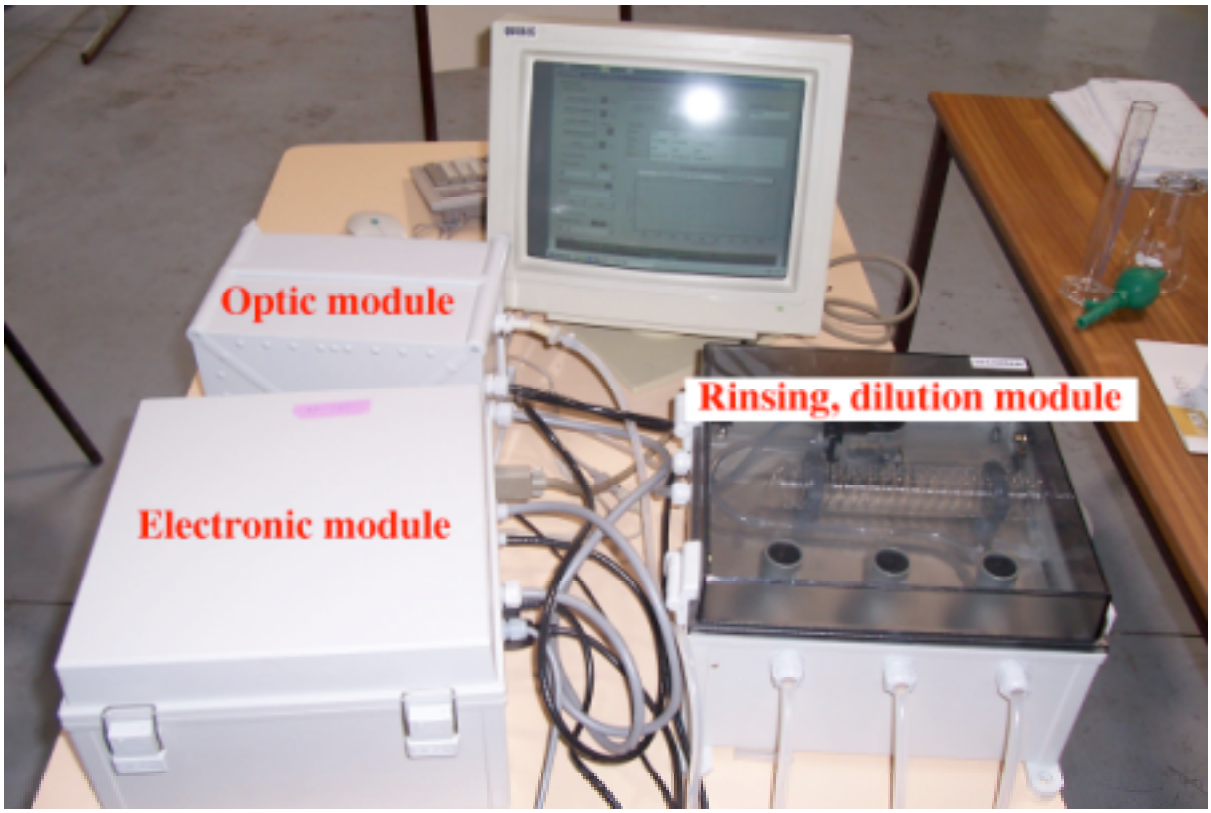


Figure 1. STAC Intrument.



Overview of the STAC spectrophotometer

Optic module

Rinsing and dilution module

Figure 2. Pictures of the STAC modules.

The electronic module contains an embedded card with Windows XP, and an dedicated version of UV-Pro software, that allows the complete control of the instrument, the deconvolution of the spectra, and the recording of the spectra and of the results in text files, that can be used for the EOLI control process.
The screen capture below shows, on the left hand, the process parameters, on the top the chosen deconvolution model, and the sepctrum and the results of, here, nitrate, nitrite and soluble COD. These three parameters were defined previously in the deconlution model.

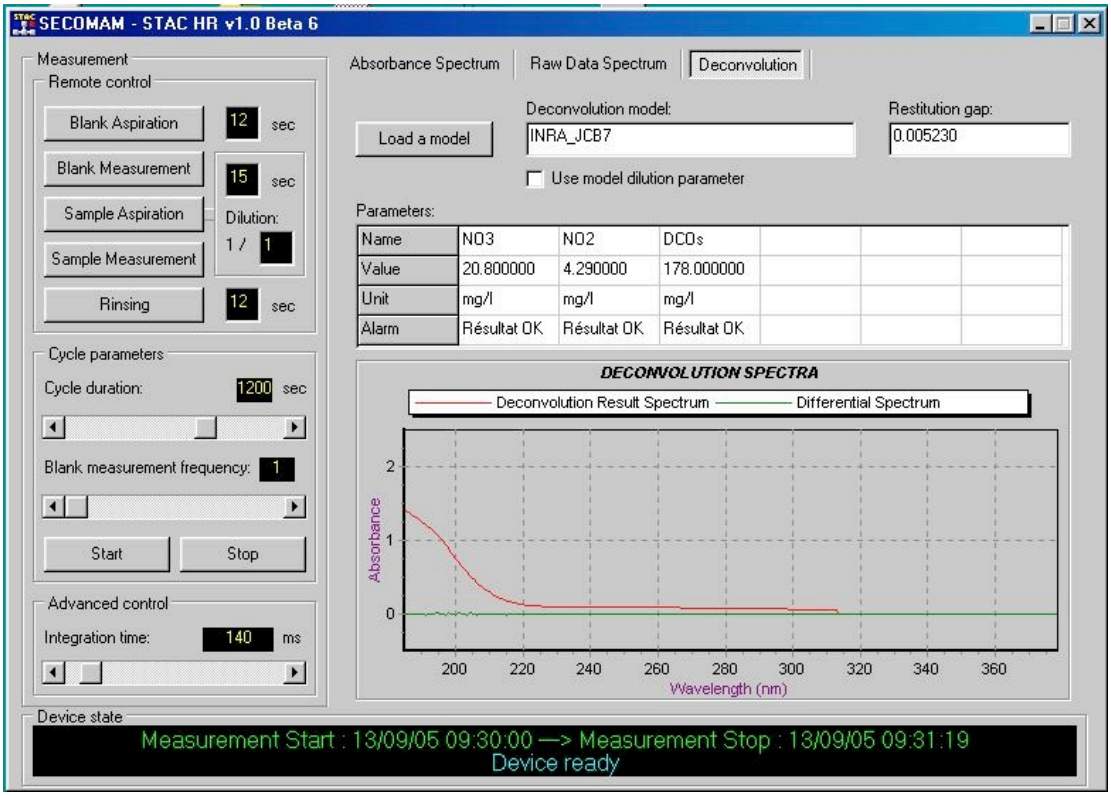


Figure 3. Front panel of the UV-Pro software.

III – Implementation of the UV-spectrophotometer sensor at LBE-INRA

The on-line spectrophotometer was implemented at the LBE-INRA SBR, in Narbonne as illustrated below. A 60 µm on-line filter and a settling column were installed in a recirculation loop allowing particle-free samples for the UV-measurement as shown in Figure 4.

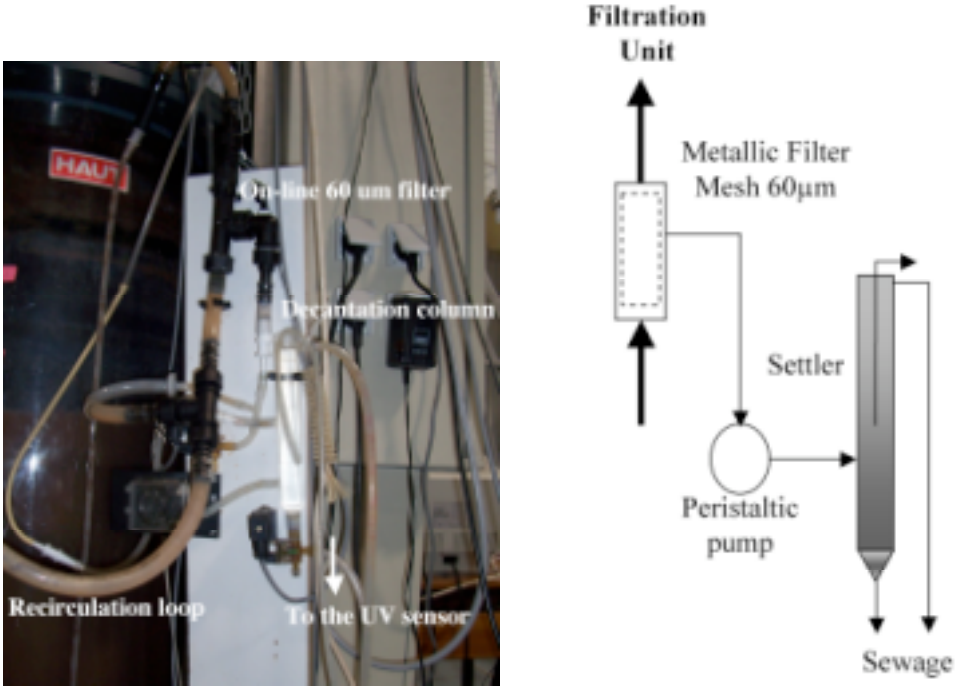
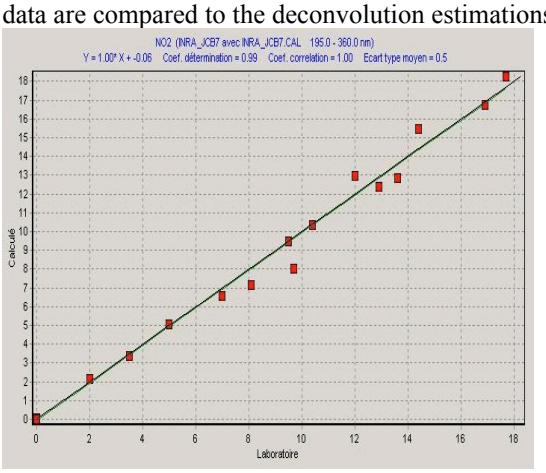


Figure 4. Description of the filtering system.

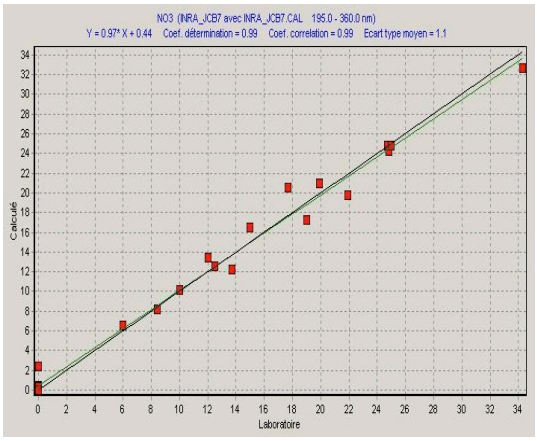
IV – On-line monitoring of nitrate, nitrite and COD

Two types of signal processing were tested: a Partial Least Square regression method and the spectral deconvolution developed by SECOMAM (UV-Pro software). The two methods were calibrated based on spectram from the LBE-INRA bioreactor.

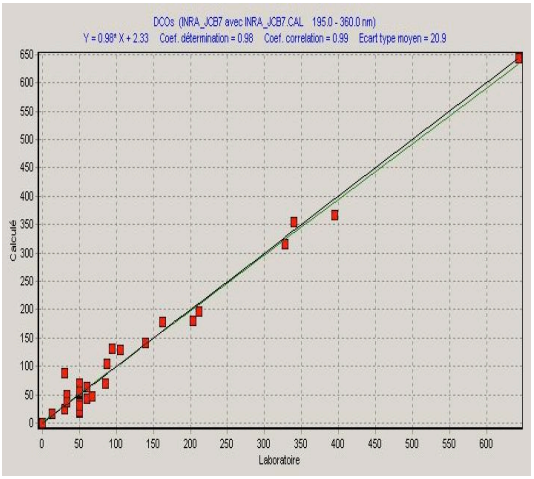
The three figures below show the calibrations regressions for nitrate, nitrite and sCOD. 20 sets of experimental data are compared to the deconvolution estimations.



Calibration for nitrate
y = 0.98 exp. + 0.44; r=0.99



Calibration for nitrite
y = 1.00 exp – 0.06, r=1



Calibration for sCOD
y = 0.98 exp + 2.3, r = 0.99

The experimental results obtained from 28 cycles were therefore used to validate the model. Table 1 below indicates that:

- For nitrate and nitrite, good correlations were obtained for the UV-Pro software, as well as for PLS regression. A PLS mc (mild-centering) was also tested. Both PLS regression methods sometimes exhibit negative values, that have never been found with the UV-Pro deconvolution.
- Fot soluble COD, all regression methods again show good correlations with the experimental data, with again an advantage for the UV-Pro software that never provides negative values. It can also be noticed that experimental data were sometimes suspicious, especially for the low values, indicating the limits of the analytical technique for such a reactor.

The yellow, orange and red background colors refer respectively to suspected experimental values, suspected predicted values, and aberrant values.

Table 1. Validation of thePLS and spectral deconvolution models

Lab	UVPRO	PLS none	PLS mc	Lab	UVPRO	PLS none	PLS mc	Lab	UVPRO	PLS none	PLS mc
23.6	24.5	24.4	23.8	19.0	78.0	77.3	45.7	0.0	0.1	-0.1	0.4
0	0.7	2.3	2.4	34.0	172.0	65.2	77.1	0.0	0.7	0.6	0.4
15.2	15.4	15.4	15.4	14.0	62.0	60.2	57.2	11.1	11.4	11.6	11.6
25.9	27.2	27.1	27.1	12.0	24.0	34.3	42.8	10.6	11.8	11.9	11.8
26	24.6	25.9	25.4	50.0	80.0	74.8	45.1	0.0	0.2	-0.1	0.4
5	0	1.4	1.1	395.0	366.0	394.9	360.3	0.0	0.0	-0.6	-0.1
0	0	-0.1	0.3	340.0	353.0	338.6	365.6	0.0	0.0	0.2	-0.3
0	0	1.5	1.6	328.0	317.0	294.9	311.6	0.0	0.0	-0.8	-1.0
0	0	-0.7	-0.6	162.0	178.0	183.1	204.6	0.0	0.0	-0.3	-0.6
0	0	-1.9	-1.9	109.0	95.0	111.6	124.5	0.0	0.0	0.4	0.3
0	0	-1.9	-2	109.0	92.0	103.7	102.7	0.0	0.0	0.8	0.9
2	3.2	2.5	2.4	80.0	95.0	87.9	87.9	5.0	4.6	5.2	5.2
10.5	8.3	8.4	8.4	60.0	106.0	76.6	84.6	9.0	10.5	10.8	10.7
18.5	17.7	17.7	17.9	60.0	64.0	61.0	81.6	11.6	14.2	14.4	14.1
33.6	24	23.2	23.9	50.0	83.0	-11.6	48.5	16.7	19.5	21.4	20.5
34.2	30	27.7	28.8	50.0	36.0	-60.1	26.2	16.8	23.7	26.6	25.3
45	36.9	43.9	45.5	11.0	35.8	-457.8	-289.3	0.0	15.8	15.3	12.9
0	0	-2.6	-2.4	90.0	150.0	149.8	171.4	0.0	0.0	0.6	0.2
20	20.3	19.9	19.8	50.0	81.0	76.5	74.1	11.0	13.1	13.4	13.5
36	37.2	27.2	28.6	13.0	205.0	-153.0	-31.3	15.0	16.9	28.7	26.9
	Nitrate				Nitrite				sCOD		

These results show that it is possible to on-line estimate nitrate, nitrite and sCOD contents in a SBR using UV spectral analysis. PLS and UV methods give both acceptable correlations with experimental data, especially for nitrate and nitrite. The two methods were compared using the Root Mean Square Errors of Prediction (I.E. an average of the difference between the actual a,d the predicted values). Table 2 indicates UV-Pro software provides better results (smaller values of RMSEP) so that it was chosen for the on-line monitoring of the SBR.

V – Conclusion

An on-line UV-spectrophotometer sensor was developed with SECOMAM and implemented within the LBE-INRA bioreactor. The on-line UV spectra, obtained from numerous samples, were analyzed using three different methods of spectral analysis: two based on Partial Least Square regression and one based on spectral deconvolution. Some spectra were used to calibrate the estimation of nitrate, nitrite and sCOD, and the other were used for validation. UV-Pro software finally gave the best results, and it was chosen to monitor on-line the SBR.