NITROGEN PROBLEMS IN WASTER WATER TREATMENT PLANTS AND THE BENEFITS OF ONLINE MONITORING OF NITROGEN CONCENTRATIONS

Procedencia del nitrógeno en el agua residual

Sewage Treatment Plants (STPs) receive waste water which have a high nitrogen content, which can be shown in 4 different forms mainly: ammonium – ammonia ($NH3\text{-}NH4^{+}$), nitrate ($NO3^{-}$), nitrite ($NO2^{-}$) and organic nitrogen. The main causes nitrogen content comes from are:

- Agriculture: derived from fertilizers that seeps into water aquifers.
- Animal husbandry: derived from animal excrements. Depending on the food animal industry (cattle, pigs, etc.), between 200 and 2300 mg/L as ammonia are generated.
- Air pollution: nitrogen oxides cause acid rain, whose water ends at Wastewater Treatment Plants (WWTPs)
- Industrial activity: water could contain between 300 and 2000 mg/L as $N\text{-}NH_3$ are discharged from industrial processes.

Ammonia is the most common component within all the possible forms nitrogen can be shown.

Problem: eutrophication

Eutrophication is the excess supply of nutrients (mainly nitrogen and phosphorus) to an aquatic system, leading to uncontrolled algae proliferation. The excessive growth of algae in aquatic environments such as lakes, rivers, reservoirs, etc. causes a high consumption of oxygen in the water, contributing organic matter. The resulting adverse effects are:

- Low water quality, which can cause respiratory and health problems in humans.
- Affecting fish life in the area, as the low amount of oxygen can become incompatible with the life of the fish.
- Affecting watercourses, making it impossible to navigate them.
- Indirect consequences for birds and mammals, as there are ideal situations for the proliferation of bacteria that produce lethal toxins for them.

Current legislation in Spain

Out of European Union, each country uses its own regulation to control nitrogen. In Spain, according to EU Directive 91/271/EEC, the requirements for discharges from urban wastewater treatment plants depend on the capacities of the plant, using the unit of measurement population equivalent (PE), which is the biodegradable organic load with a five-day biochemical oxygen demand (BOD 5) of 50 grams of oxygen per day. Thus:

- 15 mg/L N for plants from 10,000 to 100,000 PE.
- 10 mg/L N for plants > 100,000 PE

In addition, in both cases a minimum reduction percentage of 80% is required, which is related to the inlet flow load.

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However, due to the growing problem and concern that eutrophication causes, more exhaustive control measures are foreseen for wastewater treatment plants, especially in large urban centers and with more economic resources.

Nitrogen removal systems.

Nowadays there are few methods used to remove or to reduce nitrogen content in waste water, as nitrification – denitrification, physical – chemistry process or electrochemical oxidation. However, the first method is the most used in WWTPs.

Nitrification – denitrification process consists on:

El proceso de nitrificación – desnitrificación se divide en dos procesos:

- Nitrification process: it is a microbiological process through ammonia is oxidized by bacteria in presence of oxygen and inorganic carbon. This process does not remove ammonia but transforming into nitrate following the chemical reaction below:

$$NH_4{}^+ + 2O_2 \rightarrow \boldsymbol{NO_3}^- + 2H^+ + 2H_2O$$

- Denitrification process: the nitrate previously formed is reduced to gas nitrogen (motionless gas) thanks to heterotroph bacteria action, in a non-oxygen and presence of carbonic carbon medium, following the reaction

$$NO_3{}^- + 10H^+ + 10e^- \rightarrow \boldsymbol{N_2} + 2OH^- + 4H_2O$$

All the process requires oxygen addition during the first part through airing action. The energy consumption required to perform it is one of the most significant daily costs in STPs, being the main factor that limited the system. On the other hand, during denitrification TOC addition is required, being also an expense for the plant operation.

Advantages of online analysis and monitoring of ammonia – nitrate – nitrite concentration

As it has been explained above, energy consumption and TOC addition constitute two of the main operation expenses during nitrogen removal. This is why daily monitoring brings great economic benefits, as controlling any time oxygen demand and subsequently, optimizing the airing process, saving money on energy supply.

On the other hand, nitrate and nitrite online control during the whole process permits to have a more efficient WWTP, having a total control on the variables that affects the process, besides to control TOC addition, commonly as methanol. Thus, once again, money is saved reducing methanol consumption.

Example of economic savings

According to a research run by Comunitat Valenciana (Spain) during 2010 decade, the montly average energetic consumption was 0.42 kWh/m^3. However, the research also remarks that as bigger is the plant, lower is the average consumption. Thus, 125,000 PE plants average consumption was 0.61 kWh/m^3, 0.36 kWh/m^3 at 500,000PE plants and 0.30 kWh/m^3 at 1,000,000 PE WWTPs.

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NITROGEN CONTROL WITH INSTRAN IN SEWAGE TREATMENT PLANTS

On Sewage Treatment Plants, airing process represents between 30 and 60% of the whole plant consumption. Thus, assuming a media value of 45%, the energetic consumption to remove nitrogen compounds is within 0.2745 – 0.162 – 0.135 kWh/m^3, respectively. Assuming a 100,000 PE case studio plant, 27,450 kWh per month are needed. Finally, if ammonia control would allow a 5% improvement of the energy supplied, **the monthly savings are close to 1,370 kWh.**

Immersion probe vs analyzer comparison

There are commonly in market two main ways to control online nitrogen compounds: immersion probes and analyzers. Immersion probes have the main advantage that they can be directly sunk in sample, providing a continuous and instantaneous result of the concentration and requiring, theoretically, less maintenance. However, due to the dirty of samples treated, other compounds concentration is significantly high. Some of those elements, such as nitrite and chloride, commonly present on WWTPs, are a high interference on nitrate analysis. So, the result provided by the probes are far from the real concentration despite the probes specifications commonly establish around 5% accuracy. It causes that the probes need to be calibrated weekly or even more often, using also laboratory results for this calibration, increasing the maintenance of the equipment, besides the uncertainty of do not to be sure in any time if the result is correct. On the other hand, although the maintenance is higher, the sample could be treated before the analysis performance, protecting the analyzer – the analyzer is more robust – and removing the interferences that affect nitrate analysis, being the results got accurate and providing the control system most reliability than immersion probes, and subsequently,

	Advantages	Disadvantages
Immersion probes	• Continuous and direct result • Low maintenance	• Samples can not be treated previously • Low concentration result accuracy • Weekly comparison with lab results to re-calibrate • Uncertainty control system
Analyzer	• **Accurate concentration result** • Sample can be treated, eliminating interferences • More robust	• Maintenance required depending on analyzer features • Batch result instead of continuous result (10-15 min) • Reagents consumption

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NITROGEN CONTROL WITH INSTRAN IN SEWAGE TREATMENT PLANTS

Ammonium – Nitrate – Nitrite Instran®

The Instran online analyzer is an analyzer for monitoring different parameter concentration continuously, such as ammonium, nitrate or nitrite, with a frequency of up to 1 analysis every 10 – 15 minutes depending on the parameter measured.

The specific cleaning systems of the equipment allow to deal with dirty water from sewage treatment plants, without affecting the measurements with cross interferences in subsequent analyses. Its simple design makes it easy for plant operators to become familiar with the equipment and its maintenance is very low. All these features make the Instran analyzer unique in the market with exceptional performance for the control of nitrogen compounds in wastewater treatment plants and its consequent economic savings, as well as complying with current legislation.

Ammonium Instran®

The ammonium analyzer is silhouetted by a simply method which permits that common WWTP interference parameters affect the sample measurement. Moreover, standard known addition method used permits to correct in each analysis possible matrix sample variations, avoiding interferences. Finally, the low reagent consumption (0,5 mL/analysis) of each of both reagents needed, makes the *Ammonium Instran®* analyzer the best online analyzer in market.

Nitrate Instran®

High chloride and nitrite content in waste water makes difficult to perform a reliable nitrate analysis. As sample can not be treated when immersion probes are used, chloride and nitrite interference is difficult to be corrected. Moreover, if the concentration of the parameters mentioned are continuously fluctuating along time, the interference can not be corrected neither.

However, *Nitrate Instran®* uses an extra reagent that eliminates chloride and nitrite interference, providing a unique reliability on the result to nitrate analyzers. On the other hand, as it uses the same analytical technique than *Ammonium Instran®,* significant changings on sample matrix are also corrected.

Nitrite Instran®

The colorimetric measurement system the analyzer functionality is based on is not affected by the color of sample as a blank correction is performed before each analysis to avoid color and external interferences. Moreover, the intense pink color developed when nitrite reacts with the reagent provides a high sensitivity to determinate NO_2^- concentration. Once again, low reagent consumption (0,4 mL/analysis) of each of the reagents used makes *Nitrite Instran®* a simple and excellent option to control nitrite concentration.

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Nitrate Instran® real experience – UTE Artigas trial

From the parameters explained above, nitrate control was the most challenging one due to the several interferences that STPs sample contains, mainly chloride, which in some cases could be higher than 750 mg/L. Thus, Instrumentacion Analitica SA has been working on a reagent capable of remove chloride and nitrite interference without affecting nitrate compound. Once the reagent was developed and tested on the laboratory, the analyzer was tested continuously with real sample for 1 month in UTE Artigas Leachate Treatment Plant. The plant is located in Alonsotegui, close to Bilbao, and Vizcaya government manages it. The characteristic of the leachate plants, where sample matrix changes continuously and contains many possible metals and compounds (less controlled than WWTP sample composition) was a total challenge to *Nitrate Instran®* performance. At the same time the analyzer was working for 4 weeks, plant operators run, sporadically, nitrate analysis on the laboratory to check if the results got with Instran matched with the real one. The Figure 1 shows, on blue, the N-NO_3 behavior along time, noticing plant operators of possible spikes and to treat the sample if required. The orange dots show random laboratory measurements by Artigas UTE technicians. It corroborates that the spikes indicated by Instran were real spikes and not analyzer failures, providing a extreme reliable results.

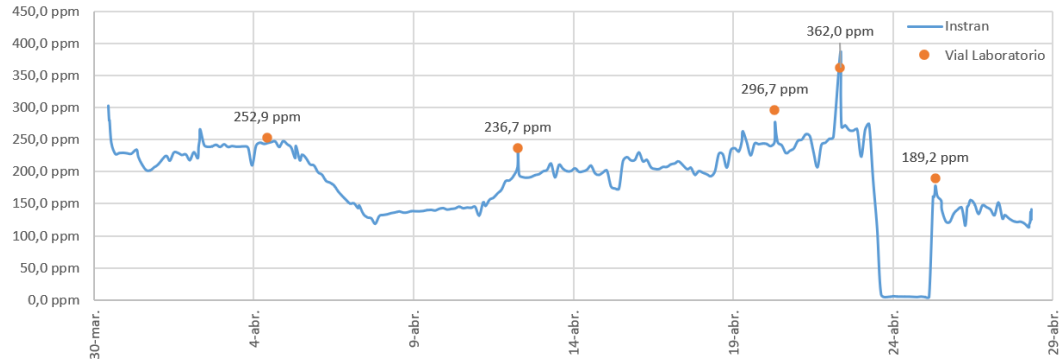

Figure 1. N-NO_3 concentration along the month trial of NItrate Instran®

For more specific information about the analyzer, please contact:
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