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Application News

No. AD-0084

TOC-LCSH with TNM-L and TOC-Control L software

Determination of Total Nitrogen in Waste Water with Oxidative Catalytic Combustion and Chemiluminesence Detection

❑ Introduction

Nitrogen is a type of nutrient pollution that comes from the microbial digestion of animal wastes or nitrogen-based fertilizers. High levels of nitrogen in bodies of water can result in harmful algae blooms, which reduces nursery habitats, kills fish and forms oxygen-starved "dead" zones [1]. Drinking water containing high concentration of nitrite (NO_2^-) or nitrate (NO_3^-) can also adversely affect infants and children as it results in methemoglobinemia, a blood disorder that interferes with the body's processes for carrying oxygen to cells and tissues [2]. Hence, it is important to monitor nitrogen level in drinking water and waste water. This application news demonstrates the analysis of total nitrogen (TN) in Certified Reference Materials (CRM) waste water samples using Shimadzu TOC-LCSH coupled with TNM-L TN analyser.

The TOC-LCSH and TNM-L measure TN according to BS EN 12260 [3]. The nitrogen compounds in water that can be measured comprises of free ammonia, ammonium, nitrite, nitrate and organic compounds. Dissolved or gaseous nitrogen (N_2) cannot be determined using this method. The TN in test solution undergoes oxidative catalytic combustion at 720ºC to nitrogen oxides. After the nitrogen oxides reacts with ozone, the nitrogen dioxides are measured by a chemiluminescence detector.

❑ Experimental

All the chemicals were purchased from Merck, Germany. Type E-1 [4] ultra pure water with resistivity of 18MΩ was used. The 1000 ppm TN standard solution was prepared according to BS EN 12260. The 1000 ppm TN standard solution was then diluted to 20 ppm.

The following samples were purchased from ERA, USA:

a) CRM Waste Water catalogue no 739 "Simple Nutrients". It contained 4.85 ppm (NO_2^- + NO_3^- as nitrogen) and 2.42 ppm ammonia as nitrogen, giving a total of 7.27 ppm TN.
b) CRM Waste Water catalogue no 741 "Complex Nutrients". It contained 14.10 ppm Total Kjeldahl nitrogen (TKN) which is equivalent to TN concentration.

During measurement, the "Multiple Injections" function was selected and the injection volume used was 40 µl. The TOC-LCSH syringe was washed two times with the test solution prior to injection and each test solution was analyzed at least two times.

❑ Results and Discussion

The various standard solutions in the calibration curve was prepared from a 20 ppm standard solution by the TOC-LCSH using the in-built auto-dilution function. Figure 1 showed the calibration curve obtained.

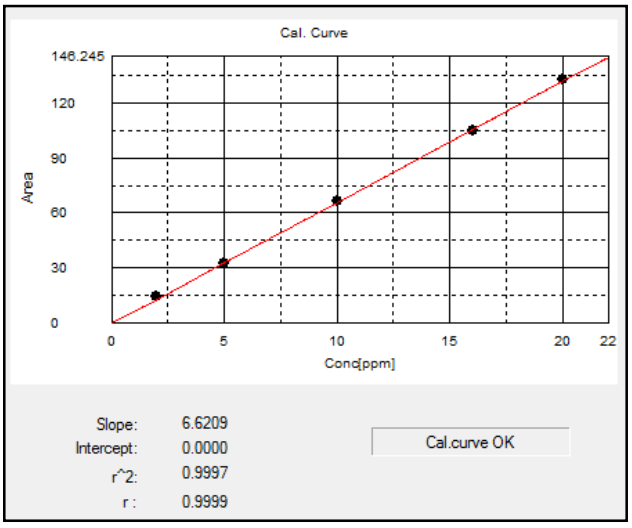

Figure 1: TN calibration curve

As the calibration curve generated have a coefficient of linear regression (R^2) of more than 0.999, this means that the TOC-LCSH can dilute and prepare the standard solutions correctly.

A 10 ppm standard solution was prepared/diluted from the 1000 ppm standard solution and analysed to check the calibration curve. The percentage recovery obtained was 97.8% (Table 1). This further showed that the calibration curve was prepared correctly by the TOC-LCSH auto-dilution function.

The results for the CRM samples were satisfactory since the percentage accuracy was from 95 to 105% (Table 1). The results also showed good reproducibility as the percentage coefficient of variation (% CV) was less than 3%.

Table 1: TN results for CRM samples

Sample	Certified Conc.	Measured Conc.	% CV	% Accuracy
CRM 739	7.27 ppm	7.62 ppm	2.6	104.8%
CRM 741	14.10 ppm	13.62 ppm	1.2	96.6%
10 ppm standard solution	10.00 ppm	9.78 ppm	2.3	97.8%

❑ Conclusions

The in-built auto-dilution and “Multiple Injections” functions in the TOC-LCSH can correctly prepare standard solutions with different concentrations from a stock standard solution for a calibration curve. Furthermore, TN in waste water was measured accurately by the TOC-LCSH and TNM-L.

❑ References

1. On-line Wastewater Nutrient Monitoring (2009). USEPA No EPA/600/S-09/028.
2. Nitrates and Nitrites (2007). USEPA, Toxicity and Exposure Assessment for Children’s Health.
3. BS EN 12260 (2003). Determination Of Bound Nitrogen (TN_b), Following Oxidation To Nitrogen Oxides.
4. ASTM D5127 (1999). Standard Guide for Ultra Pure Water Used In The Electronics and Semiconductor Industry.

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