NITROGEN OXIDES MEASUREMENTS IN HYDROCARBON GASES

Nitrogen oxides (NOx) constitute group air pollutants with economic implications in the hydrocarbon production industry. For example in olefins production, NOx may form gum products when they are combined with resins and produce explosive substances in the cold box unit. Dry colorimetry offers an affordable solution for NOx monitoring at very low concentrations. The methodology proposed for C.I. Analytics, for laboratory and on line applications, presents a detection limit of 10 ppb in hydrocarbon streams with response times near to five minutes.

1. INTRODUCTION

Nitrogen oxides are a group of oxidised species relevant for the environmental chemistry. This group of oxides, commonly named NOx, is represented by nitric oxide (NO) and nitrogen dioxide (NO_2) as the most prevalent species in the air. In fact, environmental regulatory organisms establish air quality policies as a function of NO_2 concentration [1]. The NOx importance lies in the wide participation in the chemical reactions taking place in the troposphere. NO_2 reacts with air in the presence of ultraviolet (UV) radiation to produce ozone and NO. The NO reacts with free radicals, through photochemical complex mechanisms with volatile organic compounds (VOC) present in the atmosphere. Besides, NOx in conjunction with sulphur oxides and other air pollutants contribute to the acid rain formation which has negative effects in certain ecosystems and directly affects some economic sectors.

NOx emission is a product of anthropogenic and biogenic combined activities. Anthropogenic sources are automobile emissions, electric plant boilers, incineration products, gas turbine products, cement manufacturers, nitric acid manufacturers and petroleum refineries. Natural sources of nitrogen oxides include biomass burning, lightning and soil release [2].

Further, the presence of NOx in the environment represents a public health concern. The main source exposition to NOx is through the respiratory tract. Being exposed to high NOx levels may cause irritation of the mucous membranes, fluid accumulation in the lungs and even death. Skin or eye contact with NO or NO_2 produce chemical burn in the tissues. In workplaces, the maximum exposure limits for NO was established at 25 ppm during an 8 hour workday, 40 hours per week and 5 ppm for NO_2 for an exposure time of 15 minutes according to the Occupational Safety and Health Administration (OSHA)[3,4].

In petroleum refineries, NOx levels are controlled since nitrogen compounds are an undesirable product. Nitrogen content in petroleum distillates may deactivate the acidic sites of the catalysts, reducing the cracking efficiency and some of those components have a corrosive effect. Additionally, there are safety concerns about the nitrogen oxides presence in hydrocarbon streams. At specific conditions, nitrate explosive resins may be formed in ethene production inside the cryogenic recovery unit.

Intrinsically with the emerging technologies for enhanced oil recovery (EOR), specifically hydraulic fracturing operations, there are concerns about the economical viability of the projects with the least possible impact to the environment. For example, during the Marcellus shale extraction plans academic and field studies have been performed to predict and correct the unconventional natural gas extraction effects in nitrogen oxides emissions in the United States [5].

Whether to comply with environmental standards or to control process efficiency, it is mandatory to monitor the concentration of nitrogen oxides at low concentrations. Nowadays, there is a wide market of instruments able to quantify NO_2 levels at very low detection limits. Those techniques include spectroscopic methods, such as Differential Optical Absorption Spectroscopy (DOAS), Laser induced fluorescence (LIF), Resonance Enhanced Multiphoton Ionisation (REMPI) and GC-Chemiluminescence. Although some of the analysers offer high selectivity for direct or indirect measurement of NO_2, the system components complexity as well as an appropriate operational expertise makes the cost of the projects associated to this application prohibitive [6].

Aware of the need to develop a method that produces reliable results for NOx quantitation, C.I. Analytics developed an analyser capable of measuring NO_2 at concentration levels as low as 10ppb. The principle of the analytical technique relies on the dry colorimetric method where a targeted compound produces different color intensities proportional to the concentration in the gas phase. The colorimetric detection is carried out with an Photodiode system sensing the colour changes of a chemically impregnated paper that reacts selectively to the NO_2 presence. The NO present in the original gas sample or standard (for the analyser calibration purposes) is selectively oxidised to NO_2 and the final results are reported as total NOx content. Within the advantages presented by the technique, the efficiency of the oxidation in a reasonable period of time (approximately less than five minutes of analysis time) at very low concentration levels with virtually no known interferences what are most relevant. Moreover, the fast response is achieved thanks to a catalyst that operates at temperatures below 100°C to produce NO_2.

In the next section, some experimental results are presented discussing the features that make this method unparalleled to monitor NOx content at trace levels in hydrocarbon streams.

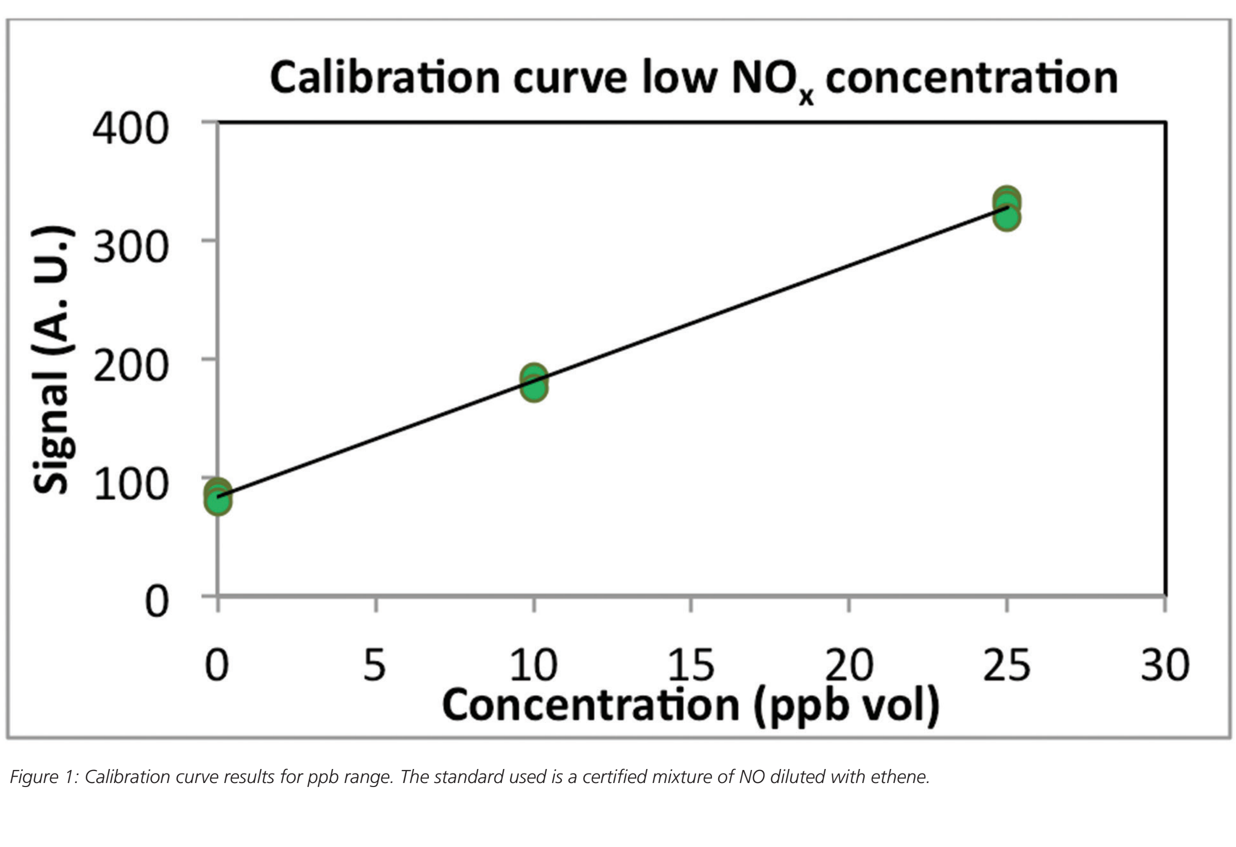
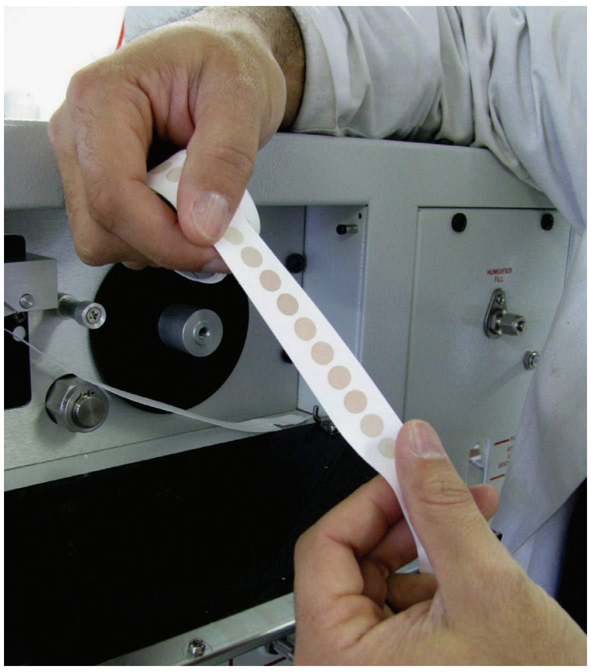


Figure 1: Calibration curve results for ppb range. The standard used is a certified mixture of NO diluted with ethene.



2. EXPERIMENTAL RESULTS

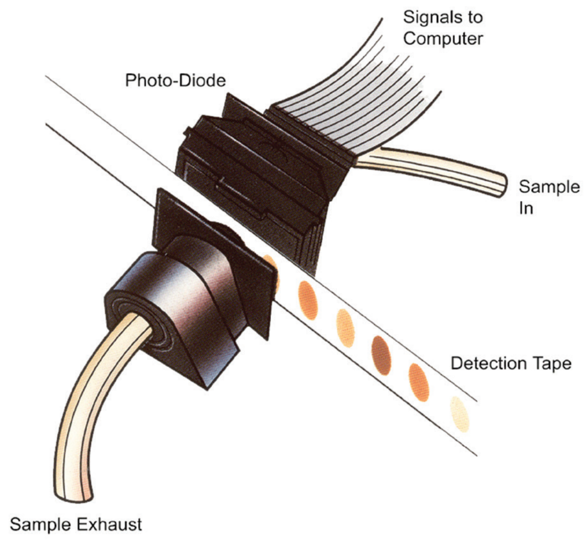
In order to produce a calibration curve avoiding any matrix effect in the quantitation, it is recommended to use a gas or a mixture of gases with a similar composition of the actual sample matrix. This is important to enhance the efficiency of the detection free from interferences. The scope of analysis for this application is extended to Liquefied Petroleum Gases (LPG) since the sample inlet is connected to a temperature controlled vaporiser unit in accordance to the customer needs.

Accordingly with the calibration range, the analyser is set for continuous injection (for concentrations up to 1 ppm vol) or loop injection type (for concentrations above 1 ppm vol of total NOx species). For process analysers, it is possible to measure continuous and loop injections simultaneously with accuracy values less than 5% full scale [F.S.]. Figure 1 presents results for a calibration curve produced using a NO standard in nitrogen balance, diluting with ethene gas. According to those results, the calibration curve presents good linearity correlation between zero and 25 ppb NOx. Additionally, resolution for 25 ppb is good enough to measure concentrations as low as 10 ppb total NOx.

Similar internal validation results have been found using propane and a mixture of propane and ethene as diluent gases, probing the robustness of the method using different hydrocarbons.

Repeatability results for 15 ppb vol total NOx are presented in figure 2. In agreement with those findings, the total nitrogen oxides analysed is very stable at low concentrations with a repeatability reported at less than 2% F.S.

The C.I. analytics NOx application in hydrocarbon streams has been extensively tested presenting high sensitivity, a broad linearity range (including low ppb concentrations), fast response, high accuracy and a good degree of repeatability and reproducibility. More importantly, it is a very versatile option since it has been designed for laboratory as well as on line monitoring of NOx, following international recognised safety standards depending on the final analyser location.



3. CONCLUSIONS

Dry colorimetric detection offers a good option for NOx monitoring at very low concentrations for laboratory and online analysis. The technique presents a low detection limit of 10ppb vol in hydrocarbon matrices. To conclude, the analytical parameters such as repeatability, reproducibility and accuracy fit the needs of clients where strict monitoring of these gases is crucial for their product process and for quality control.

4. REFERENCES

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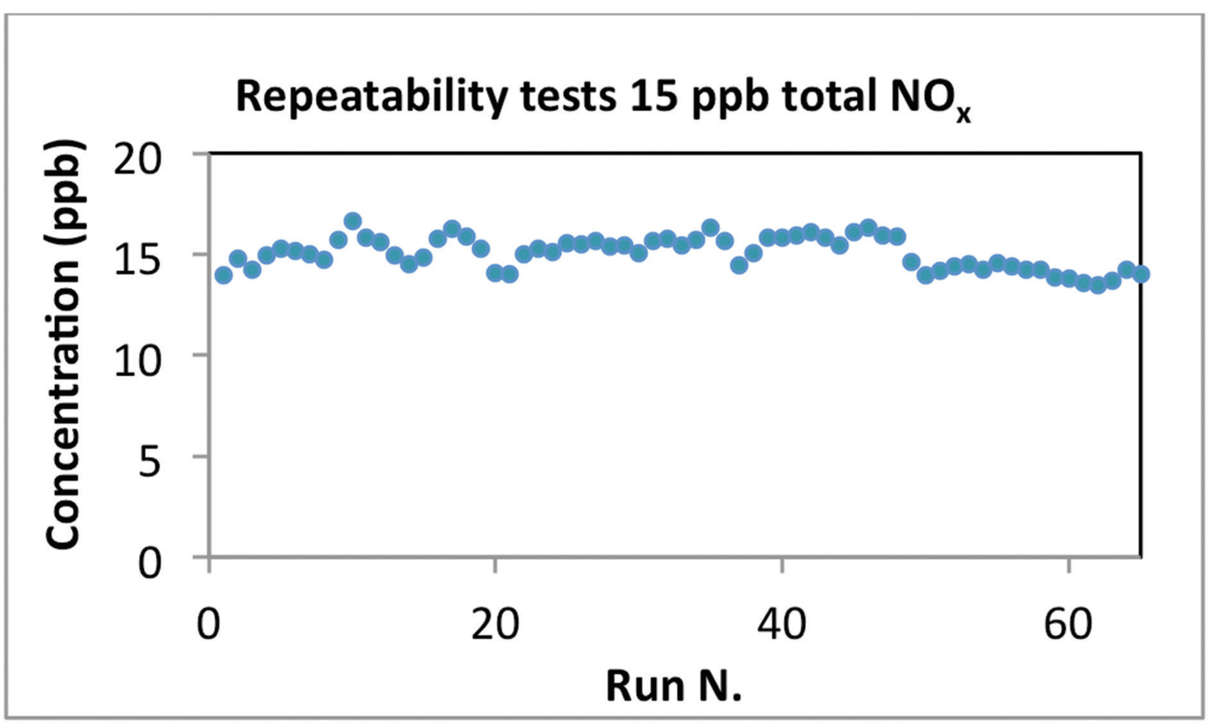

Figure 2: Repeatability tests for 15 ppb total NOx diluted with ethene. The measurements presented are consecutive, collected by the same analyst with a C.I. Analytics laboratory unit analyser.

Author Details

L. Lorena Torres, C.I. Analytics • 2085 Boulevard Industriel, J3L 4C5, Chambly, Quebec, Canada • **Web: www.cianalytics.com**