CO$_2$ analysis and monitoring

Storage of captured CO$_2$ made safe by continuous vigilance of gas purity

How continuous monitoring of CO$_2$ purity by online FTIR protects critical pipeline infrastructure

Introduction

The safe transportation of carbon (in the form of CO$_2$) captured from the atmosphere or directly from the emissions of industrial processes is commonly made via pipelines to storage locations in geological locations underground and beneath the ocean.

Preserving the safety and integrity of this pipeline infrastructure requires vigilance. Experiments have shown that elemental sulfur, sulfuric acid and nitric acid can form within a stream of carbon dioxide, if the stream contains water, NO$_x$, SO$_x$, H$_2$S, and O$_2$ in concentrations well within the limits suggested in many of the published recommendations for maximum impurity concentrations in CO$_2$.[1]

The presence of these acids presents a real risk of metal corrosion with the associated serious consequences for pipeline safety and integrity. Continuous monitoring of the gas composition can mitigate this risk. Online analysis by Fourier transform infrared (FTIR) spectroscopy offers a highly sensitive and ultra-reliable solution that provides pipeline operators confidence in the security of their infrastructure.

The greenhouse effect

Much has been said about the impact of greenhouse gases in the Earth's atmosphere. In truth, we wouldn't be here without them. Without the natural greenhouse effect, heat emitted from the Earth would literally disappear into outer space leaving our planet with an average surface temperature of -20 °C.[2]

The greenhouse effect of the Earth's atmosphere is to absorb infrared radiation from the sun, heat which is eventually lost to space while at the same time "trapping" heat in the lower atmosphere rather like a blanket, keeping the atmosphere and Earth's surface at a moderate temperature.

CO$_2$ has hit the headlines as it is the gas that (apart from water vapor) has the greatest impact on the rate of absorption and radiation of heat in our atmosphere; N$_2$ and O$_2$ which are present in much higher concentrations do not have this same characteristic effect. Atmospheric CO$_2$ levels increase the temperature of the surface of our planet, simultaneously excess CO$_2$ is dissolved into the oceans gradually lowering the water's pH, thus making the seas more acidic.

Carbon capture utilization and storage (CCUS)

As the title implies, carbon capture takes CO_2 from the atmosphere for utilization and/or storage. The most cost-efficient capture happens where CO_2 is removed from the emissions of industrial processes, such as iron and steel, chemical, and cement plants, since CO_2 emissions from these locations are relatively high. If the emitter has use for the captured CO_2, it can be utilized immediately, otherwise the next best option is to transport the gas to a storage location to prevent its release to the environment.

The captured CO_2 is conditioned to remove impurities and liquified before being pumped to permanent storage. The storage sites are geological formations that are sufficiently porous to allow the CO_2 to move freely to fill the void. The most common sites are depleted oil and gas fields and saline formations at depths greater than 1 km. The liquified CO_2 may also be used in place of water to extract oil from oil fields in a process known as Enhanced Oil Recovery.

The USA alone has anywhere from 2,000 to 20,000 billion tonnes of storage resources. Globally there is a large excess of capacity for all the CO_2 that it is anticipated we need to store.[3] The excess of storage resources available is a key factor to the future success of CCUS. Geological storage is deemed safe and secure, but the risk of leakage is an obvious concern as this would set back efforts to reduce atmospheric carbon levels. However, the International Panel on Climate Change (IPCC) considers this risk to be low and that well-selected sites are likely to retain over 90% of injected CO_2 over 1,000 years.[4]

Continuous monitoring of CO_2 by FTIR

FTIR has been employed for the online analysis of many types of gas streams in the chemical and other industries for many years. It has also been applied to the analysis of beverage grade CO_2 to ensure that carbonated drinks are free from contaminants that would adversely affect the appearance, smell, or taste of the drinks. Analysis of beverage grade CO_2 requires a rugged solution that has the sensitivity to measure impurities in parts per billion (ppb) and parts per million (ppm), while simultaneously measuring the absolute purity of CO_2.

The CO_2 that is utilized in beverages is captured in similar ways to that of the carbon capture infrastructure, resulting in similar impurities. Certain acid forming impurities, such as NO_x and SO_2, pose a risk to carbon capture pipelines as the CO_2 is pumped to permanent storage. The FTIR is a proven technology for monitoring these specific impurities in bulk CO_2. For this reason, the FTIR is a perfect fit for monitoring the impurities in CO_2 where the bulk gas is going to storage through pipelines.

The Thermo Scientific™ MAX-Bev™ CO_2 Purity Monitoring System is a fully automated solution capable of analyzing trace impurities in bulk CO_2 and absolute CO_2 purity. The system is based on the Thermo Scientific™ MAX-iR™ FTIR Gas Analyzer and includes a 10-channel multiplexer for the sequential analysis of multiple CO_2 sources.

Performance study of FTIR for captured CO_2

The MAX-Bev System was tested for the suitability to monitor CO_2, the target impurities include NO, NO_2 and SO_2. To ensure that the testing was sufficiently challenging and representative of field use, the sample also contained ~3,500 ppm of methane (CH_4) and > 95% CO_2. The inclusion of this high concentration of CH_4 and CO_2 would test the specificity of the measurement confirming that no interference to other lower concentration impurities was observed.

The limit of detection (LOD) for each impurity was defined as 3x the standard deviation of these measurements. No offsets or span factors were applied to the method, the results are shown in Table 1.

Gas	Units	LOD (3σ)
Acetaldehyde	ppm	0.002
Ammonia	ppm	0.01
Carbon dioxide	%	n/a
Carbon monoxide	ppm	0.07
Ethanol	ppm	0.05
Formaldehyde	ppm	0.09
Methane	ppm	n/a
Methanol	ppm	0.07
Nitric oxide	ppm	0.05
Nitrogen dioxide	ppm	0.003
Nitrous oxide	ppm	0.10
Sulfur dioxide	ppm	0.08
Water	ppm	0.41

Table 1: Impurity limit of detection (LOD) results.

A set of four reference gas samples were selected that contained varied amounts of NO, NO_2 and SO_2, as well as approximately 3,500 ppm of CH_4 and 95+% CO_2. The compositions are shown in Table 2.

Gas	Units	Level 0	Level 1	Level 2	Level 3
Sulfur dioxide	ppm	0.00	1.00	5.06	10.17
Nitrogen dioxide	ppm	0.00	1.03	5.01	10.00
Nitric oxide	ppm	0.00	1.04	6.21	11.22
Carbon dioxide	%	100.00	98.77	97.56	95.24

Table 2: Expected concentration levels.

Four replicate measurements of each sample were made with a measurement cycle time optimized at 1 minute, and the measured concentrations compared with the target concentrations. The linearities of each impurity and the bulk CO_2 were recorded and are shown in Figures 1 through 4 and summarized in Table 3.

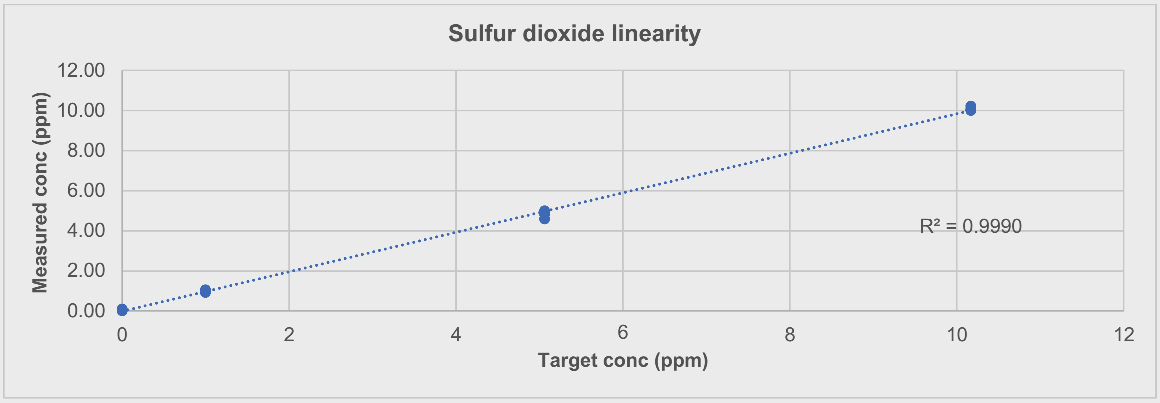

Figure 1: Linearity of SO_2.

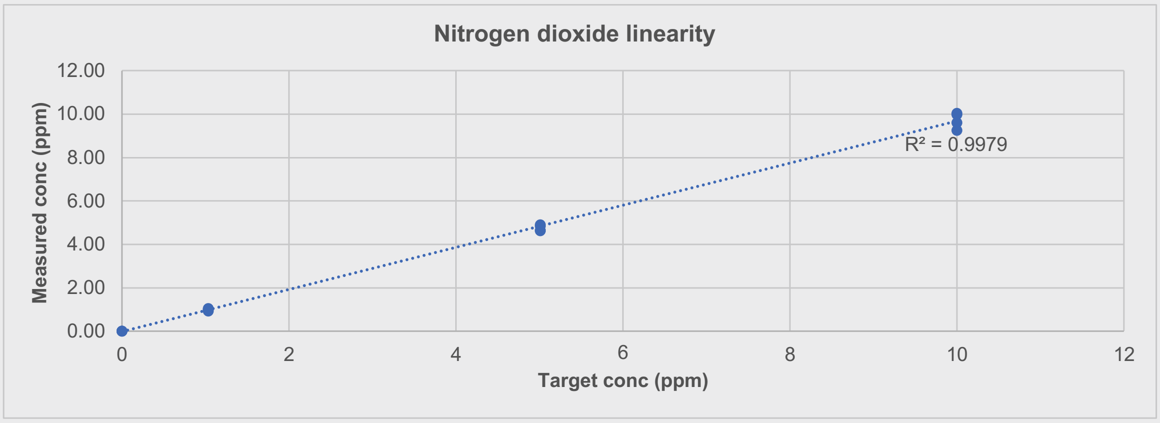

Figure 2: Linearity of NO_2.

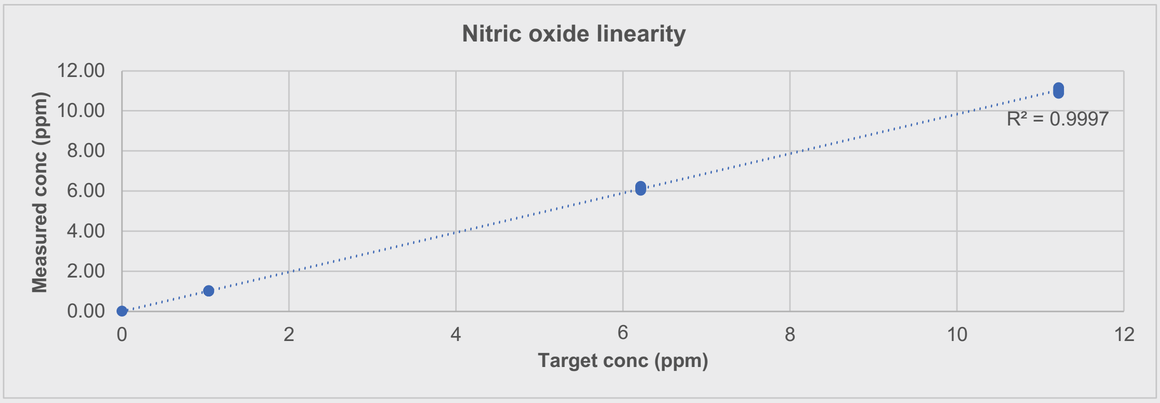

Figure 3: Linearity of NO.

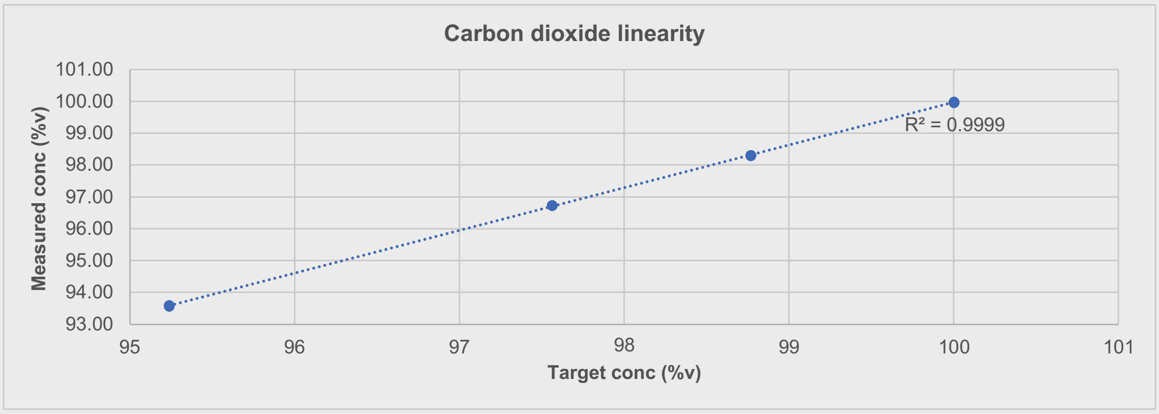

Figure 4: Linearity of CO_2.

Gas	Average percent error Level 1	Level 2	Level 3	Linearity (R^2)
Sulfur dioxide	-1.40%	-4.98%	-0.89%	0.9990
Nitrogen dioxide	-3.91%	-5.30%	-2.98%	0.9979
Nitric oxide	-0.63%	-0.99%	-1.82%	0.9997
Carbon dioxide	-0.47%	-0.85%	-1.77%	0.9999

Table 3: Accuracy and linearity summary results.

Thermo Scientific MAX-Bev CO_2 Purity Monitoring System

The MAX-Bev System is a robust and powerful online analyzer designed to provide continuous monitoring of CO_2 streams. Meantime Between Failure (MTBF) studies for this system have proven an uptime of 99.7%. This system operates independently, requiring no user intervention and is designed for 24/7 data collection. Configured for the analysis of CO_2, the MAX-Bev System has a host of features which make it the perfect choice for operators of CO_2 pipelines concerned about the purity of the CO_2 and risk from unwanted contaminants.

Factory calibrated for life

The MAX-Bev CO_2 Purity Monitoring System is based on the MAX-iR FTIR Gas Analyzer, which is calibrated at the factory and requires no field calibration for the lifetime of the analyzer installation. Calibrations are transferable, meaning that users may upgrade their analysis method to include additional gas components simply by uploading the calibration data to the analyzer.

Performance validation

At a monthly interval (or at the user's preferred frequency) the MAX-Bev System performs an automated validation check; this simple process takes less than 30 minutes, requires no operator intervention, and provides reassurance that the analyzer will continue to generate accurate results. A background measurement in a sample of pure Nitrogen (IR-inactive) followed by measurement of a set of known impurities and pure CO_2 is all that is required to maintain the analyzer accuracy.

Detector technology

The MAX-iR FTIR Gas Analyzer uses a Deuterated Triglycine Sulphate (DTGS) detector. The operating principle is that incoming IR light heats and expands the detector material changing its capacitance. This capacitance change is measured at the detector as a changing voltage. The DTGS is inherently linear, sensitive to single digit ppb concentrations and, importantly, does not require cooling either by liquid Nitrogen for thermal-electric means.

High sensitivity

The sensitivity of FTIR is in part a function of the path length through which the IR light passes through (this pathway contains the sample CO_2 and its impurities). The MAX-iR Analyzer has a high throughput multi-pass cell with an effective path length of 10 meters; this combined with the highly sensitive DTGS detector enables the MAX-Bev System to detect impurities in CO_2 at levels comfortably below the requirements for pipeline protection. For example, the minimum detectable limit of SO_2 is <82 ppb, all this is achieved while simultaneously reporting the absolute CO_2 purity to an accuracy of 100 +/- 0.02%.

Sampling and data reporting

The MAX-Bev System can be configured for the measurement of a single sample stream; alternatively, with the inclusion of a sample multiplexer, up to 10 streams can be sampled sequentially. Analysis methods can be setup for continuous monitoring or individual (batch reporting).

Results from each measurement cycle are logged in the analyzer control software as time-stamped database entries in CSV or HTML format. Rolling averages and trend views are available for review.

MAX-Bev CO_2 Purity Monitoring System.

Real-time data values including concentrations, hardware states, and alarms may be sent to Distributed Control Systems (DCS), Supervisory Control and Data Acquisition (SCADA), or Human Machine Interface (HMI), as preferred by the user. This hierarchy sampling and data acquisition can be started and stopped at the user's discretion.

Quality assurance reports can be generated at user-selected intervals (hourly, daily, weekly, monthly); these reports are saved to a local or network drive and are available in HTML and print-friendly PDF format. The standard report format includes high and low alarm concentration limits, the limits of detection, results, and pass/fail conditions.

Summary

Continuous monitoring of CO_2 purity and the reporting of trace contaminants will guard against pipeline degradation. Online FTIR based analyzers are a well proven method of providing the analysis required to meet industry needs. The MAX-Bev CO_2 Purity Monitoring System operates unattended 24/7 keeping pipeline operators informed of the purity of the CO_2 they are carrying. The system is sensitive enough to ensure that impurities are detected at levels before they become problematic and robust enough to operate in the field with minimal maintenance and no requirement for calibration. Automated validation ensures confidence in the accuracy of reported data, and the comprehensive data acquisition and reporting software informs the user every step of the way.

CO_2 storage capacity is set to grow at a rapid rate as we head towards the next decade and along with that capacity come the pipelines that will transport that gas. Protecting these pipelines will depend on constant vigilance against the presence of impurities that could, if left unchecked, result in pipeline corrosion with potentially devastating outcomes. Place the MAX-Bev System in the field, set it to run, and take comfort in knowing that your CO_2 quality assurance is in safe hands.

References

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