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GREEN TECH, HIGH SPEC, CLEAN TECH - THE ROLE OF SPECIALTY GASES IN ENVIRONMENTAL AIR EMISSIONS MONITORING

Green Tech - As we seek to maintain our industrialised way of life in a sustainable way, employing clean technologies, high tech instrumentation and high specification specialty gases has become critical and will become more so. Analytical instrumentation such as FTIR, NDIR and UV spectrometers and the Specialty gases that are required to operate and calibrate these instruments have a critical role to play in gaseous environmental emissions monitoring.

At the heart of the Linde Group specialty gases strategy is a commitment to innovation and clean technology. Dr. Roberto Parola, Global Product Manager for Specialty Gases and Equipment at Linde in Munich added: "We stand ready to support end users who need to keep pace with multiple environmental air emissions legislation changes globally. Our gases and equipment product range is in continuous development with a focus on what is required for the Marpol Annex 6 legislation for international shipping, the EU NRMM Stage 5 legislation for non-road diesel emissions, the Euro 6 transport emissions legislation and the EU IED legislation for stack emissions. Furthermore, we generate market insights into what might be required by future legislation such as Euro 7 and structure our R&D pipeline to anticipate market requirements accordingly. For example, delegates at the recent CEM conference in Budapest were able to hear about Linde's readiness to support the new MCPD EU legislation for medium combustion plant emissions monitoring with appropriate high spec specialty gas calibration mixtures".

High Spec

One of the most dynamic areas of environmental monitoring at present is the measurement and control of mercury emissions. The topic moves rapidly like the element "quick silver" its self. A particular challenge with mercury measurement is that the chemistry of mercury does not lend its self to the IR techniques such as NDIR and FTIR which can be used to detect a broad spectrum of typical pollutants such as NO_x, NH₃ and SO₂. This calls for the use of an alternative technique which is active in the UV spectrum, where mercury is active. Whilst the incremental cost of measuring an additional chemical species such as HCl or HF on an FTIR is quite affordable and relates to additional calibrations, the incremental cost of adding mercury to the analytical schedule involves a whole new analyser system.

The need for accurate and cost effective mercury monitoring systems is therefore paramount. Emilia Jyrkiäinen, CEMS Product engineer at Gasmet Technologies Oy is acutely aware of this, "As new mercury monitoring regulations are implemented, investing in a new analyser system can be necessary. To ensure that owners of our mercury monitoring systems can make an investment that will pay off, we have future-proofed our technology by recently securing the world's lowest EN15267 certified range for mercury measurement: 0 to 5 µg/m³. This results in an extremely reliable and cost effective long term solution for monitoring mercury emissions."



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Calibration of the mercury instrumentation is achieved either with commercially available gas mixtures in cylinders or with an in-situ calibration gas generator. Specialty gas calibration mixture cylinders for mercury instrumentation are available from very few suppliers, but some international players such as Linde and Praxair are able to use their global reach to make these highly specialised products available around the world. The calibration gas generators work by passing a stream of clean dry air over elemental mercury. The air which is saturated with mercury is then diluted to create the required concentration of mercury in the calibration gas mixture.

When it comes to FTIR analysers, the flexibility of the technology to measure multiple chemical species simultaneously is extremely high. For example the Gasmet CEMS II e is able to simultaneously measure 16 pollutant species in the stack emission gas stream (H₂O, CO₂, CO, N₂O, NO, NO₂, SO₂, HCl, HF, NH₃, CH₄, C₂H₆, C₃H₈, C₂H₄, CH₂O and TOC) as a standard. Jyrkiäinen added, "Gasmet FTIR analysers are used in various applications ranging from greenhouse gas research to first response. They are also perfectly at home in demanding industrial applications and stack testing procedures. And, if the end user wishes to increase their measurement scope at any stage by adding new compounds or ranges, the required changes can be made without significant additional hardware investment."

For calibration of FTIR instruments it is typical to use a suite of high precision certified calibration gas mixture cylinders. Accreditation of these calibration standards according to ISO17025 is required for many stack emissions monitoring applications. To support this calibration requirement Air Products in Europe has optimised its ISO 17025 accreditation scope to serve its users and is one of the few specialty gases companies to offer gas mixtures containing NO, SO₂, CO and CO₂ in the same cylinder. David Bryant, Air Products European Segment Programme Manager, Speciality and Medical Gases says, "These multi-component gas mixtures are ideal for CEMS applications and avoid the need for users to order and handle multiple cylinders, thereby saving time and money. Coupled with high purity nitrogen delivered with a BIP® (Built In Purifier) this system makes a great combination for FTIR calibration and purge gases." Bryant added, "Air Products has been active in the UK and European air quality monitoring industry for many years and we remain committed to support this sector with innovative products that meet both the evolving needs of end-users and the latest changes in legislation. Come and meet us at the AQE in Telford later this year to keep up with the pace of change in this sector."

Clean tech

Stack emissions monitoring is the final stage in the environmental management process and only reflects what has gone on before. The real work of "clean technology" takes place in unit operations within factories that reduce the levels of pollutant gases. And, each of these unit operations requires rigorous process control to ensure that they are doing the job that they have been built for. As an example, in many glass factories natural gas is burnt to melt the glass creating NOx emissions. To knock down the NOx levels to those

required by local environmental legislation the flue gases can be treated with a selective catalytic reduction system (SCR). Urea is added to the SCR system which decomposes at the high temperatures to form ammonia which produce the right chemical conditions to reduce the NOx back to nitrogen. To dose the appropriate level of urea it is necessary to measure the NOx levels and adjust the urea addition accordingly. But, having solved the NOx emissions problem, it is of course not acceptable to create an ammonia emissions problem, so fine tuning of the process control is achieved with ammonia slip measurement in the flue gas.

The SCR NOx reduction process referred to above is the equivalent of the addition of AdBlue® in modern diesel engines fitted with SCR units. And, to avoid the problem of ammonia slip the EU legislated with their Euro 6 transport emissions legislation that ammonia slip emissions must be less than 10ppm.

The introduction of this legislation was both an opportunity and a challenge for instrumentation suppliers and specialty gases producers since more gases and analysers would be required in automotive emissions testing, but the ammonia mixture which is required to be at + - 3% accuracy requires excellent process control and high tech gas mixture preparation techniques.

The monitoring of ammonia in the US automotive emissions legislation is not yet required. The challenges with the US legislation are, however, equally as tough. The US green house gases emissions legislation calls for N₂O measurement. Producing accurate N₂O mixtures

requires the complete absence of oxygen and therefore requires perfect cylinder purging and filling discipline. However, the peak of High-Tech is the requirement for formaldehyde measurement. With the increasing use of CNG and LNG as transport fuels, the emissions of formaldehyde are on the increase. It is produced as a combustion by product of methane. As any lab technician will testify, handling formaldehyde is something that requires extreme competence.



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