ON THE ROAD TO A GREEN FUTURE – HIGH TECHNOLOGY GASES ENABLE ENVIRONMENTALLY FRIENDLY ROAD TRANSPORTATION

Delicate eco systems… specialty gases help to keep them in balance

Bob Brown, the Australian politician once said: "The future will either be green or not at all." As we seek to maintain our industrialised way of life in a sustainable way, employing clean technologies and high specification industrial gases has become critical and will become more so. With this backdrop, Victor Chim, Specialty Gases Business Development Manager at Coregas Pty Ltd in Australia commented: "We live in a beautiful country with UNESCO heritage ecosystems such as the Great Barrier Reef and the Gondwana Rainforest which can only survive if we protect the cleanliness of our air, soil and water."

Specialty gases, related gas control equipment and analytical instrumentation all play essential roles in environmental protection. From the use of synthetic air in the analysis of VOC levels in groundwater, to the use of ammonia mixtures to produce of engine management system gas sensors, specialty gases are in use daily. Chim continues: "at the heart of the Coregas strategy is a commitment to innovation and clean technology. Enabling environmental protection is a privilege and we are proud to be making world class specialty gases that contribute to this goal."

High Spec Soil Tech

A very "down to earth" example of how high tech specialty gases are used for environmental protection is the monitoring of pollution at petrol stations in Australia. The Protection of the Environment Operations - Underground Petroleum Storage Systems (UPPS) - Regulation 2008 requires all petrol service station sites with operational underground storage to utilise groundwater monitoring wells which must be suitably positioned to detect leaks from underground petrol storage tanks and related piping systems. Groundwater from these wells must be monitored at six monthly intervals and any measurement of contaminants above the notifiable levels must be reported to the EPA, see Table 1.

Coregas specialty gases helium cylinders

Table 1: notification levels for petrol station groundwater monitoring well contamination. Source: Environmental Guidelines for Service Station Sites and Hydrocarbon Storage, Environment Protection Authority (Australia), January 2014.

Parameter	Criteria
pH	6.5 – 8.5
Total Petroleum Hydrocarbons	
C6 – C9	No criterion set at this time
C10 – C40	600µg/L
BTEX (total)	
Benzene	950µg/L
Toluene	300µg/L
Ethyl Benzene	140µg/L
Xylenes	
o-xylene	350µg/L
m and p-xylene	200µg/L
Ethanol	1400µg/L
Lead(Total)	3.4µg/L

The main Contaminants of Potential Concern in Table 1 include petroleum hydrocarbon fractions in the range of C6 to C40 which will be analysed as total recoverable hydrocarbons (TRHs). The term 'TRH' has replaced the term 'TPH' (total petroleum hydrocarbons) and it represents the combination of biogenic and petrogenic (petroleum) hydrocarbons extracted by selected solvents. Most laboratory methods, such as GC-FID techniques, will detect the full range of TRHs and therefore a silica gel pre-separation should be used if significant levels of non-petroleum hydrocarbon interferences are suspected. In such cases, the result should be tagged as 'TRH-silica'.

In addition to analysis of groundwater samples every six months, it is required to take soil samples at suitable intervals. To determine where best to take samples, a combination of human sensory observations and analytical techniques are used. Field observations would include sample colour, staining or the presence of odours. Analytical techniques would, for example, use an organic vapour analyser such as a photo-ionisation detector (PID) to detect VOCs which are characteristically emitted to the nearby air from contaminated soil. Periodic calibration of such PID detectors with specialty gases calibration mixtures containing hydrocarbons will be required to ensure reliable and accurate operation.

Environmental contract labs play a pivotal role

Analysis of petrol station groundwater monitoring samples is bread and butter work for many environmental contract laboratories operating across Australia. The analytical equipment employed for this work will often be a gas chromatograph fitted with a flame ionisation detector (GC-FID). To operate this system a carrier gas will be used to transport the sample over the chromatography column. Helium 5.0 grade or hydrogen 5.0 grade would be the most common specialty gases to use as carrier gases in GC-FID applications. However, if there is any suspicion that some of the double-bonded hydrocarbons may undergo a reaction in the presence of the hydrogen carrier gas at the high temperatures present in the gas chromatograph oven, then helium should be selected in favour of hydrogen.

In addition to the carrier gas for chromatographic separation of the sample components, detector gases will be required to operate the flame in the FID. The two detector gases which are most commonly used for hydrocarbon environmental applications are Instrumentation grade air, which is also referred to as synthetic air and is actually a blend of high purity oxygen and nitrogen, and Hydrogen 5.0 grade. When hydrocarbon species are detected using the FID technique in the automotive sector it is common to dilute the hydrogen to 40% in a balance of helium, which is highly thermally conductive, to avoid hot spots in the flame. This

is however not general practice for soil and water environmental hydrocarbon VOC measurement where pure hydrogen is prevalent.

For highly sensitive measurements, with dilute samples requiring low detection limits, it will be necessary to upgrade the above Hydrogen or Helium gas from 5.0 grade (99.999% purity) to 6.0 grade (99.9999% purity). Also, a "Low Hydrocarbon" grade of air should be specified, such as a Zero Grade Air.

Beyond the specialty gases referred to above, which are required for daily operation, a calibration gas mixture will also be essential for periodic calibration events to ensure that the sample measurements are accurate and traceable. Many environmental contract labs are ISO 17025 accredited as testing laboratories and, to conduct water sample analysis under such a scheme of accreditation, they will need to calibrate their GC-FID with specialty gases calibration mixtures which are also accredited to ISO 17025. Or, still one step better, to use ISO Guide 34 reference materials. Victor Chim reflects on this requirement with the comment that "accredited specialty gas mixtures which are traceable to national standards are essential for many legislatively driven environmental applications. At Coregas, we have regular contact with NATA and they have audited our specialty gases production and analysis processes to demonstrate compliance to both ISO 17025 and ISO Guide 34. This is a dynamic area for us and in 2018 we will be working with NATA to introduce the latest ISO 17034:2016 accreditation into our laboratory in Yennora, close to Sydney."

The road to green relies on blue

The potential pollutants stored at roadside service stations in past decades have included petrol and battery acid. With the introduction of SCR catalysts in trucks in Australia, the use and storage of urea in the form of AdBlue® is now also common with several major oil companies in Australia offering AdBlue® at more than 100 of their petrol station outlets. Whilst the storage of AdBlue® represents an additional potential environmental issue, its use is intended to keep our ambient air quality clean and green.

When diesel is combusted with air in truck engines, the production of various oxides of nitrogen (NOx) is inevitable. To reduce the NOx levels to those required by environmental legislation, the combustion gases are processed using selective catalytic reduction (SCR). AdBlue® is added to the SCR system and urea, which is the active ingredient of AdBlue®, decomposes at the high temperatures in the flue gas to form ammonia which reduces the NOx back to nitrogen over the SCR catalyst. To dose the appropriate level of AdBlue® it is necessary to measure the NOx levels and adjust the injection rate 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 final exhaust gas emitted from the SCR.

In a modern diesel engine, both the NOx and ammonia levels will be measured using gas sensors and the data will be processed in the on board diagnostics or engine management control system. Production of these engine gas sensors relies on extremely tight blend tolerance specialty gases mixtures for quality control. Chim explains what that means for his team at Coregas: "for some calibration gas mixtures it is traceability, accreditation or low measurement uncertainty that might be the critical factor, but in the case of low blend tolerance mixtures, hitting the exact requested gas mixture concentration is the core customer requirement. To achieve that, we use high precision gravimetric filling techniques to make sure that we can hit the bullseye every time and deliver the exact products that our customers need."

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