

Benzene – It's Time for Continuous, Real-Time and Specific Monitoring

Duncan Johns, Managing Director at Ion Science discusses how the previously secret documents that have come to light in lawsuits filed against benzene manufacturers and suppliers are likely to impact the petrochemical industry. He also looks at the latest technology available for the implementation of new standards proposed by the US Environmental Protection Agency for the monitoring and control of benzene concentration levels around the perimeter of all US oil refineries.

Benzene is formed from both natural and human processes and it is a critical industrial chemical. It is a constituent of crude oil and becomes gaseous during petrochemical processing. Benzene is extremely hazardous and a recognised human carcinogen.

Aromatic compounds produced by oil refineries and petrochemical plants form the building blocks for numerous important materials, including dyes, detergents, solvents, adhesives, plastics, synthetic rubbers and pharmaceuticals. However, the aromatic compounds produced in these environments, such as benzene, are also highly toxic.

Benzene is formed from both natural and human processes and it is a critical industrial chemical. It is a constituent of crude oil and becomes gaseous during petrochemical processing. Benzene is extremely hazardous and a recognised human carcinogen. Exposure to high concentrations in the 10,000 to 20,000 parts per million (ppm) range will result in death, whilst chronic exposure to ppm levels significantly increase the likelihood of leukaemia. With the risk of either chronic or acute exposure, legislation has been put in place across the globe to ensure exposure is kept to a minimum, typically a TWA of 1ppm (OSHA).

As this exposure limit is so low, its concentration alone usually defines the toxicity of vapours in the petrochemical industry as a whole. As a result, it is essential that sub ppm benzene concentrations can be measured rapidly in the presence of the hundreds of aromatic and aliphatic compounds encountered throughout the industry.

Latest Developments

The Centre for Public Integrity (CPI), Columbia University's Mailman School of Public Health and The Graduate Centre at the City University of New York have teamed up to make some 20,000 pages of benzene documents that have surfaced during litigation open for public inspection.

A new searchable database (<http://www.publicintegrity.org/2014/12/04/16319/exposed-decades-denial-poisons>) archives previously secret oil and chemical industry memoranda, emails, letters, presentations and meeting minutes that will grow over time.

In a recent article in The Guardian, Kristen Lombardi from the CPI said that "these suggest that major petrochemical companies, in conjunction with their trade association, the American Petroleum Institute (API), spent at least \$36 million on research, which was "designed to protect member company interests," as one 2000 API summary put it, and keep further restrictions at bay". Kristen went on to say that "many of the documents chronicle a systematic attempt by the petrochemical industry to influence the science linking benzene to cancer and childhood leukaemia in particular".

In May 2014, the US Environmental Protection Agency (EPA) estimated that some five million Americans, not counting those with workplace exposures, face heightened cancer risks from



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benzene and 68 other carcinogens released into the air by the nation's 149 oil refineries. This is greater than a one in one million lifetime cancer risk (Table 10 pg.277).

Making it clear that the cancer and other health risks posed by petroleum refineries on nearby communities are unacceptable, monitoring and control of benzene concentration levels around the perimeter of all US oil refineries has been proposed by the US EPA under the 'Residual Risk Program'.

The proposed rule would revise emission control requirements for flares, storage tanks and coking units at petroleum refineries and require monitoring around refineries to ensure that neighbouring communities are not being exposed to hazardous air pollution. This proposal would also set maximum achievable control technology standards for delayed coking units, which the EPA described as a "significant" unregulated source of hazardous pollutant emissions at refineries.

The EPA said it anticipates the proposal will have a "minimal" economic effect on the refining industry but could reduce emissions of hazardous air pollutants such as benzene and xylene by an estimated 5,600 tons per year.

The API and American Fuel & Petrochemical Manufacturers both released statements following the EPA's announcement questioning whether the costs associated with the proposal are justified by the expected reductions in air emissions.

The API also said these new proposals "will dramatically increase the paperwork and recordkeeping burden on refineries and cost the industry hundreds of millions of dollars per year, increase safety risk and may impact fuels production and cost with production outages likely to occur".

Sampling options for refinery perimeter monitoring vary depending on monitoring objectives. Recommendations range from placing samplers every 15° around the plant (25 sampling

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locations) to every 22.5° (16 sampling locations and every 40° (nine sampler locations). Additional sampling locations may also be required around satellite installations (if these are thought to be responsible for >10% of total refinery emissions), points upwind / downwind of the plant and / or in local centres of population - for example, nearby villages, schools, homes, etc. Fence-line sampling locations are typically deployed at evenly spaced angular intervals around the refinery perimeter.

In June 2014, California officials lowered the long-term exposure level to benzene and the state is also considering classifying benzene not just a human carcinogen, but as a "toxic air contaminant which may disproportionately impact children".

In the recent Guardian article, the CPI's Kristen Lombardi goes on to write about "how the science linking benzene to cancer and leukaemia in particular has preoccupied the petrochemical industry for a long time". She highlights a 1948 API profile of the chemical that discussed "reasonably well documented instances of the development of leukaemia as a result of chronic benzene exposure" and cautioning that "the only absolutely safe concentration is zero".

Through the 1960s and early 1970s, studies of Italian shoe and leather workers indicated a relationship between the chemical and cancer. In 1977, the National Institute of Occupational Safety and Health (NIOSH), part of the Centres for Disease Control and Prevention, launched a seminal study of two Goodyear plants in Ohio that made Pliofilm, a thin rubber wrap. The results of the research quantified the leukaemia risk for workers exposed to benzene prompting OSHA to set a stricter occupational exposure limit at 1ppm.

In 1997, the National Cancer Institute (NCI) published a landmark study on benzene-exposed workers in Shanghai. The results reinforced past research that showed the chemical causes leukaemia. In 2004, the NCI released the results of a second study which found that Chinese shoe makers inhaling benzene in amounts below the OSHA limit had fewer white blood cells than unexposed workers.

Detecting Benzene and Total Aromatic Compounds (TACs)

There are many ways to detect benzene in line with regulatory requirements. There are pros and cons for each method but preferentially benzene has been monitored using hand-held photoionisation detection (PID) instruments fitted with a benzene pre-filter tube.

In 2011, Ion Science introduced the Tiger Select, a hand-held detector with two-mode operation for the rapid detection of benzene and total aromatic compounds (TACs) providing the most accurate data available. Benzene is typically present in a cocktail of aromatic and aliphatic compounds, with the aromatics being the most harmful. Typically, PIDs are sensitive to all of these compounds but by using the proprietary high output Ion Science 10.0 eV system the aliphatics are not detected giving a Total Aromatic Compound reading – TAC mode.

Should TACs be detected above the regulatory limit, a Draeger benzene pre-filter tube can be easily attached to Tiger Select to ensure rapid detection and selective measurement of benzene – tube mode.

Should the benzene reading exceed the regulatory limit, a 15-minute short-term exposure limit (STEL) can be immediately initiated. This three-step process provides instantaneous TAC readings, minimises tube usage when benzene levels are low and gives real time exposure levels.

Throughout the measurement process, Tiger Select continues to display real-time data, ensuring worker safety in case high levels are detected before the final concentration is reached during the tube measurement. With its high sensitivity, benzene concentrations are displayed down to ppb levels. Its unique MiniPID™ VOC sensor incorporates both anti-contamination and Fence Electrode technology for extended operation in humid and dirty working environments typically encountered in the petrochemical industry. Tiger Select is also capable of providing eight-hour TWAs for TACS as well as 15-minute STELS for benzene.

Although these instruments are an adequate method of measuring benzene, they only provide a short term benzene measurement. The new EPA proposals under the Residual Risk Program and ever increasing awareness of the dangers of benzene exposure means that there is an urgent need for 24/7 continuous, benzene specific monitoring to ensure real-time protection of workforce, environment and plant. The Tiger Select is specific but it doesn't provide long-term monitoring which is required for the fence line.

Titan – the solution

Ion Science has just launched 'Titan' – the world's first continuous benzene specific monitor. It has been designed for the accurate and reliable detection of ambient benzene in petrochemical applications where the traditional methods suffer from cross sensitivity interference.



As the first truly selective wall-mounted benzene monitor, the 'Titan' is set to be a real game changer for the petrochemical industry – especially in view of EPA proposals. Incorporating the well proven Ion Science MiniPID technology at the heart of the instrument, 'Titan' is highly sensitive and capable of detecting benzene levels down to 0.1ppm and up to 20ppm. It continuously samples and analyses the environment to provide real-time feedback of ambient benzene levels.

In Summary

There's no doubt that the international petrochemical industry should prepare itself for even closer scrutiny following the release of the previously secret documents by the CPI. Kristen Lombardi quotes Peter Infante, former director of the office that reviews health standards at OSHA as saying "there is still evidence of an elevation of risks of leukaemia's and lymphomas among occupational groups exposed to the chemical, as well as populations being polluted from these benzene sources".

It is also highly likely the US EPA proposals on monitoring and control of benzene emissions around the boundaries of refineries will be implemented across Europe and the rest of the world. Global oil and chemical giants and the relevant trade associations now have the technology at their disposal for continuous, real-time benzene specific monitoring to ensure the ultimate long-term protection of workers, plant, the environment and local communities.

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Waste Management Specialist Rates Portable Analyser for Landfill Gas Extraction Monitoring

Their four MWM-Deutz TBG 620 V16 engines generate a total of 5MW. The site has been in operation since 2006, with power generation driven by 3000 m³/h of landfill gas, drawn from boreholes across the landfill site. Gas is pumped through a horizontal pipeline network and fed to a cooling, de-humidifying and cleaning station before reaching the engines. The electricity produced is fed to the Greek power grid from a 20kV station.

Helektor has used Geotech's (UK) landfill gas analysers over the last 20 years, including the GA94 and GA2000. "The GEM5000 is a leading biogas analyser that allows us to take fast, reliable measurements and to adjust the Tagarades landfill gas field to optimise operation of the power plant," comments Mr. Christos Chasapopoulos, manager of the Thessaloniki Tagarades LFG to electricity plant.

"I particularly like the low weight and size, as well as the easy-to-read display", Mr. Chasapopoulos adds, "and would certainly recommend this analyser. "We have a fleet of Geotech's analysers now and the GEM5000 is a useful tool for our technical personnel to accomplish their work quickly and accurately in a demanding environment such as landfill." Helektor also uses the Gas Analyser Manager (GAM) software for download, analysis and evaluation of gas readings.

HELECTOR S.A. is the Waste Management arm of the ELLAKTOR Group and a waste management specialist in South Eastern Europe, also active in Germany. The company has built a large number of Mechanical Biological Treatment, Anaerobic Digestion and leachate treatment sites and operates many landfill and landfill waste to energy sites.

The Geotech GEM5000 was designed specifically for the landfill gas extraction application. Landfill gas composition (primarily methane and carbon dioxide, although the analyser can measure up to six gases) and gas flow are measured. These are used to calculate a figure for the energy generated by the gas, shown in KW or BTU.



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