‘On-Line’
Odour Measurement & Control

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Proprietor: The Canary Company Pty Ltd

• Issues:

- **This paper addresses various advantages in continuous hydrogen sulphide monitoring of sewage scrubbers, how use of the technique might reduce potential odour complaints and attempts to demonstrate where use of latest technology has overcome earlier concerns with the method.**
- **In addition, the profile of continuous H2S odour monitoring as a direct means of process control and auditing is raised for consideration by interested odour action groups.**
- **Critical issues posed by the need for frequent calibration and on-going maintenance are also addressed.**

• Licensing:

•Odour control measures, under such licenses, were to demonstrate that nominated scrubbers would perform within the agreed terms of the license through the monitoring and recording of source hydrogen sulphide concentrations at the scrubber's outlet stack.

•Sewage scrubbers nominated under such licenses operated continuously and therefore required a monitoring protocol which would provide adequate sensitivity to odour concentrations of H_2S being detected 'on-line', in order that a continuous record of scrubber performance could later be demonstrated via the plant's SCADA system.

• Requirement:

•In 1997, the Protection of the Environment Operations Act replaced the NSW Clean Air Act. Designated sewage treatment plants were licensed by the EPA to maintain agreed source odour emissions.

• Reporting Techniques:

•For any licensing protocol to work in the aggressive field environment around a sewage treatment plant (STP), a non-hazardous ‘user friendly’ technique was required.

•Approved detection methods based on using a naked hydrogen flame were precluded, due to the potential risk of explosive concentrations of methane being present at an STP.

•Sampling/analysis techniques gaining wide acceptance, such as olfactometry, failed to provide the continuous monitoring and recording protocols necessary to fulfill the self-auditing component of agreed licensing.

•A niche in the market was created for interested suppliers to adapt and develop other sensitive detection principles more suitable to continuous operation

•Electrochemical sensors provided one solution.

• ‘On-Line’ Techniques:

•Contenders for this market were electrochemical detection techniques and a principle based on packaging of chemically impregnated lead acetate paper into a continuous 30 day tape

•The strengths and weaknesses of each method have required careful consideration before selecting either

•Ease of frequent maintenance in sometimes remote and difficult field locations, consumable monthly cost, and the desirability of demonstrating calibration efficacy have been voiced as important conformance issues.

•NSW’s major water authority has in agreement with the EPA identified in its “needs specification” that the electrochemical sensor will be its preferred method for continuously detecting and recording hydrogen sulphide odour emissions from its scrubbers.

• Sewage Odour Detection Methods:

- **‘On-line’ techniques for monitoring sewage odours are not presented as competing directly with approved sampling/analysis methods such as FPD, GC/FID, wet chemistry or olfactometry.**
- **The strengths of current electrochemical sensing are compared only to its popular use as an ambient diffusion sensor.**
- **Weaknesses of its application in sewage scrubbers are discussed only for the purposes of addressing resolutions**
- **The author purposes to raise greater interest in the use of continuous ‘on-line’ hydrogen sulphide monitoring of sewage odours in places other than New South Wales**
- **Due to issues of commercial confidence this paper comprises a mostly non-technical presentation**
- **No product comparisons are critically made.**

• Agreed Method for Logging H_2S Odour:

•Use of the electrochemical sensor to detect odour concentrations of H_2S is approved only after agreement between a licensee and the EPA in NSW.

• It does not automatically follow that 'agreed' use under license of the electrochemical sensing technique translates into its conformance with the EPA's "Approved methods for the sampling and analysis of air pollutants in New South Wales".

•The approved EPA method for H2S determination is routed back to the US EPA's method #15 flame photometric detection

•It is therefore pertinent to clarify that the use of electrochemical sensing techniques for the purposes of recording hydrogen sulphide odours is not preferred by the New South Wales EPA but approved by them in written agreement with a licensee for their prescribed purposes.

• Methodology Milestone:

- **Approval for use of the electrochemical H2S sensor under EPA license should however be recognised as a key milestone.**
- **Australian Standard AS3580 'Methods for sampling and analysis of ambient air' approves the use of some electrochemical instruments.**
- **Method 4.1 for sulphur dioxide (SO_2) and 7.1 for carbon monoxide (CO) include electrochemical instruments as approved choices.**
- **Method 8.1 the sampling/analysis of hydrogen sulphide by contrast excludes the use of electrochemical instruments, identifying the GC/FID technique as the only method for determination of H2S concentrations in ambient air. This is unfortunate however:-**
- **Exclusion of electrochemical instrumentation from AS3580 method 8.1 for H2S is understandable as in 1990 electrochemical sensing techniques were typically cross sensitive to CO**
- **As method 8.1 targeted the suitability of instrumentation for ambient air analysis, several ppm of CO co-existing with H_2S would certainly interfere with sensor response thus justifying the 1990 method.**

• Improved H_2S Sensor:

- **Monitoring of H2S odour in scrubbers is performed in a totally closed loop and not exposed to ambient air**
- **Also now since 1990 and due to particular requirements of the waste water industry, a more specific hydrogen sulphide sensor has been developed**
- **CO interference is now reduced to 2%**
- **Sensor technology in 21st century has advanced well ahead of concerns presumed in 1990 which excluded the electrochemical H_2S sensing instrument as a choice from AS3580/1990 Method 8.1.**
- **Perhaps now a timely review of method 8.1 is in order to meet current needs of technology and the marketplace ?**

• Continuous Monitoring Options:

- **Electrochemical sensors are widely recognised for their linear response to gas, loop powered operation, low cost, and capability to detect a variety of hazardous substances with high sensitivity**
- **Common usage is 'ppm' detection of workplace safety concentrations**
- **Would this measurement technique be successful in odour monitoring at sub-ppm levels and under conditions where previously it had failed?**
- **How would electrochemical sensors, having been tried previously in wet-well monitoring and due to poor response and reduced cell life - failed, now conform to sensor manufacturer's specifications?**
- **Concurrent with local market need in the mid-90's however came technological improvement in sample flow engineering hardware enabling solutions to previously experienced problems**
- **Repeatable "on-line" detection of total sulphurs as H_2S down to less than 30 parts per billion (ppb) became possible.**

• Calibration Traceability:

- **Supporting the development of ultra low range reactive gas sensing techniques required internationally acceptable calibration standards at sub-ppm levels to prove conformity to AS3580-1990 Method 2.1.**
- **NIST traceable permeation tubes, commercially available, made the best choice for both flexibility and sensitivity considering, the likely requirement for a calibration gas source at sub-ppm concentrations**
- **Reputation of early permeation tubes suffered from poor repeatability, were difficult to ship and store before exceeding their "use by" date.**
- **Now permeation sources are readily available and individually traceable devices giving long storage life, good stability and repeatability. These calibration sources are now reliable used in the field at levels necessary to validate repeatable sensor response.**
- **Calibrant consistency over time, has served to confirm the low span drift of gas sensors operating in Canary odour monitoring systems**
- **Repeated conformity with wet chemistry method as to the veracity of readings has increased user confidence – both sensors and calibrants.**

• Sampling Difficulties:

•Sample gases entering and exiting sewage scrubbers provide a highly aggressive atmosphere in which to continually expose the humble electrochemical sensor, without drastically reducing its life expectancy.

•A significant proportion of The Canary Company's development of this technique for odour detection has been allocated just to sample preparation.

•Challenges to overcome - keeping the sensor alive, optimising detection limitations, and sensor selectivity to interfering gases like organic sulphurs and chlorine, have largely been resolved in the development objectives of the latest 'SmarTox O' product.

• Monitoring of Sulphur Odours:

•Odour group interests are currently united in the single goal of finding agreement for an international set of protocols relating to dynamic olfactometry

•As a result are some odour interest groups neglecting to acknowledge the importance of other technological advancements which may benefit community concerns for reduction and elimination of odour ?

•'On-line' scrubber monitoring of outlet H2S is one of several performance indicators available but the only one directly representative of NSW license compliance and elemental sulphur breakthrough as H2S.

•Reduction of odour, prior to a source emission developing into a complaint is now possible in spite of 'on-line' odour monitoring having rated little attention .

• Partial Solution:

•The Canary Company Pty Ltd has developed a continuous odour detection strategy to comply with agreed sewage treatment plant licensing by the EPA.

• In addition to a monitoring only role the technology is poised to offer more features - identify scrubber adjustment requirements in real time, monitor the effectiveness of changes, assist in self-auditing of fugitive emissions

•Provide an overview of environmental credits due in sulphur recovery where both foul air and the scrubbed source are monitored.

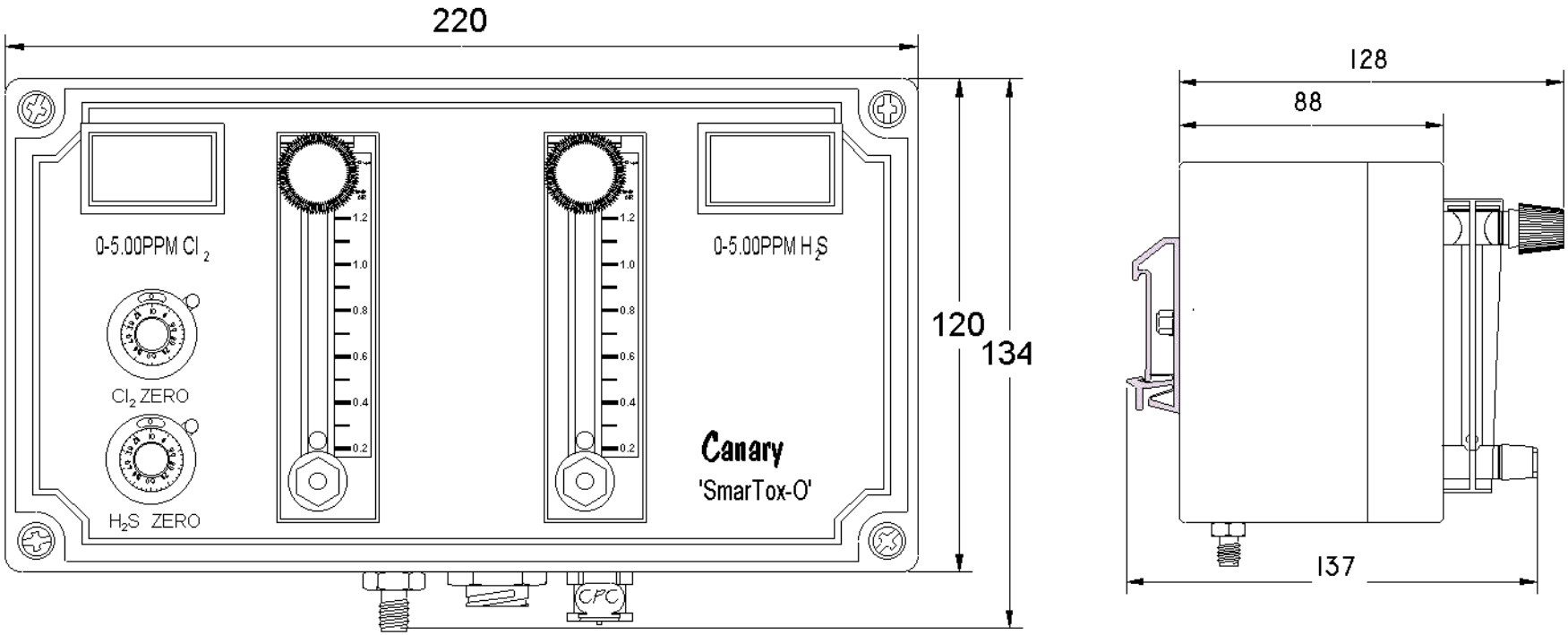
• From an immovable working prototype developed in 1993 the concept has now developed into a totally modular system

•Modules are easily exchanged in the field for the express purpose of frequent bi-monthly maintenance of high duty items, off site.

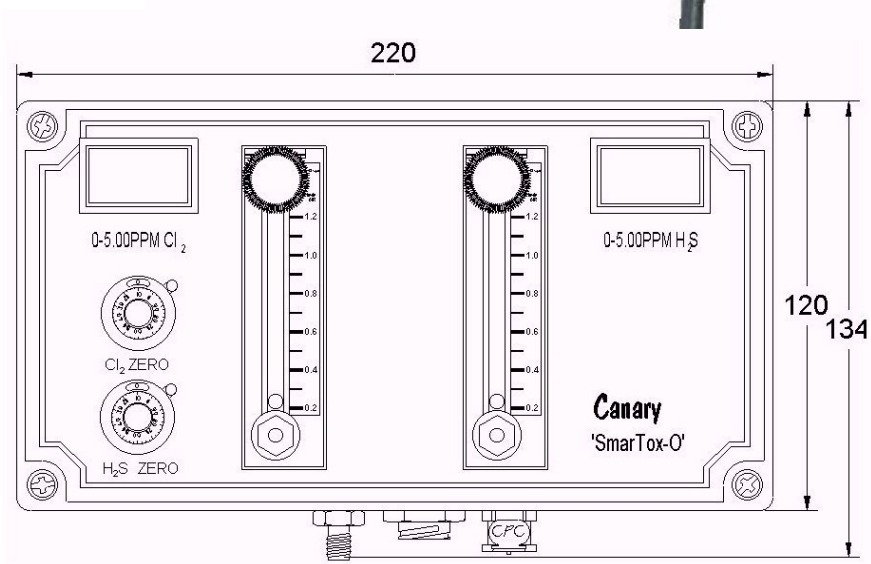
•The latest design Canary 'SmarTox-O' resolves sulphurs detected as H_2S down to 0.01 ppm (10 ppb) and continuously sends a proportional 4-20mA output signal to a remote computer (SCADA type) system.

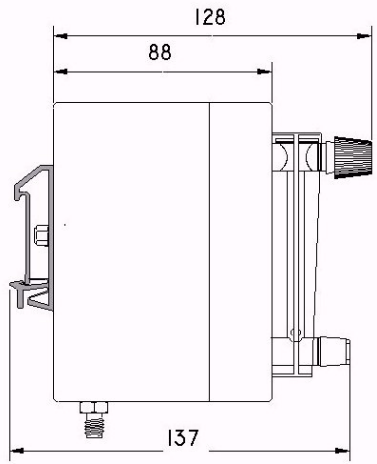
•Canary electrochemical sensing modules now carry full warranty normally expected from ambient air diffusion type applications.

- **Schematic ‘SmarTox-O’ Dual Gas Sensing Module:**



• Continuous Monitoring Options:





• Schematic ‘SmarTox-O’ Dual Gas Sensing Module:

•Features of the most recent Canary design offer a user-friendly concept, suitable for specifying into a system panel with other process instrumentation for maintenance by outside contractor.

• The product features sample flow conditioning and control, local display of concentration, temperature set-point indication, and remote sample ‘’on/off’’.

•The module is easily detached from a DINrail panel as a single unit, for service back in a clean-room environment and is replaced in seconds with a freshly calibrated module using non – instrument trained personnel employed at site.

•Because of its small size, it is a cost effective monitoring solution to purchase, transport and maintain. The Canary ‘SmarTox-O’ modular design is a hybrid concept in gas detection – placed between the portable safety and fixed application instrument markets.

• Intermittent to Continuous Operation Strategy:

•Following prototyping in 1993 an invitation to tender for supply and installation of two separate ‘on-line’ systems monitoring inlet and outlet of two large scrubbers was let, to be situated at an environmentally sensitive ocean outfall site.

•Proportional 4-20mA output signals from each ‘on-line’ system were to be re-transmitted back to the plant’s SCADA system.

•The original specification was met and won by the author.

•Two systems were manufactured in 2 metre high field enclosures, early ‘90’s technology requiring a “bigger is better” approach.

• Installation necessitated the use of a crane to locate each cabinet. By comparison today’s modules are miniaturised - only a fraction of the original transmitter dimensions

•Odour sensing transmitters were required to pass performance testing by an accredited 3rd party laboratory.

• Blueprint for the Future :

- **Immediately following original system startup, H2S gas monitoring identified scrubber failure**
- **Then "just proven" outlet H2S transmitter identified elemental sulphur breakthrough by displaying an H2S 'over-range' and thereby identifying a process problem.**
- **Investigation of the scrubber process using a series of colorimetric gas detector tube tests then revealed in what "ballpark" the outlet emissions really were. With each successive detector tube, selected for its increased ppm measurement range**
- **Tubes finally revealed a scrubber outlet venting 50 ppm hydrogen sulphide as compared to full scale deflection of 1 ppm accepted in the tendered offer.**
- **Importantly, just moments after system startup the monitoring technology justified its cost to the public by detecting sulphur breaking through a scrubber system operating way over its design criteria.**
- **For the first time operators at this STP had a link to sulphur recovery measured directly as H_2S for identifying with and in this instance requiring their immediate action.**
- **Several unidentified inconsistencies proving lethal to longterm sensor performance were revealed during first weeks of operation including the potential for gas sensor failure due to saturating sample conditions**
- **Under these conditions good sensor response would be limited to perhaps just a few days gradually reducing to nil response over a couple of weeks. Negative customer reaction would follow as customers's became disappointedly aware that the pleasing and stable sensor zero they were observing did not equate to 100% scrubbing efficiency but more likely to a 'drowned' sensor.**
- **This initial experience led to a re-view of sampling techniques needed to keep electrochemical sensors alive and solutions for overcoming earlier difficulties implemented**

• Scrubber Failure Detected:

Improvements implemented:

- **Increasing the outlet gas sensor range to allow for moderate over-range conditions.**
- **Use only PTFE Teflon® or 316 Stainless Steel wetted materials in contact with sample gas to minimise contamination by dilution but also use Teflon® dropout pots (not plastic or anodized) with automatic drainage**
- **Sample tubing was given sufficient fall to drain and dropout pots were situated at the lowest points**
- **Heat tracing to ensure sensor response remained temperature stable against wide daily swings and further reduce non-condensing sample moistures.**

• Wet Chemistry Testing:

- **Though not always but in spite of expected interferences, the 'SmarTox-O' electrochemical measurement strategy has agreed well with standard wet chemistry testing methods, being specific for H_2S.**
- **Results from several sets of independent analyses the Canary 'SmarTox-O' modules since early 2000 have provided good to excellent agreement (best within +/-0.2%) with the method.**
- **Recording of the continuous electrochemical signal compared later to grab sampling occurring every 40 minutes and tracking scrubber outlet emissions up and down from 0.04 ppm to 0.6 ppm exceeded the expectations of all concerned, particularly as two scrubbers were compared separately at the same site.**
- **With this sort of correlation possible the use of the technology for scrubber control purposes becomes viable whilst, the cost of system ownership remains unequivocally the lowest in the market**

• Calibration/Maintenance:

•Due to the closed loop and aggressive operating environment a frequency re-calibration and operational checking regime is vital to the successful use of electrochemical techniques.

•A bi-monthly interval is recommended, requiring a pre-calibrated replacement module to be held on rotation.

•Removal & replacement of our modular design is simple enough for a non - instrument trained employee to perform.

•An ‘out of service’ module can be replaced with a spare, freshly calibrated, ‘SmarTox-O’ module in seconds.

•The ‘out of service’ module is easily couriered, due to its small size, to and from a remote location to Canary Company’s premises based in Sydney.

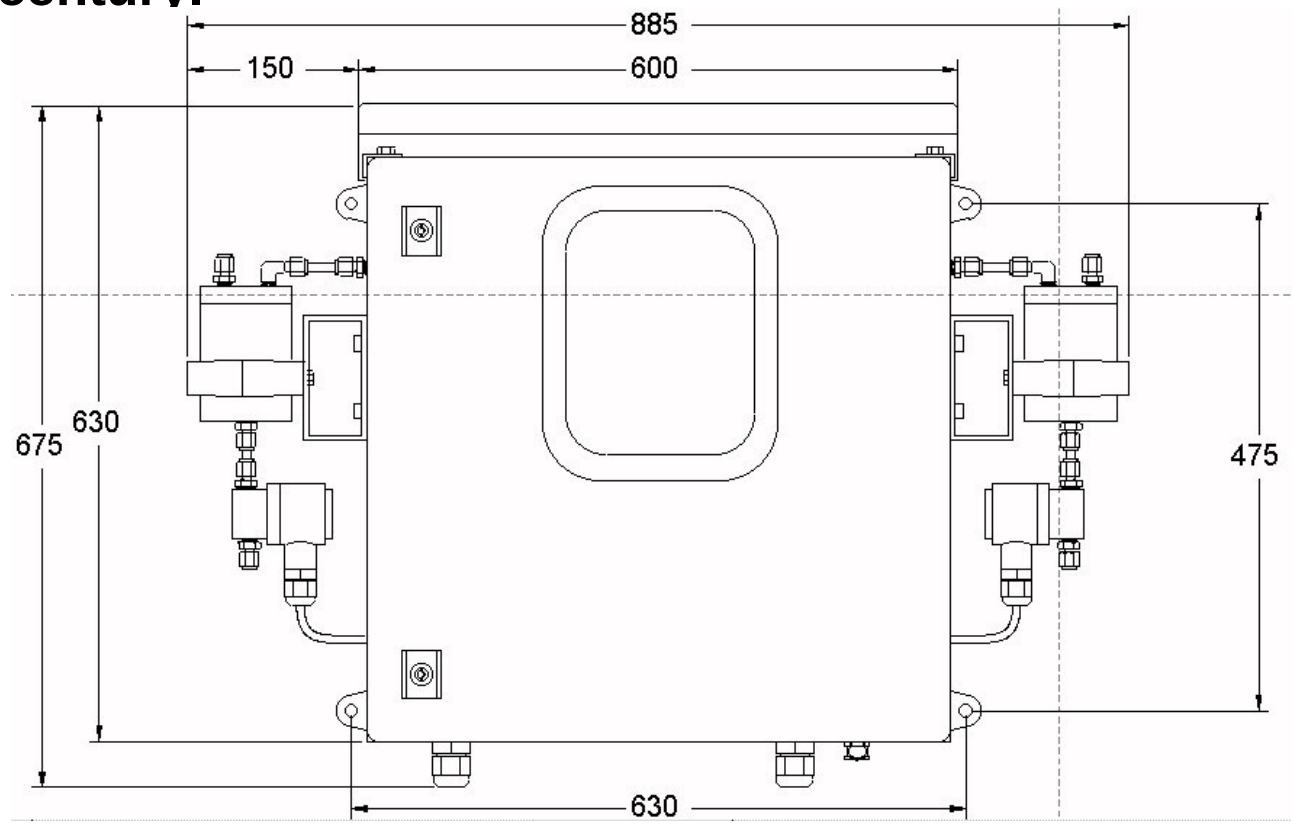
•No other on-line odour monitoring technique offers such flexibility, Canary Co has achieved this DINrail concept in a rugged design.

• Summary:

- For a variety of field considerations, neither EPA approved FPD flame photometric detection method #15, dynamic olfactometry, nor AS3580 Method 8.1 GC/FID ambient air analysis of H_2S provide feasible 'on-line' monitoring solutions required by a growing market to meet specified needs of sensitivity and simplicity.
- A feasible solution is found utilising the humble electrochemical (coulometric) sensor to meet this demanding odour measurement & control requirement.
- In spite of recent technological advancements made in specificity, some may still regard this method of gas detection as too unsophisticated.
- This simple detection device, employed correctly into a sample stream, has been since 1994 and is now more effectively able to fulfill the important role of policing odour in a most rugged environment otherwise known to fail more complicated analysis methodologies.

• Closing Remark:

The author concludes that the use of low cost monitoring techniques such as electrochemical H2S sensors, to continuously audit scrubber efficiency provide a most valid and useful advancement in any odour control policy and should be considered as an advancement toward further reducing fenceline odour in the cleaner world environment of our 21st century.



Thank you.

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• Calibration/Maintenance:

User Benefits

New ‘SmarTox-O’ modules are easily shipped by courier to/from local, interstate and overseas customers - as frequent maintenance checks do not require routine service by a Canary representative at site.

Calibration efficacy is improved long term as the internal integrity of ‘SmarTox-O’ enclosure is not being continuously exposed to corrosive atmospheres found typically around sewage treatment works.

Calibration accuracy to zero and low ppb NIST traceable span gases, and other test function checks, are more repeatable in the controlled workshop environment than in the field.

Cost of ownership - to purchase and maintain new ‘SmarTox-O’ system - is low.

• Calibration/Maintenance:

User Benefits

Frequency and cost of site visits by service personnel to rectify gas detection faults are mostly eliminated.

‘Out of Service’ modules can be returned to Canary Co by courier for recertification in-house and a spare freshly calibrated module kept on the user’s shelf is immediately re-connected into the system panel via 3 quick-connect fittings.

All work on highly sensitive instrumentation can be performed away from contaminated scrubber atmosphere in a clean environment where precise checks can be effected reliably.

• Sensor Interference:

Foul air entering a sewage scrubber may contain organic sulphurs in addition to inorganic H_2S. Positive interference from organic sulphurs on the H_2S calibrated sensor has been determined at between 10 & 20% for the cumulative effects of Dimethyl sulphide, COS & SO_2. Mercaptans is the exception to this with a significantly higher interference of 40%. Cross-sensitivity may also vary between individual sensors whilst chlorine interference typically provides a negative interference of up to 20% but typically around 10% of Cl_2 concentration. Accepting the worst case scenario, as normal, makes further consideration to adapt electrochemical techniques to odour monitoring a complete waste of time. However, observations made over a 7 year period of on-line odour detection, confirmed by colorimetric detector tube testing, have shown good agreement with target gas sensor readings. In other words potential interference levels expected had a nulling effect on sensor output when exposure to potential interferents was averaged over 15-30 minute intervals.

• Sensor Interference:

In short :

- **Does concern over issues like electrochemical sensor interference preclude its usefulness?**

- **In the day to day world of scrubber operations which may involve a variety of process anomalies, how critical is positive sensor interference displaying 0.2ppm outlet concentration instead of perhaps an actual 0.1ppm when scrubber mass/flow is typically 10 cubic metres/second at the source and in consideration of the downwind dilution effect of pluming 1-200 metres away at the fence line?**

- **Is not the primary goal of any on-line measurement strategy to ensure a sensor is alive and can detecting real changes in concentration?**