Application Note 6

Chlorine Dioxide Measurement with a 7CLH CiTiceL

Chlorine is widely used in industry as a sterilising and bleaching agent, and used in large quantities in water treatment. Water authorities worldwide are increasingly looking for alternatives to chlorine, as the chlorination of organic substances found in waste water can lead to the formation of carcinogenic halogenated compounds. Chlorine dioxide is a more acceptable alternative since there is less chance of toxic by-products being formed . It is also a more effective sterilant, so the quantity needed to achieve sterilisation is smaller.

The U.K. occupational exposure limits for chlorine dioxide are as follows:

Long term exposure limit: 0.1 ppm
Short term exposure limit : 0.3 ppm

(Figures are taken from HSE Guidance Note EH 40/93.)

American Conference of Governmental Industrial Hygienists (ACGIH) TLV figures (1984) for ClO_2 are:

TWA (8 hour) : 0.1 ppm
STEL (15 minute) : 0.3 ppm

TWA figures for other countries include:

	TWA		**TWA**
Belgium :	0.1	Brazil:	0.08
Denmark:	0.1	Finland:	0.1
Italy:	0.1	Mexico:	0.1
Netherlands:	0.1	Switzerland:	0.1

Figures are taken from AIHA Occupational Exposure Limits - Worldwide, W.A.Cook, 1987.

A programme of work was carried out at City Technology to examine the feasibility of detecting chlorine dioxide electrochemically. Theoretical calculations predict complete reduction of chlorine dioxide will readily occur in the acid medium of an electrochemical cell according to the following equation:

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$$

Unfortunately a usable supply of chlorine dioxide was not commercially available at the time, due to its tendency to explode under pressure, and had to be generated in house.

7CLH chlorine sensors were used as the electrode material favours the reduction of chlorine dioxide. The sensors were found to respond readily to chlorine dioxide, with 10ppm ClO_2 output between 30.4 and 32.1 μA.

The conclusion drawn from this testing was the sensitivity of the 7CLH to chlorine dioxide is approximately 3.1μ A/ppm ±25%. This is a reducing signal, i.e. the output has the same polarity as when responding to chlorine. The minimum output resolution of the 7CLH in a fixed monitoring application is 0.15 μA, corresponding to a chlorine dioxide concentration of approximately 0.05 ppm. Therefore with suitable precaution and signal processing, a chlorine dioxide monitor could be set to alarm at the STEL of 0.3 ppm chlorine dioxide.

For calibration, it is recommended that chlorine dioxide is generated electrochemically using the method given below and that chlorine is used as a surrogate gas for occasional sensor verification.

Summary:

Sensor	Sensitivity to ClO_2	Sensitivity to Cl_2
7CLH	3.10 ± 25% μA/ppm	1.0 ± 0.25 μA/ppm

NOTE: Chlorine dioxide may be prepared industrially by electrolysis of a $NaClO_2$/NaCl solution using a graphite anode and a copper or nickel cathode. It can also be generated by passing chlorine gas through a column of sodium chlorite. The method used at City Technology involved the electrolysis of a solution of 2% $NaClO_2$, 0.2% $CuSO_4$, 0.3% tri-sodium citrate, 5% Na_2SO_4. The pH was adjusted to 8.3 with 0.1M sodium hydroxide.

Alternatively, chlorine dioxide generating equipment is available from a number of suppliers. Please contact City Technology for advice.