

## Application Notes



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# Chlorine Dioxide Measurement

## 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<sub>2</sub> are:

TWA (8 hour) : 0.1 ppm

STEL (15 minute) : 0.3 ppm

TWA figures for other countries include:

	<u>TWA</u>		<u>TWA</u>
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:



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<sub>2</sub> 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 3.1 µA/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  $\mu\text{A}$ , 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:

<u>Sensor</u>	<u>Sensitivity to <math>\text{ClO}_2</math></u>	<u>Sensitivity to <math>\text{Cl}_2</math></u>
7CLH	$3.10 \pm 25\% \mu\text{A/ppm}$	$1.0 \pm 0.25 \mu\text{A/ppm}$

**NOTE:** Chlorine dioxide may be prepared industrially by electrolysis of a  $\text{NaClO}_2/\text{NaCl}$  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%  $\text{NaClO}_2$ , 0.2%  $\text{CuSO}_4$ , 0.3% tri-sodium citrate, 5%  $\text{Na}_2\text{SO}_4$ . 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.

# Intrinsic Safety Considerations

## Currents & Open Circuit Voltages for Intrinsic Safety Considerations

### Introduction

Electrochemical sensors are generally devices which only produce very small voltages and currents and are not able to store large quantities of energy. In certain circumstances, therefore, it may be possible to consider them as simple apparatus as defined in BS 5501. Paragraph 1.3 of the 'general requirements' states that:-

*"Devices in which, according to the manufacturer's specifications, none of the values 1.2V, 0.1A, 20μJ, or 25mW is exceeded need not be certified or marked."*

To consider whether the sensors can be covered by this statement we need to look at:-

- A) The electrical characteristics of the sensors in normal operation
- B) The possible fault conditions and what they might produce.

**Note:** Previously much attention has been focused on the potential short circuit currents which might be produced if a sensor is open circuit, exposed for a period to a high level of an electrochemically active gas and subsequently shorted out. It is worth noting that this condition requires two countable faults to occur with the exception of the condition of replacing the sensor in a hazardous area.

### Oxygen Sensors

#### A) Currents and voltages generated under normal operation at 20°C.

##### 1) Current outputs

Current outputs in dry, ambient air are:

**7OX** : 0.4mA maximum

**7OX-V** : 0.4mA maximum

These sensors are non-linear and show increasing sensitivity at oxygen concentrations above normal ambient air levels of 21%. Maximum currents of 10mA are observed in pure oxygen.

##### 2) Open circuit voltages

In tests carried out at City Technology, measurements made of open circuit voltages over the range 10-100% O<sub>2</sub> were less than 0.8 volts for all oxygen sensors. Therefore there is no known way that the open circuit voltage can exceed 0.9 volts.

#### B) Max. current on short circuit from an open circuit condition.

Peak current values of 200mA maximum were recorded on oxygen sensors over the concentration range 10 to 100% O<sub>2</sub>. These peaks decay rapidly, within a few seconds, to the normal operating currents as oxygen within the cell is consumed and further ingress is controlled by the capillary diffusion barrier.

Peak short circuit currents are primarily a function of the open circuit voltage generated and are similar for all oxygen sensor types. Variations might be expected on testing larger sample sizes, but it is unlikely that currents would ever reach significantly greater values than 200mA and a reasonably safe limit to quote would be = 500 mA.

### Summary on Oxygen Sensors.

Maximum current in normal operation (pure O<sub>2</sub>) = 0.01 Amps.

Maximum open circuit voltage (10 to 100% O<sub>2</sub>) = 0.9 Volts.

Maximum peak short circuit current (10 to 100% O<sub>2</sub>) = 0.5 Amps.

## Toxic Sensors.

### A) Currents and voltages generated under normal operation at 20°C.

#### 1) Current outputs

All sensor types are linear over the recommended operating range of gas concentration and the current generated is given by the equation:

$$\begin{array}{ccccc} \text{cell sensitivity} & \times & \text{gas concentration} & = & \text{cell output} \\ (\mu\text{A/ppm}) & & (\text{ppm}) & & (\mu\text{A}) \end{array}$$

How a sensor behaves when exposed to concentrations above its recommended range depends on whether it has two or three electrodes. In both cases, exposure to such high concentrations results in severe polarisation at the *counter* electrode.

**(a) Three-Electrode Sensors** - The *sensing* electrode is controlled, relative to an unpolarised *reference* electrode, by an external operational amplifier circuit. Unlike two-electrode sensors, the *sensing* electrode potential is independent of the *counter* electrode polarisation. Tests on these sensors have shown a linearly increasing output with gas concentration until the output current exceeds the saturation current of the controlling external amplifier. At this point no further current change is possible with increases in gas concentrations. The maximum current limitation of amplifiers commonly used with a three-electrode sensor control is unlikely to exceed 50mA.

#### 2) Voltages generated

**a) Three electrode sensors** - In normal operation the cell potential will be the sum of the *sensing-reference* and *reference-counter* potentials. There are two cases to consider:

- i) For zero bias sensors the *sensing-reference* potential will be zero

(<10mV). The *counter* electrode potential, however, is free to float relative to the *reference* electrode and will polarise as it produces the required cell current. The degree of polarisation is dependent on time and concentration. However once a polarisation of 1.05V has occurred the *counterelectrode* will begin to evolve hydrogen and no further polarisation can take place. This means the maximum theoretical cell voltage for an unbiased sensor is 1.05V.

ii) The above consideration of *reference-counter* potential applies equally to biased sensors, but the *sensing-reference* potential may be greater than zero. The current recommended bias settings are:

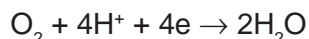
**7ETO:** +300mV;      **7NT:** +300mV  
**7AM:** +300mV;

Therefore the maximum theoretical cell voltage for biased sensors is 1.35V. However in practice *counter* electrodes do not polarise as far as hydrogen evolution (e.g. at its maximum overload of 5000ppm NO, measurements made on a 3NF/F show a stable polarisation voltage of 800mV, giving a total cell voltage of 1.1V). It is therefore true to say that, in practice, even in biased operation cell voltages are normally less than 1.2V.

## B) Maximum values of open circuit voltages

The MAXIMUM POSSIBLE potential is given by the NERNST equations for the electrochemical reactions at the *sensing* and *reference* electrodes.

The *reference* electrode is essentially the oxygen electrode reaction:



This reaction is irreversible and the true Nernst potential is never observed, even on very active electrocatalysts such as platinum. Maximum observed potential for City Technology *reference* electrodes is about 1.05 volts on the Normal Hydrogen Electrode Scale (N.H.E.). In some sensors lower potential references are used and this is taken into account when deriving the figures below.

The following maximum possible potentials of the various *sensing* electrode reactions are calculated against the observed *reference* oxygen potential. The figures assume the subject gas reactions achieve the NERNST potential:

$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	1.25 V
$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_3 + 2\text{H}^+ + 2\text{e}^-$	0.75 V
$\text{H}_2\text{S} + 3\text{H}_2\text{O} \rightarrow \text{SO}_3 + 8\text{H}^+ + 8\text{e}^-$	0.76 V
$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	1.05 V
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	0.80 V
$\text{NO} + \text{H}_2\text{O} \rightarrow \text{NO}_2 + 2\text{H}^+ + 2\text{e}^-$	0.37 V
$\text{NO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O}$	0.20 V
$12\text{NH}_3 + \text{I}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{IO}_3^- + 12\text{NH}_4^+ + 10\text{e}^-$	0.60 V (see note)

**Note:** Ammonia sensors employ a unique electrolyte. The  $\text{NH}_3$  reaction mechanism in this electrolyte is different to the oxidation and reduction techniques used in other sensors. However the maximum possible potential is still calculable.

From these equations we see that the maximum open circuit voltage will be less than 1.2V in all cases except CO. The theoretical maximum for CO is 1.25V, which corresponds to 100% CO. At lower concentrations the voltage will be reduced by 60mV/decade (e.g. giving 1.19V @ 10% CO).

In practice, however, the above estimates of MAXIMUM POSSIBLE open circuit voltage are unlikely to be achieved for the following reasons:

- (a) Many of the reactions, particularly that of CO, are irreversible, so the full NERNST potentials are never realised.
- (b) The presence of oxygen at the *sensing* electrode creates a mixed potential which reduces the *sensing-reference* potential difference.
- (c) In the open circuit condition, reactant gas can diffuse to the *reference* and *counter* electrodes causing an equalisation of potential differences (e.g. a 3H sensor introducing to 100%  $\text{H}_2\text{S}$  in an experiment produced no measurable cell potential).

Measurements made at City Technology show that the above factors do in fact limit the open circuit voltages quite substantially, even with exposure to very high concentrations. For example, 0.75V was recorded on a CO sensor exposed to 20% CO and 0.36V was recorded on a  $\text{H}_2\text{S}$  sensor in 900 ppm  $\text{H}_2\text{S}$ . Since these potentials vary according to the logarithm of the gas concentration, open circuit voltages will not vary greatly at higher concentrations.

In summary, although it is theoretically possible to generate more than 1.2V in an open circuit situation, in practice this is never observed.

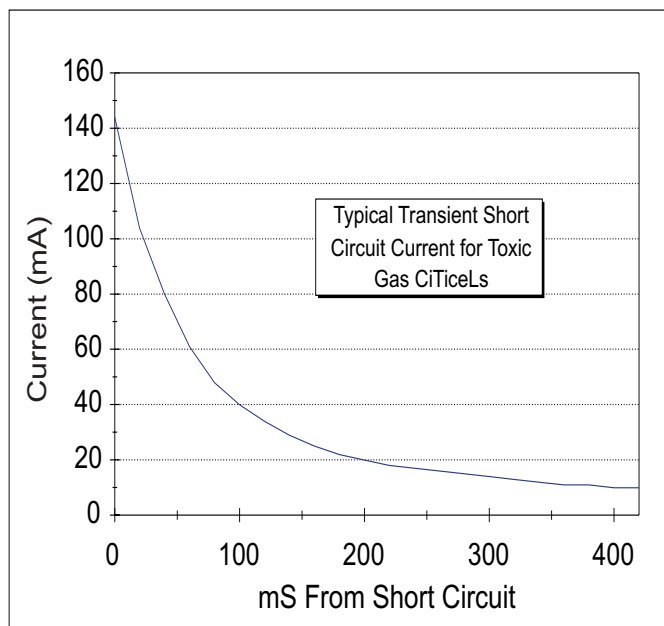
### **Max current on short circuit from an open circuit condition**

As for oxygen sensors, peak short circuit currents will be a function of the open circuit potential developed during the open circuit. The maximum measured value in tests at City Technology, in 20% CO, was 0.47 amps from an open circuit potential of 0.75 volts. The maximum possible potential is 1.2 volts and therefore we can deduce that the MAXIMUM POSSIBLE short circuit current would be 1 amp.

## Summary on Toxic Gas Sensors.

Maximum current possible in normal operation = 0.05 Amps.  
Maximum cell voltage possible in normal operation = 1.2 Volts  
Maximum open circuit voltage possible = 1.2 Volts.  
Maximum peak short circuit current possible = 1 Amp.

**Figure AP2.1**  
Short Circuit Currents





# Phosphine Measurement

## Phosphine Measurement Using 7E and 7SH CiTiceLs

### Introduction

Phosphine is a colourless, flammable, toxic gas which smells like garlic or decaying fish. It is a volatile gas with a high vapour pressure, a specific weight comparable with that of air and a low molecular weight. All these properties favour the use of phosphine in fumigation applications, the major use of the gas over the last 60 years. However another increasingly important application for the gas is in semiconductor manufacture. These two applications have vastly different requirements, and so require different sensors.

<b>Phosphine -</b>	Chemical Formula:	PH <sub>3</sub>
	Molecular Weight:	34.1
	Lower Explosive Limit:	1.79 - 1.89% volume in air
<b>Toxicity:</b>		
> 2000ppm	Lethal to man in a few minutes	
400-600ppm	Dangerous to life after 30-60 minutes	
100-190ppm	Maximum that can be tolerated for an hour	
7ppm	Maximum that can be tolerated for several hours without symptoms	
0.3ppm	Short Term Exposure Limit (Source: HSE GN EH40/93)	
	Threshold Limit Value (Source: ACGIH 1983)	

### Fumigation

Grain and other foodstuffs in storage have always been susceptible to attacks by pests. The FAO (Food and Agriculture Organisation of the United Nations) estimates that between 10 to 20% of the world's harvest is destroyed by insects and rodents. Toxic gas fumigation provides an effective solution to the problems of foodstuff storage and transportation. First used in 1935, phosphine is today one of the most widely used fumigants in the world.

For successful fumigations using phosphine it is important that the concentration and flow of phosphine are carefully monitored and controlled; too low a concentration can lead to eggs and pupae surviving the fumigation; too high a concentration can lead to a phenomenon known as 'phosphine narcosis' whereby insects enter a torpid state in which they are resistant to phosphine gas.

### Semiconductors

Whereas the measurement of phosphine in fumigation applications provides a means of process control, its use in semiconductor manufacture is personnel protection. Unlike fumigation processes, which involve large, enclosed spaces

which can be 'flooded' with gas, semiconductor manufacture requires 'hands on' supervision. Therefore the legal requirement to protect the work force requires monitoring of TLV levels. Clearly the levels needed to exterminate a barn full of insects is going to be a lot higher.

## Detection

In the past phosphine concentrations have been traditionally determined by glass tube detectors. Although these can determine concentration, they suffer from poor accuracy and, when used in large scale or in-transit applications, high cost. In addition the technique is unsuitable for continuous monitoring or control applications.

For these reasons the use of an electrochemical carbon monoxide CiTiceL as a phosphine sensor was investigated<sup>[1]</sup>.

Theoretical calculations predict that complete oxidation of phosphine will readily occur in the acid medium of an electrochemical cell according to the following equation:



## 7E Carbon Monoxide CiTiceL

One sensor suitable for this reaction is the 7E uncompensated Carbon Monoxide CiTiceL. Inbuilt filters and other features used on other Carbon Monoxide CiTiceLs preclude their use as phosphine sensors. Tests have indicated that with a 1000ppm  $\text{PH}_3$  the sensitivity of a batch of 7E sensors varied between 230 and 239 $\mu\text{A}$ . With a 10 Ohm load resistor connected a 90% response time of under 60 seconds was measured.

The conclusion drawn from our testing is the sensitivity of the 7E to phosphine is approximately 235nA/ppm  $\pm$  36nA, with the resolution at 20°C approximately 0.2ppm  $\text{PH}_3$ . As such it would not be feasible to use the 7E for determining regulatory health exposure limits, as the set level is commonly 0.3ppm  $\text{PH}_3$  for a certain period of time. However the 7E would certainly indicate whether an area (such as a grain silo or tanker hold) had a lethal amount of phosphine. In addition it should be possible to use the 7E in an actively controlled system whereby the build up of phosphine is accurately measured and controlled. The 7E, therefore, could be suitable for most fumigation applications but not for semiconductor manufacture.

Cross sensitivities to other gases, recorded as a percentage of the reading for  $\text{PH}_3$ , at 100ppm and 20°C have been measured as:

	$\text{PH}_3$	$\text{CO}$	$\text{H}_2$	$\text{SO}_2$	$\text{H}_2\text{S}$	$\text{CO}_2$	$\text{NH}_3$	$\text{CH}_4$
%	100	33	<15	28	112	0	0	0

<sup>[1]</sup> Initial Investigations: Ducom P., Bourges C. "Determination of phosphine concentrations with an electrochemical cell", Laboratoire Denrées Stockées, Ministère de l'Agriculture, 33152 Cenon, France

## 7SH Sulphur Dioxide CiTiceL

An alternative to the 7E capable of measuring phosphine down to TLV levels is also required. Of the sensors thought likely to respond, in tests the 7SH Sulphur Dioxide CiTiceL gave the best results. When subjected to the same tests as the 7E sensors, a batch of 7SH CiTiceLs showed a response to 5ppm of phosphine of approximately 4.75µA/ppm. The 7SH sensors also showed a 90% response in under a minute with a 10W load resistor.

Clearly this gives a much higher response to phosphine than the 7E. The resolution at 20°C is better than 0.1ppm and hence very capable of detecting the TLV level of 0.3ppm. In addition, the sensor shows virtually no cross-sensitivity to hydrogen or carbon monoxide, both of which are commonly present in semiconductor manufacture. Hence the 7SH is a far more suitable sensor for such applications where the prime concern is personnel safety.

Cross sensitivities to other gases, recorded as a percentage of the reading for PH<sub>3</sub>, at 100ppm and 20°C have been measured as:

	PH <sub>3</sub>	CO	H <sub>2</sub>	SO <sub>2</sub>	H <sub>2</sub> S	CO <sub>2</sub>	NH <sub>3</sub>	CH <sub>4</sub>
%	100	0	0	25	35	0	0	0

## Summary

### Type 7E:

Gas	CO	PH <sub>3</sub>
<b>Sensitivity</b>	0.075 ± 0.010 µA/ppm	0.235 ± 0.036 µA/ppm
<b>Minimum Range</b>	0-20ppm	0-10ppm
<b>Maximum Range</b>	0-2000ppm	0-2000ppm
<b>Resolution at 20°C</b>	0.5ppm	0.2ppm

### Type 7SH:

Gas	SO <sub>2</sub>	PH <sub>3</sub>
<b>Sensitivity</b>	1.25 ± 0.25 µA/ppm	4.75 ± 1.0 µA/ppm
<b>Minimum Range</b>	0-3ppm	0-1ppm
<b>Maximum Range</b>	0-100ppm	0-25ppm
<b>Resolution at 20°C</b>	0.1ppm	<0.1ppm

See also 4PH phosphine sensor which is manufactured and tested with phosphine



# Health and Safety Guidelines

## Electrochemical Gas Sensors

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### General

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CiTiceL electrochemical gas sensors are supplied as sealed units and in normal usage represent no chemical hazard in the sense of the "Control of Substances Hazardous to Health (COSHH) Regulations" and the Health and Safety at Work Act 1974. Chemical hazard can however arise if CiTiceLs are misused or abused when leakage may occur. Leakage may also occur in the event of a manufacturing fault. In order to avoid potential problems the following notes should be observed on storage, usage, handling and the disposal of unwanted CiTiceLs.

### Oxygen CiTiceLs

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Oxygen CiTiceLs contain a 4-molar potassium acetate solution which is corrosive. Normally this material would only leak out as a result of either mechanical damage (crushing or piercing) or by electrical misuse for example by attempting to input electrical charge. These CiTiceLs also contain small amounts of lead, lead oxide, platinum, silver, carbon and antimony some of which are toxic and/or mutagenic. If the user comes into contact with the Oxygen CiTiceLs contents the affected area should be washed with a copious supply of water. Obtain medical advice.

As these sensors contain some highly toxic compounds, irrespective of physical condition they should be disposed of according to local waste management requirements and environmental legislation. They should not be burnt as they may evolve toxic fumes.

### Toxic Gas CiTiceLs

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The majority of Toxic Gas CiTiceLs contain sulphuric acid electrolyte and the chemical hazard is mainly related to the corrosive nature of this compound. These sensors also contain platinum, ruthenium, gold, silver and carbon, some of which are toxic. Any skin or eye contact with the contents of these CiTiceLs should be washed immediately with copious amount of water. Obtain medical advice.

### Design and Use

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CiTiceLs are sealed units containing an aqueous electrolyte and a combination of other substances as detailed above. Provided these CiTiceLs are used only for their intended application they do not represent a chemical hazard.

CiTiceLs must not be exposed to temperatures outside the range -50°C to 60°C. Toxic gas CiTiceLs should not be exposed to organic vapours which

may cause physical damage to the body of the sensor, for example 1, 2 dichloroethane, acetone and chloroethylene.

## **Storage**

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For maximum shelf life CiTiceLs should be stored in the containers in which they are supplied in clean dry areas between 0°C and 20°C.

CiTiceLs must not be stored in areas containing organic solvents or in flammable liquid stores.

## **Carriage**

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CiTiceLs are classified under UN 2800 (Batteries - Wet non-spillable) and conform to the special provisions, section 4.5, paragraph A67 of the dangerous goods regulations. As such CiTiceLs are classed as non-dangerous and may be transported without special packing, labels, etc. It is, however, important to check any local regulations.

## **Damage**

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Should any CiTiceL be so severely damaged that leakage of the contents occurs then the following procedures should be adopted.

- a) Avoid skin contact with any liquid or internal component through use of protective gloves.
- b) Disconnect CiTiceL if it is attached to any equipment.
- c) Use copious amounts of clean water to wash away any spilt liquid. This is particularly important in equipment where the CiTiceL involved contains sulphuric acid or phosphoric acid because of the corrosive nature of these electrolytes.

## **Disposal**

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All CiTiceLs contain toxic compounds irrespective of physical condition. They should be disposed of according to local waste management requirements and environmental legislation. They should not be burnt since they may evolve toxic fumes.

# **Combustible Gas Sensors**

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## **General**

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CiTipeL combustible gas sensors should at all times be operated according to the instructions from the manufacturers, City Technology Limited, as laid down in the relevant section of the Company's 'Product Data Handbook' Issue 1.6, or any later issue, taking into account any guidelines or warnings the company may issue from time to time. If operated in this way, CiTipeLs represent no chemical hazard in the sense of the "Control of Substances Hazardous to



Health (COSHH) Regulations” and the Health and Safety at Work Act 1974.

Where it is necessary to operate CiTipeLs in a manner other than stated by City Technology Limited, advice should be sought from the company before proceeding.

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## **Design**

The pellistor bead of active elements in a CiTipeL contain very small traces of toxic chemicals. The amounts involved are so small they do not represent any safety hazard. However they should still be handled according to any guidelines laid down by relevant safety bodies regarding the handling of toxic chemicals.

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## **Use**

These sensors are designed for use in applications where the build up of combustible gases could threaten safety. It is therefore essential the sensors operate as intended, and the greatest threat to this is ‘poisoning’ of the pellistor bead by exposure to certain compounds.

CiTipeLs can be operated either in a diffusion mode or in a flow through stream. Whichever mode is used, the sensors must be mounted in a suitably designed head, meeting the required approval standards of the relevant safety bodies.

CiTipeLs should be protected from exposure to concentrations of silicones, chlorinated hydrocarbons, and compounds containing lead or sulphur, all of which can cause an irreversible decrease in sensitivity. Similarly, halogenated hydrocarbons may temporarily inhibit sensor performance, and should also be avoided.

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## **Storage**

Any area used to store CiTipeLs should be free from catalytic poisons

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## **Disposal**

CiTipeLs should be disposed of in accordance with guidelines laid down by any relevant safety bodies as well as in accordance with local regulations.

# Warranty

## Statement of Warranty

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Unless stated otherwise on the data sheet, City Technology products are warranted for a period of 12 months from date of despatch, against defects in workmanship, materials, and construction. A credit note will be raised against the appropriate account where a sensor has failed within these criteria. A summary of the procedure for Handling of Warranty Failures is set out below.

## Warranty Failures

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The Quality Department has computerised the handling and control of warranty failures. Part of this process requires the support of our customers in implementing the following guidelines:

1. Should a product fail to meet the performance requirements set out in this handbook or exhibit other defects please contact in the first instance, a member of City Technology's technical staff or the Quality Returns Technician.
2. Subject to a discussion with CTL staff, return of sensors to CTL for evaluation may be authorised. Receipt of sensors by CTL is not an admission of liability.
3. Once a warranty failure is received at City Technology, a unique reference number will be issued and an acknowledgement containing this number will be faxed within 24 hours. Thereafter the defect is fully investigated and reported on to the customer by letter with, where appropriate, a credit note for the defective product.
4. The sensing and referencing electrodes of biased operation CiTiceLs must not be shorted together when returned. **All other** toxic gas CiTiceL types must have their sensing and reference electrodes shorted out.
5. Please identify clearly why each sensor failed **or** why it is being returned. Only those within the warranty period should be despatched.
6. Please wrap each sensor individually to prevent any damage in transit. This is most important because failure to protect each cell may cause damage to the critical capillary mechanism during transit.
7. Products containing PCB interface electronics should be stored and transported in antistatic bags.
8. When returning goods under warranty all accompanying documentation should clearly state that they are defective goods and of 'no commercial value'.



## Connection to Sensors

### Connection to Sensors with PCB Pins

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**Under no circumstances** should 7-Series CiTiceL pins be soldered to, as this can cause leakage of electrolyte. Connection should be made via a PCB mounting socket. **WARNING: SOLDERING TO PINS WILL RENDER YOUR WARRANTY VOID.**

Details of recommended sockets are given below:-

Supplier:

**Wearnes Cambion Ltd.**

Peveril House

Mill Bridge

Castleton

Hope Valley

S33 8WR

Tel: +44 1433 621555

Fax: +44 1433 621290

e-mail: [cambionsales@cambion.co.uk](mailto:cambionsales@cambion.co.uk)

<http://www.cambion.co.uk>

Suggested part, order code:

450-5301-01-xx-00

(where 'xx' is the finish of the sockets)



## CiTiceL Colour Coding

### Colour Coding for Toxic Gas CiTiceLs

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All 7-Series Toxic Gas CiTiceLs can be identified by a coloured band. The colour of this band denotes the gas measured, with a different colour used for each gas. This additional feature allows easier identification of the sensors without affecting the performance characteristics or overall dimensions of the sensors.

The full range of colours are as follows:

Carbon monoxide (CO)	-	Red
Hydrogen sulphide (H <sub>2</sub> S)	-	Dark blue
Sulphur dioxide (SO <sub>2</sub> )	-	Green
Nitric oxide (NO)	-	Orange
Nitrogen dioxide (NO <sub>2</sub> )	-	Black
Chlorine (Cl <sub>2</sub> )	-	Brown
Hydrogen (H <sub>2</sub> )	-	Yellow
Hydrogen cyanide (HCN)	-	Light blue
Ammonia (NH <sub>3</sub> )	-	Purple
Ethylene oxide (C <sub>2</sub> H <sub>4</sub> O)	-	Aqua blue

## CiTiceL Handling

Toxic Gas CiTiceLs have a rugged design and are relatively insensitive to mishandling. Following these few simple guidelines will ensure correct operation in service:

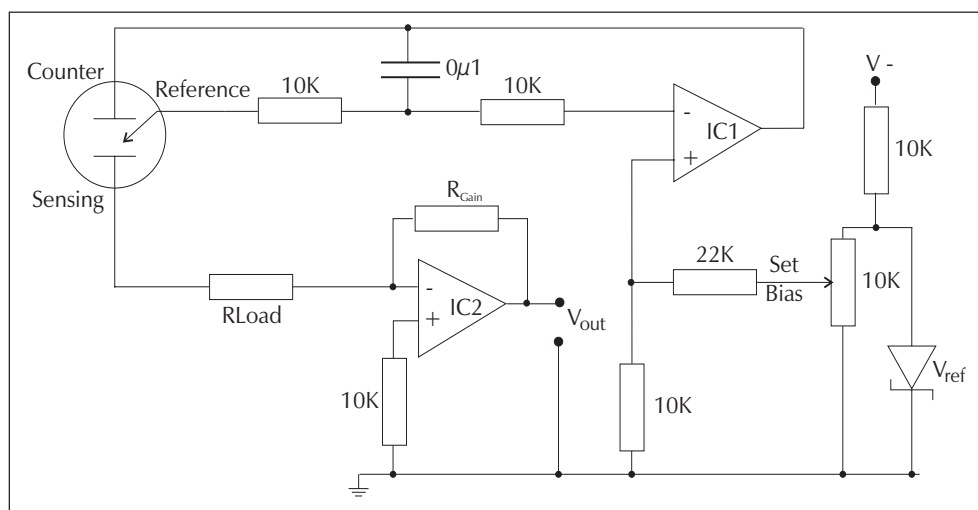
1. The CiTiceL must not be subjected to any pressure when clamping or handling.
2. The protective mesh should not be removed, and the underside cover-slip (where present) and capillary region must not be poked or prodded.
3. The CiTiceL contains a small volume of strong mineral acid. In the unlikely event of a leak, the contaminated parts should be rapidly and thoroughly rinsed in water.
4. Do not use glue directly on or near the CiTiceL as the solvent will cause crazing of the plastic and damage to the electrodes can result from high concentrations of solvent vapours.
5. CiTiceLs must not be stored or assembled in areas which contain solvent vapours. This includes aerosols used in the environment such as air-freshener, wax polish, window cleaner and all organic solvents. Formaldehyde, for example, is known to temporarily inhibit the operation of nitric oxide sensors. Other solvents are known to create false high baselines and in some cases may damage the electrodes. When using sensors with printed circuit boards, degreasing agents in particular should be avoided.
6. Sensors in which the PTFE membrane is clearly visible must not be stacked on top of each other as the capillary region is particularly susceptible to damage from PCB pins.
7. Never solder connections directly on to gold PCB pins of a CiTiceL
8. If for any reason a sensor is removed from its PCB, care must be taken not to bend the pin connections.

## Biased Operation of 7H Sensors

The rate at which chemical reactions proceed can usually be increased by adding energy to the reactants. For most chemical reactions this can be achieved in one of two ways, either by raising the temperature or increasing the pressure at which the reaction takes place. In an electrochemical cell, where for example  $H_2S$  is oxidised electrochemically, there is a third option, namely applying a **bias potential**.

To apply a bias voltage to a three electrode sensor the following circuit is required.

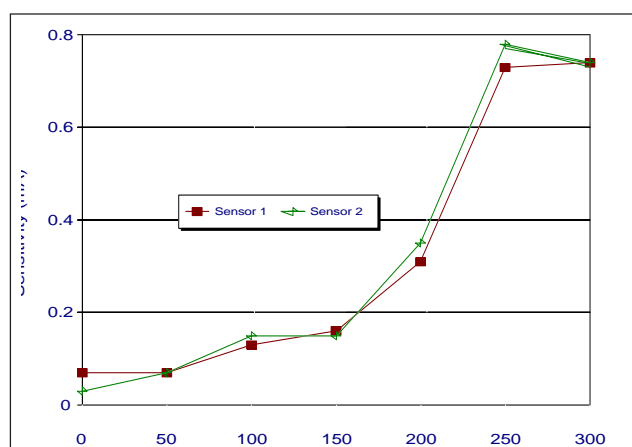
**Figure AP9.1**  
Recommended circuit for  
'biased' CiTiceL operation



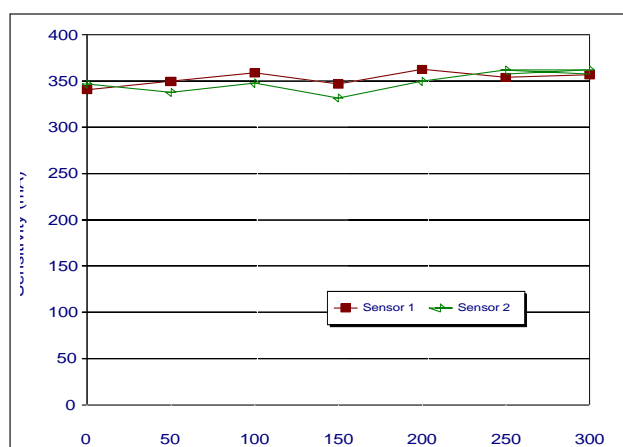
For further details on this circuitry please refer to the circuitry notes in the Operating Instructions section.

The performance characteristics of 7H  $H_2S$  CiTiceLs were studied when bias voltages between 0 and +300 mV were applied. At each increase in bias, the baseline, sensitivity, response time, and cross sensitivity to a range of gases was measured for each sensor tested. The results of these measurements are shown in figures AP9.2 to AP9.5.

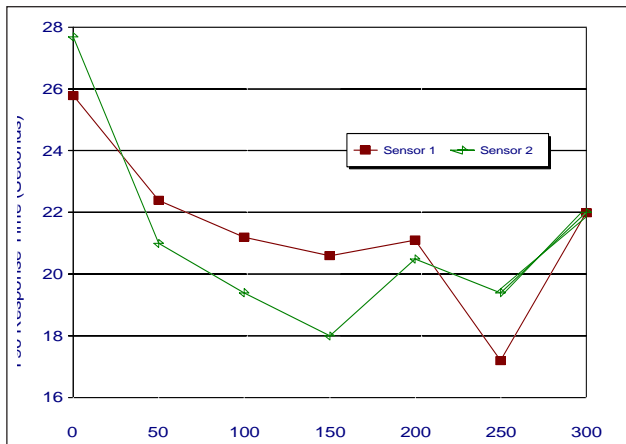
**Figure AP9.2**  
Baseline vs Bias



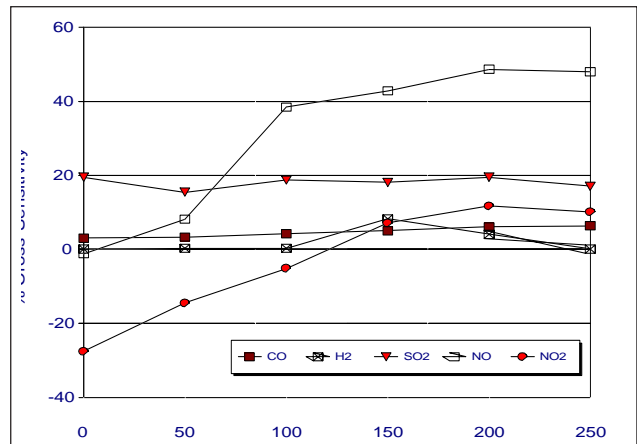
**Figure AP9.3**  
Sensitivity vs Bias



**FigureAP4.**  
Response Time vs Bias



**FigureAP5.**  
Cross Sensitivity vs Bias



## Summary

### Response Time:

On examining the data obtained, it is clear that one of the main advantages to be gained by running the sensor at bias is the response time is faster. At 250mV bias  $T_{90}$  response times below 20 seconds were observed for both sensors tested.

### Sensitivity:

The overall sensitivity to H<sub>2</sub>S showed no significant variation with bias potential.

### Baseline:

As expected, sensor baselines showed an increase as the bias potential was increased. The steady state baselines were recorded once the sensors had settled as the application or change of a bias potential causes rapidly decreasing baselines.

### Cross-sensitivity:

It is interesting to note that the NO<sub>2</sub> response is negative below 170mV and positive above. The other significant variation is in the NO response which becomes more appreciable as the bias potential is increased.