为什么要用以空气作背景气的标准气校验电化学毒气传感器？

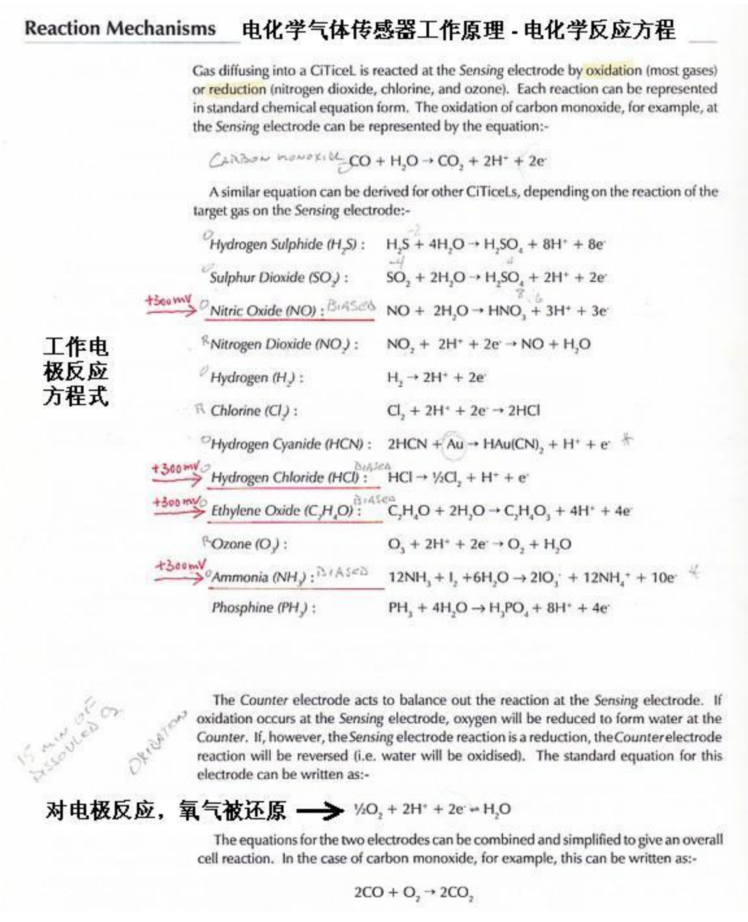
1）用于标定和测量电化学传感器的标准气必须用空气作背景气（或称余气）。如果用以氮气作背景气的标准气则会产生误差和影响传感器正常工作。其原因是，电化学传感器内部的对电极上发生耗氧的还原反应，需要电解液中有氧气参与反应（见下表，主流电化学毒气传感器反应方程式）。空气的主要成份是 21%氧气和 79%氮气。如果用以氮气作背景气的标准气，因为标准气中的氧气偏压为零，当此标准气通过传感器时会将传感器内部电解液中的氧逐渐吸走，使传感器不能正常工作。

2）国际上通行的要求是电化学传感器须使用以空气作背景气的标准气（二氧化氮、氯气、臭氧三个氧化性气体除外）。早前传统的毒气探测报警器使用半导体传感器，不要求标准气以空气作背景气，故普遍使用以氮气作背景气的标准气，这种习惯在有些国家沿用至今，是不正确的。**参见国外标准机构对使用电化学毒气传感器要求使用以空气作为背景气（见图 2-4）**

3）有毒气体报警器真正工作时是用于检测环境中的毒气（即空气气氛中的毒气），而不是纯氮气中的毒气。所以，用以空气作背景气的标准气进行标定和测量也更接近实际应用情况。

4）即使用以氮气作背景气的标准气进行标定、测量时没发现误差，也不能保证在真正应用场合下（是在空气气氛中测量）的测量是准确无误的。

图 1、电化学毒气传感器的电极反应



Reaction Mechanisms　电化学气体传感器工作原理 - 电化学反应方程

Gas diffusing into a CiTiceL is reacted at the *Sensing* electrode by oxidation (most gases) or reduction (nitrogen dioxide, chlorine, and ozone). Each reaction can be represented in standard chemical equation form. The oxidation of carbon monoxide, for example, at the *Sensing* electrode can be represented by the equation:-

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

A similar equation can be derived for other CiTiceLs, depending on the reaction of the target gas on the *Sensing* electrode:-

工作电极反应方程式

Hydrogen Sulphide (H_2S) :	$H_2S + 4H_2O \rightarrow H_2SO_4 + 8H^+ + 8e^-$
Sulphur Dioxide (SO_2) :	$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$
Nitric Oxide (NO) :	$NO + 2H_2O \rightarrow HNO_3 + 3H^+ + 3e^-$
Nitrogen Dioxide (NO_2) :	$NO_2 + 2H^+ + 2e^- \rightarrow NO + H_2O$
Hydrogen (H_2) :	$H_2 \rightarrow 2H^+ + 2e^-$
Chlorine (Cl_2) :	$Cl_2 + 2H^+ + 2e^- \rightarrow 2HCl$
Hydrogen Cyanide (HCN) :	$2HCN + Au \rightarrow HAu(CN)_2 + H^+ + e^-$
Hydrogen Chloride (HCl) :	$HCl \rightarrow \frac{1}{2}Cl_2 + H^+ + e^-$
Ethylene Oxide (C_2H_4O) :	$C_2H_4O + 2H_2O \rightarrow C_2H_4O_3 + 4H^+ + 4e^-$
Ozone (O_3) :	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$
Ammonia (NH_3) :	$12NH_3 + I_2 + 6H_2O \rightarrow 2IO_3^- + 12NH_4^+ + 10e^-$
Phosphine (PH_3) :	$PH_3 + 4H_2O \rightarrow H_3PO_4 + 8H^+ + 4e^-$

The *Counter* electrode acts to balance out the reaction at the *Sensing* electrode. If oxidation occurs at the *Sensing* electrode, oxygen will be reduced to form water at the *Counter*. If, however, the *Sensing* electrode reaction is a reduction, the *Counter* electrode reaction will be reversed (i.e. water will be oxidised). The standard equation for this electrode can be written as:-

对电极反应，氧气被还原 → $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

The equations for the two electrodes can be combined and simplified to give an overall cell reaction. In the case of carbon monoxide, for example, this can be written as:-

$$2CO + O_2 \rightarrow 2CO_2$$

图 2、加拿大国家标准对便携式毒气探测仪的标准气要求以空气作背景气

National Standard of Canada *CAN/CSA-Z433-M92*

Portable Gas Monitors

Prepared by
Canadian Standards Association

6.9 Step Change Response

以空气为背景气的标准气

6.9.1 Toxic Gases

Beginning with the gas instrument in clean air, it shall be suddenly exposed to a prepared mixture of gas in air having a concentration corresponding to the initial calibration gas. From the instant of exposure to this gas mixture, the instrument shall indicate 50% of the gas concentration in less than 10 s, and 90% of the gas concentration in less than 30 s.

Note: *For sample-draw type or manually aspirated type instruments the times specified do not include the transport time required for the gas sample to reach the instrument from a remote sampling point.*

18 *April 1992*

图 3、EXERA 对毒气探测仪的标准气要求以空气作背景气

EXERA

EVALUATION REPORTE3897X08

Publié par l' EXERA, Avril 2008

Index de classification 5.3

VERSION PROJECT

Détecteur de Sulfure d'Hydrogène

6. TESTS METHOD

The values and stabilities of the ambient temperature, the relative humidity and the pressure are measured when testing.

While testing, and apart from special specifications, the following conditions must be respected:

- constant temperature of 2℃ in a range of 15 to 35℃,
- constant relative pressure of ± 10 % in a range of 86 to 108 kPa,
- constant relative humidity of ± 10 % HR in a range of 30 to 70 % HR

用以空气为背景气的硫化氢标准气

6.1. Tests Gas

The reference test gas is hydrogen sulfide (H_2S) at 12 ppm, the sensors chosen having a measure scale of 0-20 ppm.

Except any special condition, the test gases are made of a mix of compressed air and H_2S. The mixes are made with a maximum uncertainty of the concentration of ± 4 % volume.

The tests were performed with the help of a calibration mask provided by the manufacturer. The gas flow is the one of the calibration recommended by the manufacturer.

The gas tests are used dry.

The tests are performed in the following order. Before each test (except the storage non current carrying test), the sensor is tested with the reference test gas
.

6.2. Storage non current carrying

Every part of the device must face successively the following conditions (in air)

- temperature of (–20 ± 2)℃ during 24 hours,
- temperature of (20 ± 5)℃ during at least 24 hours,
- temperature of (40 ± 2)℃ during 24 hours,
- temperature of (20 ± 5)℃ during at least 24 hours.

6.3. Prepairing the material

The devices are calibrated and the alarms are set to 5 ppm and 10 ppm by the manufacturer.

The usual recommendations concerning the periodic calibration are established by the manufacturer. .

图 4、IEC 描述电化学毒气传感器需要氧气参与才能正常工作

IEC

31/696/FDIS

FINAL DRAFT INTERNATIONAL STANDARD
PROJET FINAL DE NORME INTERNATIONALE

	Project number / Numéro de projet: IEC 60079-29-2 Ed. 1.0	
	IEC/TC or SC CEI/CE ou SC: TC 31	Secretariat / Secrétariat: United Kingdom
☒ Submitted for parallel voting in CENELEC / Soumis au vote parallèle au CENELEC	Distributed on / Diffusé le: 2007-05-18	Voting terminates on / Vote clos le: 2007-07-20
Also of interest to the following committees / Intéresse également les comités suivants	Supersedes document / Remplace le document: 31/620/CDV and 31/678/RVC	

Functions concerned / Fonctions concernées

☒ Safety / Sécurité　☐ EMC / CEM　☐ Environment / Environnement　☐ Quality assurance / Assurance de la qualité

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Title
IEC 60079-29-2 Ed. 1.0: Explosive atmospheres - Part 29-2: Gas detectors - Selection, installation, use and maintenance

Titre
CEI 60079-29-2 Ed. 1.0: Atmosphères explosives - Partie 29-2 : Détecteurs de gaz - Sélection, installation, utilisation et maintenance

A.5.1 Common applications

Electrochemical cells are compact, require little power, and have a high sensitivity to certain gases.

Electrochemical cells are not available for detecting most hydrocarbons (for example the alkanes, methane, ethane, propane, etc.)

However, there are a limited number of applications of this type of sensor for explosion prevention. They are suitable for measuring concentrations of hydrogen or carbon monoxide up to the LFL, and oxygen up to 25 % v/v. There are also sensors available for up to 100 % (v/v oxygen).

Additionally, these sensors are commonly used for measuring gas concentrations down to low parts per million levels, for example, in leak detection and personal monitoring for many specific toxic gases (as opposed to vapours), such as H_2S, CO, HCN, NH_3, PH_3, SO_2, NO, NO_2 and ethylene oxide. Although they may be specified for a particular gas, they may detect other interfering gases.

Portable apparatus for the detection of flammable gases, using other types of sensor described in this standard for their 0-100 % LFL ranges, frequently have such electrochemical toxic gas sensors and electrochemical oxygen sensors fitted in a multi-gas configuration.

A.5.2 Limitations

Temporary, loss of sensitivity occurs in moving a cold sensor of this type into a warmer high humidity situation due to water condensing on the membrane, partially blocking it. This is particularly noticeable on oxygen sensors where a normal reading of just under 21 % can drop for this reason and give an alarm for a few minutes. Contamination by non-volatile liquids or adhesive solids can hav

电化学毒气传感器需要氧气参与电化学反应。溶解于电解质中的氧只能支持短时间，因此要在无氧的环境下延长操作时间是不可能的。

Dependent on the sensor, oxygen may be required for the electrochemical reaction. In such cases dissolved oxygen in the electrolyte will last for short periods, but prolonged operation in oxygen-free situations is not possible.

The electrolyte or one or more of the electrodes will usually limit the life of the sensor. The sensitivity will usually fall with time, requiring periodic recalibration or response checking.

Dependent on the type of sensor and the gas to be measured, the sensor may have a shortened life or a drop in response due to an overload of gas. This can happen particularly with oxygen sensors used in high oxygen concentrations, where a lead electrode is consumed proportionally to the oxygen exposure.