
**Gas analysis — Preparation of calibration
gas mixtures using dynamic volumetric
methods —**

Part 11:
Electrochemical generation

*Analyse des gaz — Préparation des mélanges de gaz pour étalonnage
à l'aide de méthodes volumétriques dynamiques —*

Partie 11: Génération électrochimique



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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 6145-11 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

ISO 6145 consists of the following parts, under the general title *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods*:

- *Part 1: Methods of calibration*
- *Part 2: Volumetric pumps*
- *Part 4: Continuous syringe injection method*
- *Part 5: Capillary calibration devices*
- *Part 6: Critical orifices*
- *Part 7: Thermal mass-flow controllers*
- *Part 8: Diffusion method*
- *Part 9: Saturation method*
- *Part 10: Permeation method*
- *Part 11: Electrochemical generation*

Part 3 to ISO 6145, entitled *Periodic injections into a flowing gas stream*, has been withdrawn by Technical Committee ISO/TC 158, *Analysis of gases*.

Introduction

This part of ISO 6145 is one of a series of standards dealing with the various dynamic volumetric methods used for the preparation of calibration gas mixtures.

Electrochemical gas generation can be used to produce calibration gas mixtures containing calibration components which, because of their corrosive nature or low content, are unlikely to be stable in high-pressure cylinders.

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Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods —

Part 11: Electrochemical generation

1 Scope

This part of ISO 6145 specifies a method for the preparation of calibration gas mixtures by using electrochemical generation of a calibration component and introduction into a complementary gas flow. By alteration of the gas flow or the charge passed through the cell electrolyte, it is possible to change the composition of the gas mixture. The relative expanded uncertainty of the calibration gas content, U , obtained by multiplying the relative combined standard uncertainties by a coverage factor, $k = 2$, is not greater than 5 %.

The method described in this part of ISO 6145 is intended to be applied to the preparation of calibration gas mixtures in the volume fraction ranges $(0,1 \text{ to } 250) \times 10^{-6}$.

NOTE 1 Gases that can be produced by electrochemical generation are oxygen (O_2), hydrogen (H_2), hydrogen cyanide (HCN), hydrogen sulfide (H_2S), chlorine (Cl_2), bromine (Br_2), chlorine dioxide (ClO_2), ammonia (NH_3), nitric oxide (NO), nitrogen (N_2), carbon dioxide (CO_2), phosphine (PH_3), arsine (AsH_3) and ozone (O_3).

NOTE 2 The merits of the method are that a stable calibration gas mixture can be quickly prepared within minutes.

NOTE 3 Gas blending systems based on electrochemical generation and thermal mass flow controllers, with the facility of computerization and automatic control, are commercially available. An example is given in Annex A.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*

ISO 6145-7:2001, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers*

3 Procedure

3.1 Principle

Electrochemical gas generation is a fundamental method in which the quantity of the calibration gas component generated is proportional to the charge passed. The proportionality factor is the reciprocal of the Faraday constant [the electrical charge carried by one mole of electrons (or singly charged ions)], which is equal to the product of the Avogadro constant (N_A) and the charge of an electron ($-e$).

$$F = N_A \cdot e \quad (1)$$

where

F is 96 485,341 5 C/mol with a relative uncertainty of $4,0 \times 10^{-8}$ (see References [1], [2] and [3]).

The passage of accurately determined electrical current through a cell determines the gas output provided the conditions given in Clause 5 are applied.

3.2 Complementary gas

The flow rate of complementary gas shall be determined by one of the methods given in ISO 6145-1.

3.3 Electrolytic systems for gas generation

Table 1 lists some examples of gases which can be prepared in quantitative yield by direct electrolysis, using platinum and other electrodes. Also included is an example of the suppression of an unwanted constituent by adsorption on activated carbon surrounding the appropriate electrode.

Table 1 — Electrolysis systems for gas generation

Gas required	Electrolysis system	Gas liberated at other electrode	Yield mole of required gas per charge numerically equal to Faraday number
O ₂ or H ₂	Pt, H ₂ SO ₄ , Pt Pt, K ₂ SO ₄ , Pt Pt, KOH, Pt	H ₂ or O ₂	1/4 (O ₂) 1/2 (H ₂)
O ₂	Pt, H ₂ SO ₄ , Hg ₂ SO ₄ , +C, Hg Pt, neutral solution, active C Pt, KOH, HgO, +C, Hg Pt, KOH, CdO, Cd	nil	1/4
N ₂	Pt, N ₂ H ₄ , H ₂ SO ₄ , Pt	H ₂	1/4
Cl ₂	Pt, NaCl, Pt	H ₂	1/2
CO ₂	Pt, H ₂ C ₂ O ₄ , Pt	H ₂	1
NO	Pt, (NOH)SO ₄ , + H ₂ SO ₄ , Pt ^a	O ₂	1

^a This system has also been used for the generation of nitrogen dioxide [4].

3.4 Apparatus

3.4.1 Cell construction

Cell construction shall be designed to ensure that the generated calibrated component is transferred into the complementary gas stream at maximum efficiency suitable for calibration purposes. Some of the conditions that shall be fulfilled for the operation of an electrolytic cell used for this purpose are given in Clause 5. Examples of electrolytic cells are given in Figures B.1 and B.2.

3.4.2 Current supply and gas flow control

3.4.2.1 The content of the calibration gas produced from the system is dependent on three factors:

- a) the current supplied through the cell which generates a volume flow rate of the calibration gas component;
- b) the (volume) flow rate of the complementary gas; and
- c) the cell efficiency.

NOTE Cell efficiency is the fraction recovery of calibration component over the calculated quantity generated by the current supplied to the cell (see 4.2.3). It depends on the design of the cell. Practical hints on design are given in Clause 5 and an example is given in Annex C.

3.4.2.2 A battery, capable of supplying voltage in the range 0,5 V to 1,0 V, and a milliamperemeter with a measurement range of 0,5 mA to 5,0 mA with an uncertainty of 1,0 %, are suitable. DC generators are an alternative but may pass an AC ripple, which can affect the electrolysis process.

3.4.2.3 A flow measuring unit (e.g. a thermal mass-flow meter) that has been calibrated for the complementary gas between a volume flow rate of 0,2 l/min and 5,0 l/min with an uncertainty of 1 % is suitable.

NOTE Methods for the measurement of the flow rate of the complementary gas are given in ISO 6145-1, which also describes the procedure for calibration of the thermal mass-flow meter.

3.5 Gas mixture preparation

3.5.1 Complementary gas

The calibration gas mixture shall be prepared by passing the chosen complementary gas through the calibrated thermal mass flow controller, set at known flow, through the cell. If the complementary gas is air, the supply to the controller may be managed with a small air pump. Other complementary gases may be chosen by using a regulated supply from a high-pressure cylinder to the controller. The complementary gas shall be allowed to purge out the cell for 2 min and then the cell voltage supply required for the electrolysis shall be switched on.

The purity of the complementary gas shall be established before use, particularly with regard to any impurities that may cross respond or react with the gas being generated. If pumped air is chosen as the complementary gas, then suitable purification shall be used to remove any interfering substances.

3.5.2 Voltage supply

The applied voltage to the cell from the battery shall be slowly increased to the point at which gas bubbles appear at the electrode. The value at that point is termed the decomposition potential. This is the point at which electrolysis occurs and the calibration component is produced at its electrode. The reading of the milliamperemeter is noted when the value has become stable. Decomposition potentials for various electrolytes are given in Table D.1.

Different values of the content of the calibration gas mixture can now be obtained by variation of the flow rate of the complementary gas or the current passed through the cell. It would be advisable to select that parameter which is nearest to the middle of its range.

3.5.3 Calculation of gas mixture content

The volume fraction of the calibration component, φ_A , in the calibration gas mixture is calculated from the relation:

$$\varphi_A = \frac{q_A}{q_A + q_B} \quad (2)$$

in which q_A and q_B are the volume flow rates of the calibration component and the complementary gas, respectively.

The contribution of the calibration component may be neglected in consideration with the flow of the complementary gas, in which case Equation (2) will become:

$$\varphi_A = \frac{q_A}{q_B} \quad (3)$$

q_A is calculated from Equation (4) and q_B is the complementary gas flow rate in millilitres per second (ml/s).

$$q_A = \left(\frac{I \cdot K \cdot V_m}{z \cdot F} \right) \cdot \left(\frac{T_1}{T_R} \right) \quad (4)$$

where

q_A is the calibration gas volume flow rate in millilitres per second (ml/s);

I is electrical current in amperes (A);

V_m is the molar volume of gas generated by the charge numerically equal to the Faraday number in litres per mole (l/mol);

F is the Faraday constant (see 3.1; 96 485,341 5 C/mol);

z is the number of electron charges carried by one ion;

T_1 is the temperature of the cell, usually ambient;

T_R is the reference temperature, usually 273,15 K.

K is dimensionless factor determined by cell efficiency and electrolysis reaction (see Table 1), usually delivered by the manufacturer or determined by experiment.

Equation (4) is based on the following:

$$n = \frac{Q}{z \cdot F} = \frac{I \cdot t}{z \cdot F} \quad (4a)$$

where

n is the amount of substance in moles (mol);

Q is the electric charge in coulombs (C);

t is the time in seconds (s).

$$I \cdot t = Q = n \cdot z \cdot F = \frac{V}{V_m} \cdot z \cdot F \quad (4b)$$

where

V is the volume of generated gas in litres (l);

V_m is the molar volume of gas generated by the charge numerically equal to the Faraday number in litres per mole (l/mol).

$$q \approx \frac{V}{t} = I \cdot V_m \cdot \frac{1}{z \cdot F} \quad (4c)$$

Including a dimensionless factor K [determined by cell efficiency and electrolysis reaction (see Table 1; usually delivered by the manufacturer or determined by experiments)] and a temperature correction factor results in Equation (4).

EXAMPLE

In the production of a bromine mixture in nitrogen gas, the following data were obtained.

- 1) Electrolyte was 1 mol/l zinc bromide solution in water with platinum electrodes.
- 2) Decomposition potential, V_d , was 1,81 V. (See NOTE 1 below.)
- 3) Electrical current, I , passed through cell, was 0,1 mA.
- 4) Ambient temperature / cell temperature was set at 20 °C, reference temperature, T_R , was 0 °C.

Calculation of the volume flow rate of the calibration component, q_A (cell electrolysis): Bromine is diatomic, therefore $z = 2$. The cell efficiency factor, K , is 0,998. With Equation (4), q_A is given by:

$$\begin{aligned} q_A &= \left(\frac{0,1 \text{ mA} \times 22,4 \text{ l/mol} \times 0,998}{2 \times 96\,485,34 \text{ As/mol}} \right) \times \left(\frac{293,15 \text{ K}}{273,15 \text{ K}} \right) \\ &= \left(\frac{0,1 \times 10^{-3} \times 22,4 \text{ l} \times 0,998}{2 \times 96\,485,34 \text{ s}} \right) \times \left(\frac{293,15}{273,15} \right) \\ &= 12,5 \times 10^{-9} \text{ l/s} = 12,5 \times 10^{-6} \text{ ml/s} \end{aligned}$$

The complementary gas flow rate, q_B , measured by a thermal mass-flow controller is 5 l/h = 5 000 ml/3 600 s = 1,39 ml/s.

Using Equation (3), the volume fraction, φ_A , of calibration gas in the mixture is given by:

$$\varphi_A = \frac{q_A}{q_B} = \frac{12,5 \times 10^{-6} \text{ ml/s}}{1,39 \text{ ml/s}} = 8,99 \times 10^{-6}$$

NOTE 1 Strictly speaking, the voltage across the cell, measured by the voltmeter V_d , is greater than the decomposition potential by the quantity $I \cdot R$, where I is the current flowing in amperes and R is the resistance in ohms. However, since I is very small and R is not very large, the quantity $I \cdot R$ may be neglected, and the voltage measured on V_d , although marginally larger by 0,1 %, taken as the decomposition potential.

NOTE 2 Verification of the final calibration gas mixture may be carried out by reference to a standard mixture prepared by a national body, using the comparison method given in ISO 6143. This procedure also identifies bias from other sources and establishes traceability against standard mixtures.

NOTE 3 Verification of the calibration mixture may be carried out by some analytical procedure. For example, a determined volume of the gas mixture may be absorbed in a suitable solution and the bromine content determined by volumetric titration. If the results of this procedure are used to assign volume fraction or mass concentration values to the calibration gas mixture, then the uncertainty of the analysis should be included as part of the overall uncertainty assessment.

4 Uncertainty evaluation

4.1 Introduction

The volume fraction of the calibration component, φ_A , in the calibration gas mixture is given in Equation (2):

$$\varphi_A = q_A / (q_A + q_B) \quad (5)$$

in which q_A and q_B are the volume flow rates of the calibration component and the complementary gas, respectively.

4.2 Sources of uncertainty

4.2.1 Complementary gas flow

When the flow rate of the complementary gas is measured by a method given in ISO 6145-1, due consideration shall be given to the uncertainty associated with the method. The thermal mass flow controller is one of the types of apparatus recommended to control the complementary gas flow into the cell. Details of its use for preparation of calibration gas mixtures are given in ISO 6145-7, but in the method described in this part of ISO 6145 only one controller is used. A suitable controller shall be provided with temperature and pressure compensation. The relative expanded uncertainty quoted with this method is < 1 %.

4.2.2 Gas generation

Electrochemical gas generation is controlled by the current fed through the cell. A certified milliamperemeter calibrated to 1 % of reading is suitable.

4.2.3 Absorption of generated gas in the cell electrolyte

The gas generated in an electrolyte shall be separated from the electrolyte prior to mixing with the complementary gas. This is the largest potential error contribution to cell efficiency. If not properly designed, a portion of the desired gas may escape to the bulk electrolyte instead of exiting into the mixing chamber. To prevent this, the electrolyte is generally separated from the mixing chamber by use of a semi-permeable membrane. Analytical checks shall be carried out on the gas mixture generated to assess cell efficiency. Cell efficiency, measured by analysis of the cell output against that calculated from the current flow, shall be more than 97 %.

4.2.4 Effect of moisture content

Most of the electrolytes are hygroscopic, and they will lose or gain water depending on the humidity of the complementary gas stream. Corrections for a very dry or wet complementary gas can be measured, but their effect on the uncertainty may be regarded as very much less than ± 1 %.

4.2.5 Effect of temperature

Both complementary and generated gases run at the same temperature through the cell. This temperature shall be measured to evaluate the quantity of generated gas in Equation (4). There will be a source of uncertainty in this measurement.

4.2.6 Purity of electrolytic chemicals

Impurities in the chemicals used to make the electrolytes for gas generation can introduce interfering substances during electrolysis. Chemicals used to prepare electrolytes shall be of the highest purities to avoid such effects. There will be a source of uncertainty from this effect if impure chemicals are employed.

4.2.7 Impurities in complementary gas

Impurities in the complementary gas which may respond or react with the generated gas component shall be considered as a source of uncertainty.

4.3 Uncertainty of volume fraction

The uncertainties in the volume fraction of the minor component in the calibration gas mixture, at constant temperature and pressure, can be estimated from the separate uncertainties in the flow rate of the complementary gas and the gas generation from the electrolytic cell (see NOTE 3 under 3.5.3).

The volume fraction of component A is given by Equation (1).

The relative expanded uncertainty in φ_A is then given by:

$$\frac{U(\varphi_A)}{\varphi_A} = \left[\frac{2q_B}{q_A + q_B} \right] \left[\left(\frac{u(q_A)}{q_A} \right)^2 + \left(\frac{u(q_B)}{q_B} \right)^2 \right]^{1/2} \quad (6)$$

$$\left[\frac{u(q_A)}{q_A} \right]^2 = \left[\frac{1}{I \cdot K \cdot T_1} \right]^2 \left[(K \cdot T_1)^2 u^2(I) + (I \cdot T_1)^2 u^2(K) + (I \cdot K)^2 u^2(T_1) \right] \quad (7)$$

The derivation of this formula is given in Annex C of ISO 6145-7:2001. The r.m.s. (root mean square) sum of the standard uncertainty contributions is multiplied by the coverage factor $k = 2$ to give a relative expanded uncertainty based on a level of confidence of approximately (95 %).

The standard uncertainty of $u(q_A)$ is derived from the standard uncertainties of the electrolysis process.

The standard uncertainty $u(q_B)$ in the flow rate of the complementary gas is obtained with reference to ISO 6145-1 for the selected method of flow calibration. (See NOTE 3 under 3.5.3.)

This estimate of the relative uncertainty in the composition rests entirely on the uncertainties in the measurements of flow rates. Other factors to be taken into account include the efficiency of mixing. To check the effectiveness of a mixing system to provide a homogeneous calibration gas mixture, mixtures shall be prepared by the method as described and the compositions shall be checked by the comparison method, ISO 6143. This procedure also identifies bias from other sources and establishes traceability against standard mixtures.

5 Electrochemical cell design

5.1 The materials of the cell shall be chosen with care. The cell body shall withstand both the electrolyte and reaction products, be resistant to the rigors of industrial use and be easily moulded or machined into its final stage.

5.2 The materials used for the electrodes are critical. They shall be able to withstand long term immersion in the chosen electrolyte, be resistant to the oxidation or reduction at the electrode surface, be able to be fabricated into proper shapes for use inside the cell, and be able to carry the current needed to sustain the reaction.

5.3 The efficiency of the electrode and the absence of undesirable secondary reactions should be established. This is a fundamental quality control measure. It has to be carried out for each different reaction on an individual basis.

5.4 The desired content of the calibration component sought shall be obtained without applying an excessive current or voltage. For example, when carbon dioxide is produced by the electrolysis of oxalic acid solution, oxygen may also form at the anode if a critical value of the current is exceeded. Better voltage

control can be achieved on the working electrode itself with a three-electrode system including a reference electrode (see Reference [5]).

5.5 Any unwanted gas liberated at the other electrode shall be excluded from the calibration system. This is essential in cases where the gaseous products may recombine before reaching the measuring system.

5.6 The generation of the calibration component shall be obtained rapidly and the gas produced shall be quickly and completely displaced on terminating the electrolysis; precautions may be necessary to ensure the gas is at ambient temperature.

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Annex A (informative)

Example of a commercial electrochemical cell

A.1 Electrolyte

An electrochemical device currently available is designed for the generation of chlorine for introduction into a complementary gas. The electrolyte is an acidified (HCl) solution of lithium chloride (approximately 5 mol/l) with a minor component of copper chloride (approximately 0,1 mol/l) in water.

NOTE The copper provides colour to the electrolyte.

A.2 Electrodes and cell materials

The active electrode is a dimensionally stable anode (DSA) manufactured from ruthenium oxide coated onto titanium plate. The counter electrode is a fine platinum wire. The body materials are polycarbonate with PTFE membranes heat sealed to the polycarbonate to provide venting of any hydrogen gas produced on the counter electrode. Another PTFE membrane is used to separate the electrolyte in the main body from a mixing chamber where the generated chlorine is swept away by the complementary gas. The chlorine gas is produced in close proximity to the mixing chamber membrane so that the majority of the chlorine is transferred to the complementary gas, resulting in a highly efficient cell.

A.3 Electronics/ranges

The main circuit board of the instrument provides temperature-compensated current to the generating cell over a range of 0,035 mA to 3,59 mA (standard range) or 0,003 5 mA to 0,075 mA (microrange) and is calibrated against a certified standard with a measurement uncertainty of less than 1 %.

A.4 Flow control/ranges

Flow of the complementary gas is provided by a small micro pump (for air) and is regulated via a mass flow sensor built into the instrument. The mass flow sensor has a range from 0 l/min to 6 l/min and is calibrated against a certified standard with a measurement uncertainty of 1 %. Both the current and the complementary gas flow can be controlled by the microprocessor via a digital display to provide an output range of $(0,5 \text{ to } 50) \times 10^{-6}$ volume fraction (standard range) and $(0,05 \text{ to } 1) \times 10^{-6}$ volume fraction (micro-range) at 0,5 l/min.

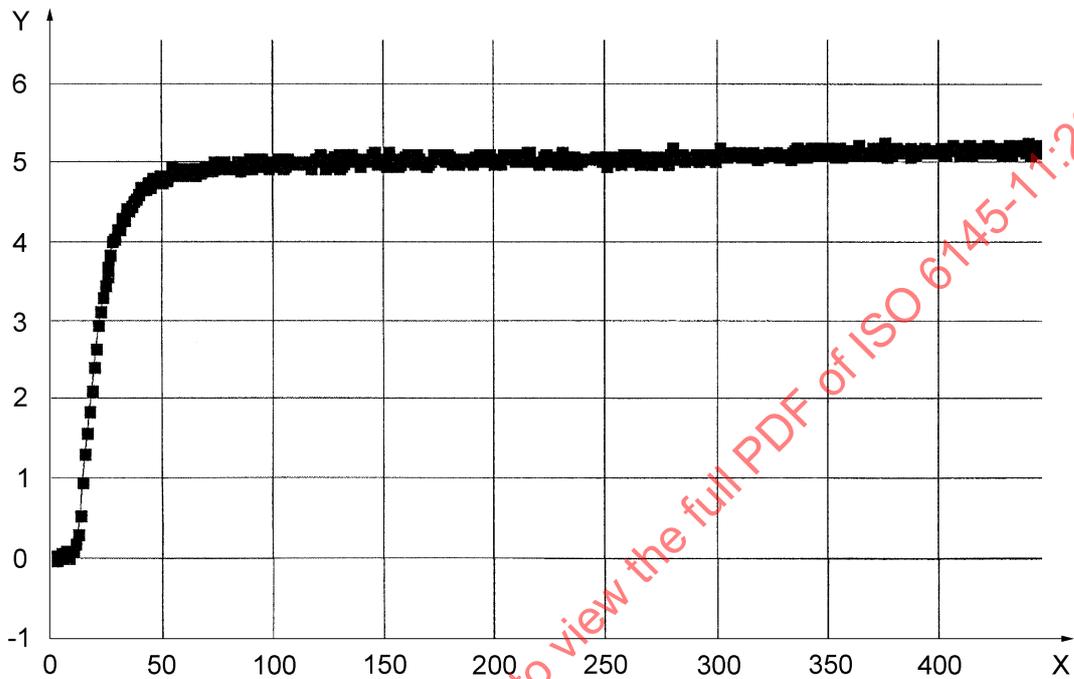
The ranges are linearly related to flow, which can be adjusted from 0,2 l/min to 1 l/min with the internal pump and 0 l/min to 3 l/min using the external pump. This gives an overall range of $(0,1 \text{ to } 250) \times 10^{-6}$ volume fraction (standard range) and $(0,01 \text{ to } 5) \times 10^{-6}$ volume fraction (microrange) over the entire flow range of 0,1 l/min to 3 l/min.

A.5 Cell parameters

The electrochemical cell will generate approximately 50 l of gas at maximum current on one filling of electrolyte. The entire unit, cell, pump, mass flow sensor, batteries, control panel and microprocessor is field usable weighing approximately 1,5 kg. Four "C" size batteries or a 9 V DC continuous operations adaptor is

used to supply the current. The typical equilibrium time for the device is approximately 5 min to achieve higher than 90 % of the desired output.

Figure A.1 shows the performance of an electrochemical cell in the generation of a gas mixture containing chlorine as a calibration component. The cell has reached > 90 % of its desired content in less than 2 min and then remains stable at the 5×10^{-6} volume fraction level after 4 min. In the example given below for the generation of chlorine at the 5×10^{-6} volume fraction level, the overall measurement uncertainty is < 5 %.



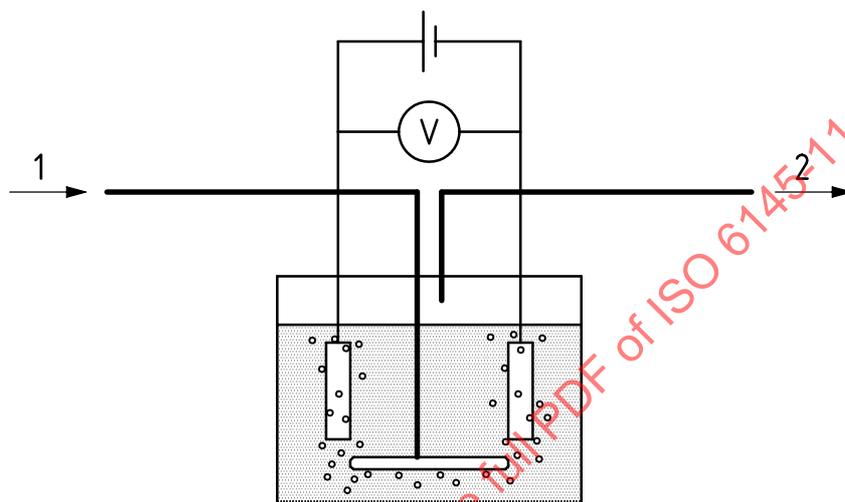
Key
X time, in seconds
Y $\varphi(\text{Cl}_2) \times 10^{-6}$

Figure A.1 — Example of chlorine generation from an electrochemical cell

Annex B (informative)

Schematics of electrolytic cells used for gas generation

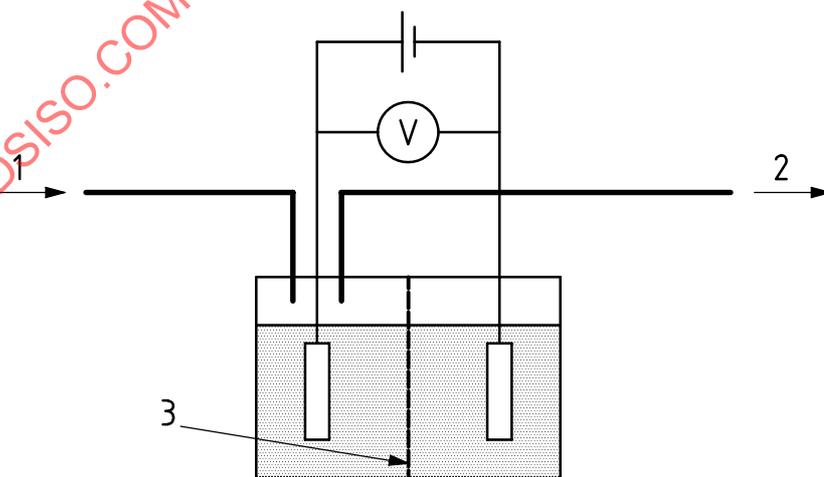
Schematic diagrams of cells are given in Figures B.1 and B.2.



Key

- 1 complementary gas in
- 2 gas mixture out
- V voltmeter

Figure B.1 — Cell with combined gas output, e.g. oxygen calibration unit



Key

- 1 complementary gas in
- 2 gas mixture out
- 3 membrane to avoid mixing of the two solutions
- V voltmeter

Figure B.2 — Cell with single output, e.g. bromine calibration unit