

On the accurate calibration of an electrochemical oxygen meter in the 10^{-7} bar range

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A method for the accurate standardization of an electrochemical oxygen meter, in the $10^{-6} - 10^{-7}$ bar range is described. The method is based on the use of an electrochemical oxygen leak and a chemical getter pump. In this manner problems connected with traces of hydrogen, originating from the pyrolysis of water, and traces of oxygen of unknown origin are overcome.

1. Introduction

The solid state, electrochemical oxygen meter, whose operating principle, is schematically illustrated in Fig. 1, can be employed, for measuring the oxygen partial pressure in inert carrier gases above 10^{-5} bar.

As the electrochemical oxygen meter is a gas concentration cell, its EMF is given, in the most general case, by the equation

$$E = \frac{1}{4F} \int_{\mu'}^{\mu''} t_{O^{2-}} = d\mu_{O_2} \quad (1)$$

(where μ_{O_2} is the chemical potential of oxygen and $t_{O^{2-}}$ is the oxygen transport number of the electrolyte) which reduces, for $t_{O^{2-}}$ constant and equal to one, to the well-known Nernst equation

$$E = \frac{RT}{4F} \ln \frac{P'_{O_2}}{P''_{O_2}} \quad (2)$$

By a suitable choice of the pressure in the reference compartment, which should be known with the best precision possible, one can then determine the oxygen partial pressure in the measuring compartment.

At pressures lower than 10^{-5} bar, although the

oxygen transport number is still constant and equal to one, the use of the oxygen meter is limited due to the fact that the step-response time is known [1] to increase appreciably and the measured EMF to be strongly dependent on the gas flow-rate. These effects originate from:

- oxygen permeability of the electrolyte;
- slow-oxygen reaction rate;
- parasitic reactions at the electrode–electrolyte interface.

While inconveniences coming from the oxygen permeability of the electrolyte could be removed by increasing the gas flow rate, and reducing the temperature while operating the gauge within the ionic conductivity domain (to avoid chemical diffusivity effects in the region of mixed ionic-electronic conductivity), disturbances coming from other origins are more difficult to eliminate and, often, cannot be eliminated at all. It will be shown however that by operating the gauge at 750°C , one realizes the best compromise between high oxygen reaction rates and low oxygen permeability, so that one has only to eliminate the disturbances coming from parasitic reactions, which could be potential-determining[†], in order to achieve the best performance of the gauge.

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† Potential-determining reactions could be the $\text{H}_2/\text{H}_2\text{O}$ reaction

$\text{H}_2\text{O} + 2e \rightleftharpoons \text{H}_2 + \text{O}^{2-}$ (in the electrolyte)

or the CO/CO_2 reaction $\text{CO}_2 + 2e \rightleftharpoons \text{CO} + \text{O}^{2-}$ (in the electrolyte).

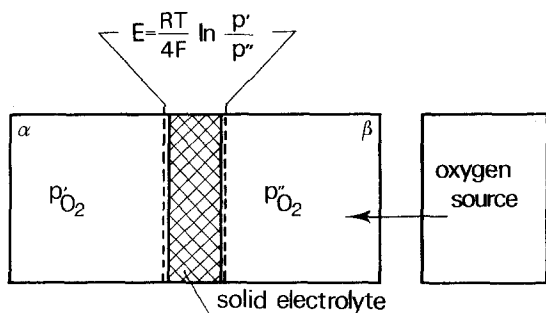


Fig. 1. Schematic drawing of an electrochemical oxygen meter. In the conventional arrangement, the (α) compartment is the measuring one which contains pure oxygen at a pressure P'_O_2 or a suitable gas mixture which buffers the oxygen pressure at the pressure P'_O_2 . The right side (β) compartment is coupled with a suitable oxygen source which maintains the pressure at the value P''_O_2 . In the potentiometric null point method the left-hand side compartment is still the measuring one, while in the right-hand side compartment the partial pressure of oxygen is gradually changed while continuously reading the EMF, when $E = 0$, $P''_O_2 = P'_O_2$.

Independently of whether the gauge is operated in the conventional or in the potentiometric null detector arrangement (see Fig. 1) investigation of these effects is only possible when proper gas mixtures of known oxygen content are available for calibration purposes.

The preparation of standard mixtures in the 10^{-5} – 10^{-8} bar range of partial oxygen pressures could be carried out in principle either by electrochemically removing oxygen from a mixture of known oxygen content [2] or by coulometrically injecting oxygen into an oxygen-free inert gas [2, 3].

The first method suffers an intrinsic kinetic limitation, as it is known that cathodic limiting currents appear when the oxygen content in the gas phase is very low. Eventually, electron injection into the electrolyte occurs when the cell voltage is not carefully controlled, causing the embrittlement of the electrolyte, the onset of electronic conductivity and therefore loss of Faradaic efficiency.

Provided oxygen is generated at 100% efficiency, the only drawback of the second method is the lower detection limit, which depends on the oxygen content left in the inert carrier gas after a suitable deoxidation cycle. Major difficulties could also arise from the presence of reducing impurities in the inert carrier gas (H_2 , CO, volatile organic compounds) which could react with oxygen in the

pump itself, the reaction being catalysed by platinum, which is generally used as the electrode material.

The essential problem to be solved in order to achieve the best performance of the gauge is then the ultimate removal of impurities and oxygen in the inert carrier gas which could be obtained by using a suitable purifying unit.

The aim of this paper is to illustrate and discuss the use of a high efficiency getter pump coupled with an electrochemical pump, which coulometrically generates oxygen in the stream of the purified inert gas, as a standard calibration method for solid-state, electrochemical oxygen meters. It will be demonstrated that accurate measurements of oxygen pressures down to 0.1 ppm can be carried out in spite of previously reported [1] controversial opinions, provided the right getter material is used.

2. Experimental

2.1. Calibration method and procedure

A schematic diagram of the standard experimental set-up is shown in Fig. 2. Ultra-pure He gas for chromatographic use enters the purification unit which is maintained at the operating temperature by means of a suitable temperature controller. The electrochemical oxygen pump and meter are connected in series with the purifier output by stainless steel tubes.

The oxygen purification unit is either a getter purifier, model 101/700 developed by SAES Getter, Milano, or a silica tube filled with zirconium or Ti chips. In this latter case, the entering gas may be previously dried with suitable traps (see later).

The SAES purifier model 101/700 uses as the active material an 84% Zr–16% Al alloy known as St 101 alloy which is already widely employed in U.H.V. applications. Details of the purifier and of its characteristics have been reported elsewhere. [4]. It consists essentially of a double walled stainless steel cylinder containing a cartridge filled with the powdered getter alloy. The relative purification efficiency for various gases is reported in Table 1.

It has been observed that at flow-rates higher than $150 \text{ NI} \cdot \text{h}^{-1}$, the efficiency of the unit

* Normal litre i.e. volume measured at ambient temperature and pressure.

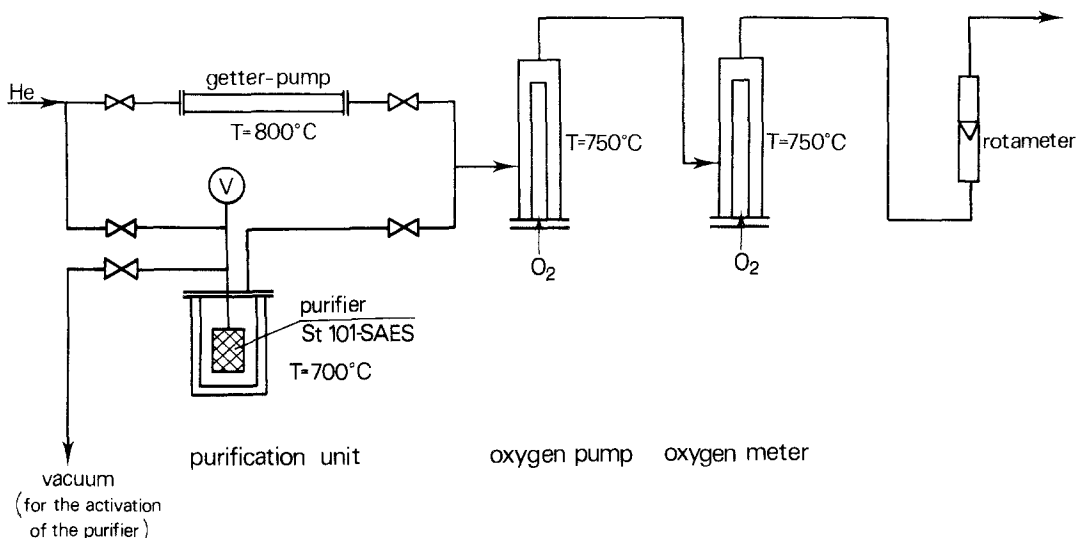


Fig. 2. Schematic diagram of the experimental set-up.

Table 1. SAES 101/700 cartridge. Purification efficiency for various gases referred to efficiency of 100 at 700°C

Temperature (° C)	Purification efficiency					
	CO	CO ₂	CH ₄	N ₂	O ₂	H ₂
25	47	2	0	0	41	0
230	77	73	13	52	52	71
400	87	82	65	73	83	96
500	91	87	78	83	97	112
600	94	93	91	88	99	121
700	100	100	100	100	100	100

decreases considerably, and therefore flow-rates higher than 60 Nl h⁻¹ have never been exceeded in the present work.

Fig. 3 shows the details of the electrochemical pump and of the oxygen meter which were constructed by coupling an YSZ (Yttria Stabilized Zirconia) tube, which serves as the electrolyte, to a brass flange by a proprietary electrowelding technique. The gas to be analysed flows in the annular chamber between the inner wall of a silica bell and the outer wall of the electrolyte tube. The silica tube is also electrowelded to the brass flange. The porous platinum electrodes were prepared by decomposing a Pt paste.

Both the reference electrode compartment of the gauge and the cathode compartment of the pump are continuously fed with air to provide constant pressure conditions. The gauge and pump

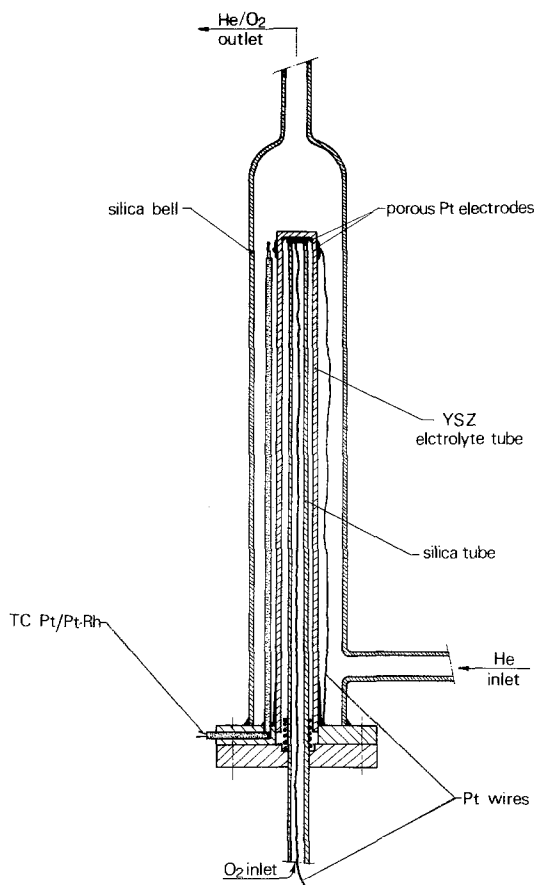


Fig. 3. Section of the electrochemical pump and/or electrochemical oxygen meter.

are heated by a heating coil directly mounted on the outer wall of the silica tube. Care was taken to ensure that the portion of the electrolyte tube covered by the platinum electrodes was in a constant temperature zone. This avoids spurious thermoelectric EMFs and mixed voltages [5].

Both units were maintained at constant temperature by means of a proportional temperature controller. The system is operated as follows. The purifier is activated by heating the getter alloy at 800°C under a rotary pump vacuum. The temperature is reduced to 700°C and the gas is allowed to flow through the purifier and the measuring line by switching the appropriate valves. Both the electrolyser and the oxygen meter are operated at 750°C.

A fixed flow-rate is established and the voltage at the meter output is measured. Oxygen is then introduced coulometrically into the inert gas stream by polarizing the oxygen pump at constant current via a constant d.c. supply: the current is normally varied between 10 μA and 10 mA. The oxygen content of the carrier gas, assuming 100% efficiency (as is the case, considering that the electrolyte works in its purely ionic conductivity

domain) is a function of the flow-rate, ϕ , and of the current according to the equation

$$\text{ppm}_{\text{O}_2} = \frac{208 \cdot 912i \text{ mA}}{\phi \text{ NIh}^{-1}} \quad (3)$$

In the present work the flow-rate has been varied between 12 and 60 NI h^{-1} .

The flow-rate is measured using rotameters, previously calibrated using the soap bubble method. Helium gas was used throughout as other inert gases sometimes caused erratic behaviour of the gauge. Nitrogen could not be used as it is absorbed in the purifying unit.

3. Results and discussion

We report in Fig. 4 typical results of experiments carried out with zirconium chips at 800°C as the getter material. One observes that the EMF read in the absence of any current passing in the oxygen pump ($E_{i=0}$) lies in the range 600–900 mV, the actual voltage depending on the life of the getter material, on the gas flow-rate and on the use of suitable traps for removing water from the gas

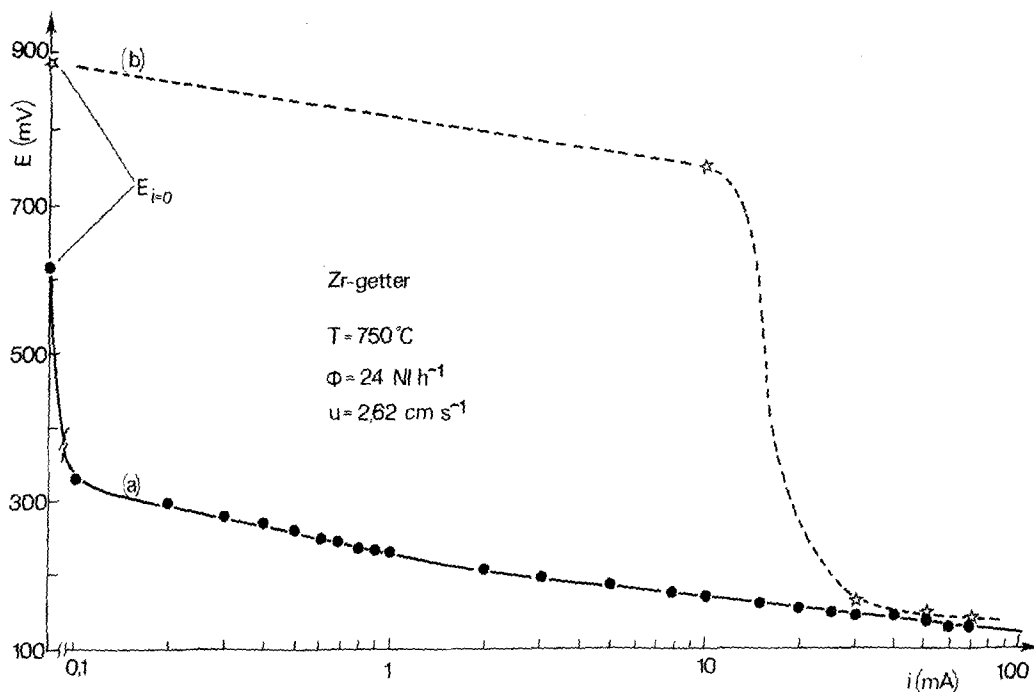


Fig. 4. Calibration of a He/O₂ mixture using Zr as the getter material for the He purification: (a) fresh zirconium chips; (b) zirconium chips after several hours of use. NI = Normal litre i.e. volume measured at ambient temperature and pressure.

mixture. These EMF values indicate a partial pressure of oxygen in the inert gas which lies between $3 \cdot 10^{-13}$ and $3 \cdot 10^{-19}$ bar, respectively.

The results obtained when injecting electrochemically generated oxygen into this mixture indicate however that such a low oxygen potential is not at all controlled by the residual (free) oxygen in the inert gas but is buffered by a chemical equilibrium. In fact a definite excess of oxygen should be introduced into the gas coming from the getter unit before the EMF read at the oxygen meter corresponds to the theoretical voltage calculated according to Equation 3.

As an example, when using fresh zirconium chips as the getter material (see Fig. 4, curve a) the EMF drops close to the theoretical voltage (solid line) when a current in excess of $100 \mu\text{A}$ (corresponding to 0.87 ppm in the experimental conditions chosen) circulates in the oxygen pump. A much larger current is needed (30 mA, corresponding to 260 ppm), when zirconium chips, which

have already been used in several purification cycles, are employed.

Essentially analogous results are obtained (see Fig. 5) when the gas, before entering the zirconium purification unit is passed through a liquid nitrogen trap, and a P_2O_5 and/or a molecular sieve trap for water vapour removal. In this last case, however, a slightly lower excess of oxygen (10 mA instead of 30 mA at about 21 NI h^{-1}) is necessary to get the theoretical oxygen content in the gas phase. Better results are obtained when using the SAES getter, as illustrated in Fig. 5 and Fig. 6.

One observes first (see Fig. 6) that in the absence of any current passing, the EMF read at the oxygen meter ranges between 350 and 240 mV, indicating a partial pressure of oxygen around $2 \cdot 10^{-8}$ and $4 \cdot 10^{-6}$ bar, respectively. Even at the lowest currents passing, moreover, especially at the high flow-rates, one remarks that the experimental EMF values range very close to the theoretical ones.

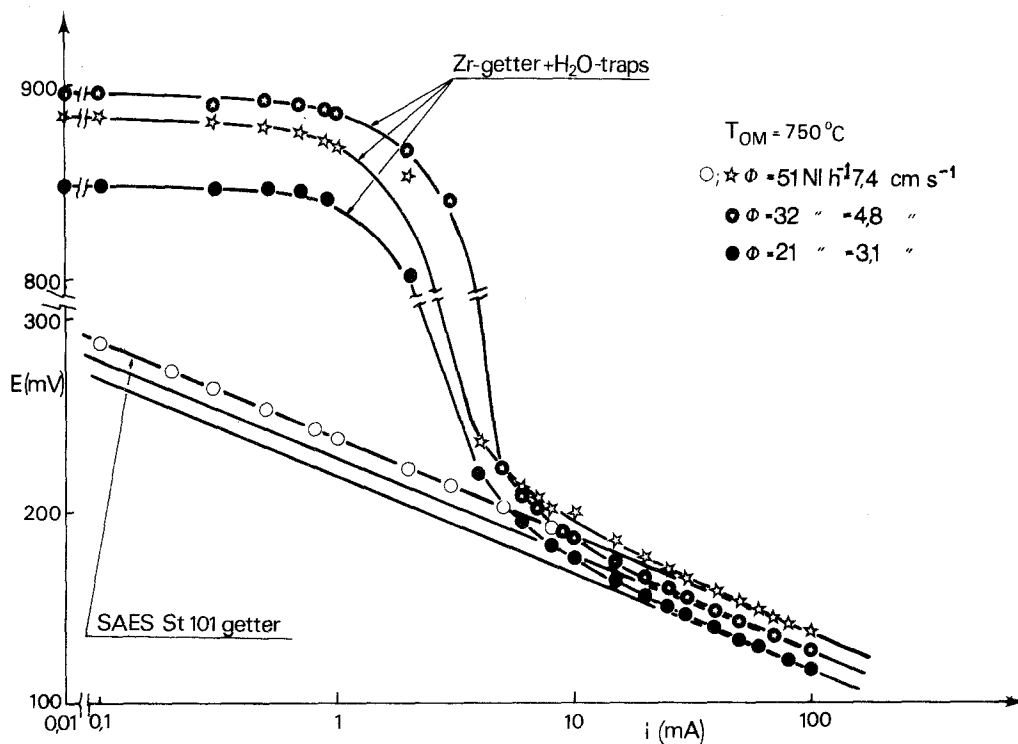


Fig. 5. Comparison between the purification efficiency of zirconium chips and SAES-getter. NI = Normal litre i.e. volume measured at ambient temperature and pressure.

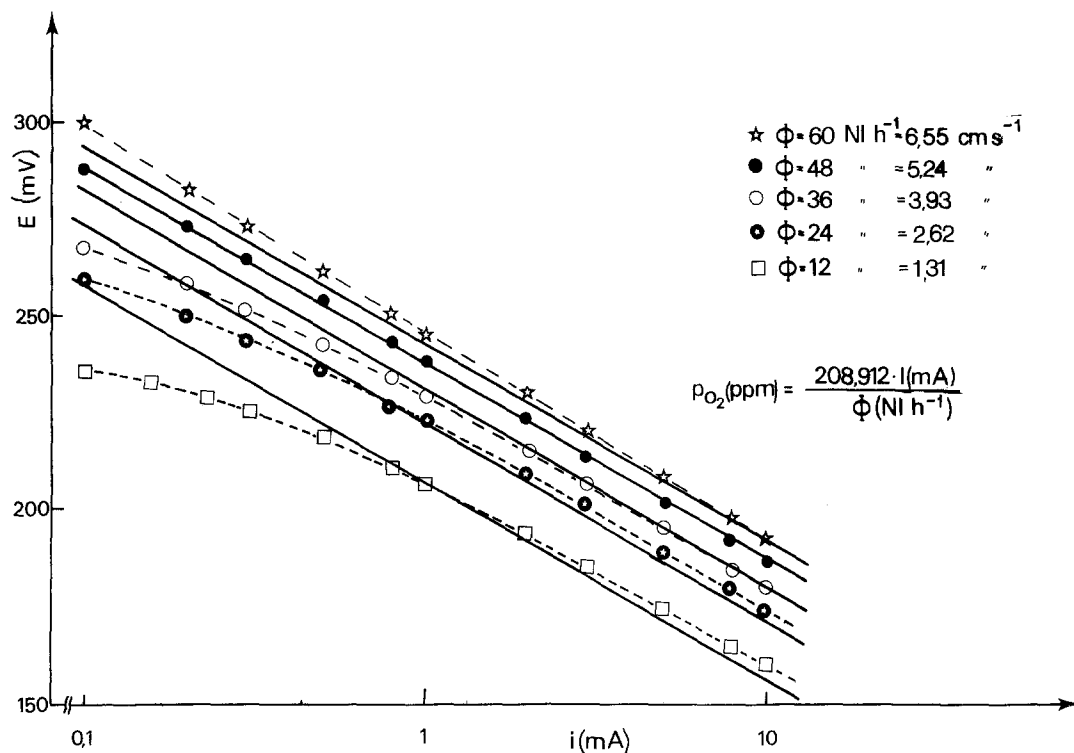
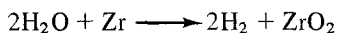


Fig. 6. Calibration of a He/O₂ mixture using SAES-getter as the trap. NI = Normal litre i.e. volume measured at ambient temperature and pressure.

In the best conditions ($u = 5.24 \text{ cm s}^{-1}$ *, $T = 750^\circ \text{C}$) a good agreement is obtained between the theoretical and the experimental EMF still at an oxygen content in the gas mixture of 0.04 ppm.

One could account for the behaviour observed with the zirconium-getter as well as for the influence of life-time on the performance of the getter material, by assuming that a part of the oxygen introduced in the purified gas stream serves for 'titrating' a reducing impurity present in the gas phase. Apparently, the reducing impurity we are concerned with is H₂, coming from water pyrolysis



and it is the system H₂/H₂O which buffers the chemical potential of oxygen in the purified gas.

A similar behaviour has been already observed when injecting oxygen into a benzene-He mixture [6], the benzene being quantitatively oxidized by oxygen which is injected coulometrically into the

* In order to report figures which could be compared with results given by other authors, the flow-rates relative to the most relevant experiments have been reported in Figs. 4-6 in terms of cm s^{-1} units.

mixture, presumably at the oxygen pump electrode surface, which is composed of catalytically active materials (Pt, V₂O₅, V₂O₅ + MoO₃).

The better efficiency and the relative insensitivity of the system to the water content in the inert carrier gas when the SAES-getter is used is accounted for by considering that at any temperature the equilibrium pressure of hydrogen in the gas phase is lower for the St-101 alloy than for pure zirconium. The hydrogen pick-up efficiency is higher for the St-101 alloy up to 700°C, (it would be better still at 600°C, as is shown in Table 1) while it is limited for pure zirconium.

A further limitation to the use of pure, massive or coarse grained zirconium comes from the formation of a surface oxide, which hinders the hydrogen diffusion into the metal.

As in the case of conventional EMF measurements carried out at higher temperatures (see for instance the results of Etsell and Flengas reported in Fig. 7a, which have been carried out on gas at 1000°C) one observes (see Fig. 7b) that at the lowest flow-rates negative deviations from the theoretical voltage are observed. These could be

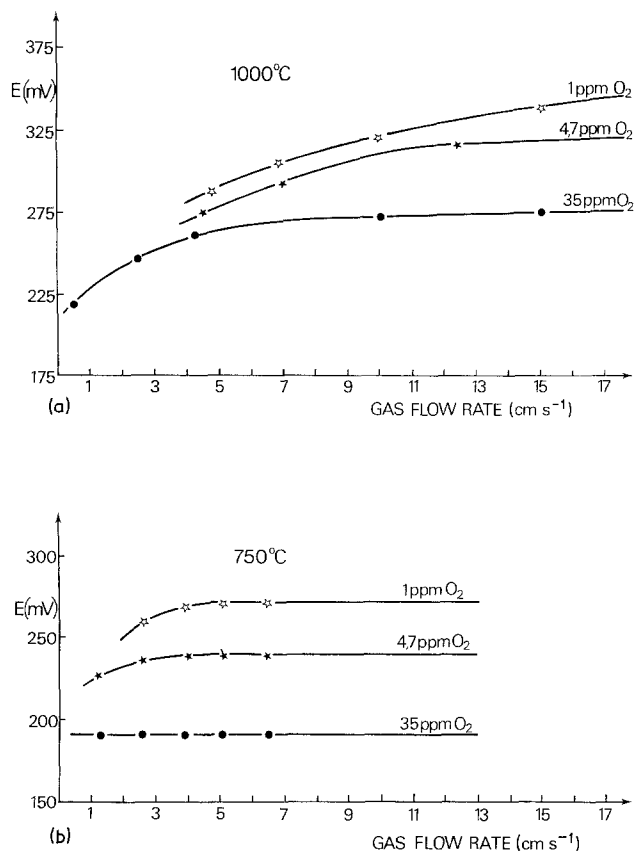


Fig. 7. Flow-rate dependence of cell e.m.f. for He/O₂ mixtures with low oxygen amounts.

interpreted as being due to oxygen permeation from the reference compartment through the electrolyte wall to the measuring compartment. This limits the detection level, at a flow-rate of 1.31 cm s⁻¹, to 10 ppm even when the SAES-getter is used.

It is, however, instructive to compare the results reported in Fig. 7a and b, which show that by reducing the temperature from 1000 to 750°C (and so reducing the oxygen permeability) oxygen pressures down to 1 ppm could be measured without particular difficulties even at moderately low flow-rates.

In considering the accuracy of the experimental results, one should first note that at the operating temperature of the electrochemical pump the Faradaic efficiency of oxygen generation is unity. Consequently the absolute oxygen pressure could simply be calculated from the current passing in the pump and the inert gas flow-rate. An external absolute standard for the oxygen pressure is therefore unnecessary. The reliability of the experimental results can be appreciated from the difference

between the actual concentration (ppm_g) read at the gauge

$$\text{ppm}_g = \text{ppm}_{\text{ref}} \exp \left[\frac{4FE}{RT} \right] \quad (4)$$

(where ppm_{ref} is the oxygen concentration in the reference mixture) and the oxygen concentration (ppm_{el}), calculated according to Equation 3 from the amount of oxygen introduced coulometrically.

Provided this oxygen content is corrected for the initial oxygen content (ppm^o) in the mixture, which is determined from the EMF read in the absence of any current passing

$$\text{ppm}^o = \text{ppm}_{\text{ref}} \exp \left[\frac{4FE_{i=0}}{RT} \right]$$

it appears that in the range 10⁻⁷ to 10⁻⁵ bar the values of the absolute deviations ($\Delta\text{ppm} = \text{ppm}_g - \text{ppm}_t$, where ppm_t = ppm^o + ppm_{el}) fall within the interval 0.01–0.5 ppm, while the relative deviations, which are systematically negative, range around a maximum of 6% at 3.93 cm s⁻¹ (see Table 2).

Table 2. Accuracy of the experimental determination of the oxygen partial pressure in helium-oxygen mixtures. The gas was first deoxygenated with the SAES-getter

i (mA)	ppm _{eI}	ppm _g	ppm _t	Δ ppm	Δ ppm%	$\phi = 36 \text{ Nl h}^{-1}$ $w = 3.93 \text{ cm s}^{-1}$
0	0	0.57 [†]				ppm _t = ppm _{eI} + ppm ^o Δ ppm = ppm _g - ppm _t Δ ppm% = $\frac{\Delta \text{ppm}}{\text{ppm}_t} \times 100$
0.01	0.06	0.62	0.63	-0.01	-1.59	
0.02	0.12	0.66	0.69	-0.03	-4.35	
0.03	0.17	0.71	0.74	-0.03	-4.05	
0.04	0.23	0.76	0.80	-0.04	-5.00	
0.05	0.25	0.82	0.86	-0.04	-4.65	
0.06	0.35	0.87	0.92	-0.05	-5.43	
0.07	0.41	0.92	0.98	-0.06	-6.12	
0.08	0.46	0.99	1.03	-0.04	-3.88	
0.09	0.52	1.02	1.09	-0.07	-6.42	
0.1	0.58	1.10	1.15	-0.05	-4.35	
0.2	1.16	1.69	1.73	-0.04	-2.31	
0.3	1.74	2.30	2.31	-0.01	-0.43	
0.5	2.90	3.47	3.47	-0.00	-0.00	
0.8	4.64	5.18	5.21	-0.03	-0.58	
1	5.80	6.47	6.37	+0.10	+1.57	
2	11.60	12.26	12.17	+0.09	+0.74	
3	17.41	18.12	17.98	+0.14	+0.78	
5	29.01	30.12	29.58	+0.54	+1.83	
8	46.42	47.86	46.99	+0.87	+1.85	
10	58.04	59.61	58.61	+1.00	+1.71	

[†] ppm^o = 0.57 ppm

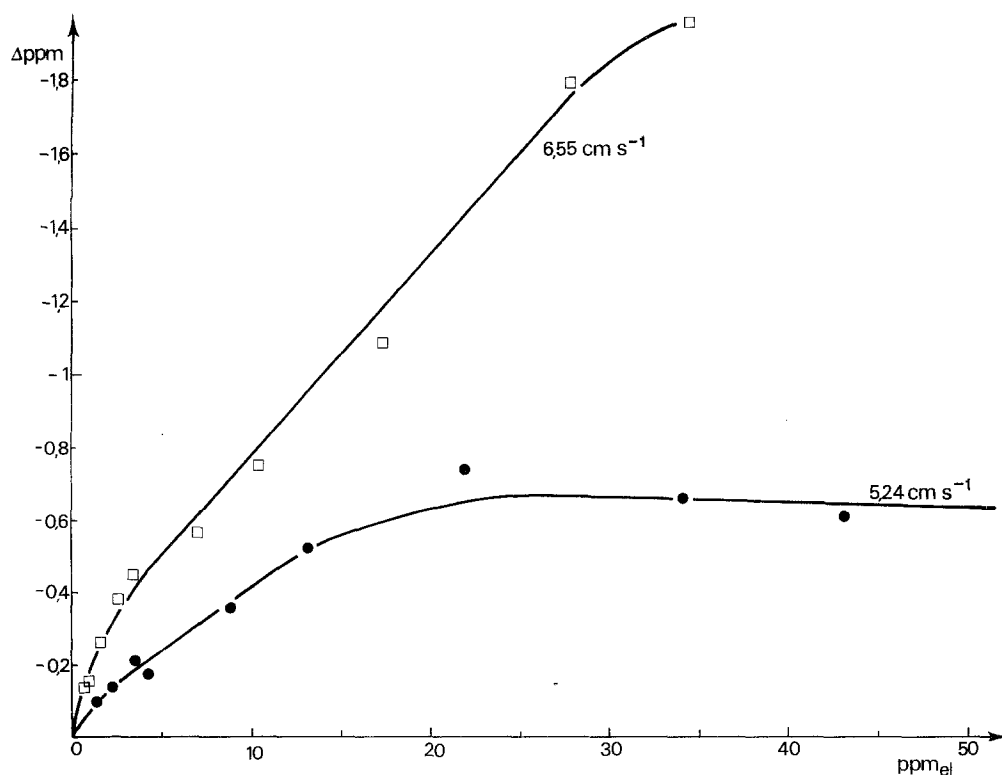


Fig. 8. Absolute deviation (Δ ppm) versus ppm of oxygen electrochemically introduced into the inert gas stream.

At a higher flow-rate, the absolute deviations Δ ppm, which are reported in Fig. 8, appear definitely higher and are systematically negative even at the highest oxygen partial pressures. The negative deviations can be accounted for, since Kleitz [7] has shown that the equilibration times, at partial oxygen pressures of about 10^{-6} bar at 700°C , are of the order of 2 h with platinum. We have demonstrated, however, that these tremendously long time-lags do not have much influence on the accuracy of a gauge because the relative and absolute deviations are small or negligible especially at the lowest flow-rates.

4. Conclusions

In spite of the influence of the water dissociation reaction and reduced hydrogen pick-up on the performance of the purification unit, an oxygen content as low as 0.1 ppm could be determined without any particular precautions, and with very good accuracy (about 10%) and relatively short step-response times.

It is apparent that the use of two getter purifiers similar to the SAES St 101/700 model, one working at 700°C for optimum O_2 pick-up and water dissociation and the second working at 600°C for the most efficient H_2 pick-up would further

improve the performance of the system. The use of purification units, however, requires a careful study of the behaviour of the particular getter material, in order to interpret correctly the EMF output of the electrochemical gauge.

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