

Coulometry of oxygen, hydrogen and moisture molecular impurities in inert gases

I A Kondratyev¹, A A Shakhmatov², P V Melnikov³, A V Ragutkin³,
G Yu Dalskaya³, V P Pirog⁴, A A Sukhov⁴, L F Nosenko⁴

¹Chief engineer, Experimental design bureau of automation, Angarsk, Russia

²Chief of department, Experimental design bureau of automation, Angarsk, Russia

³Associate professor, Moscow Technological University (MIREA), Moscow, Russia

⁴Engineer, Experimental design bureau of automation, Angarsk, Russia

E-mail: fisika@mail.ru

Abstract. This paper studies the method of simultaneous measurement of oxygen, hydrogen and water impurities that is based on combining moisture coulometric and solid electrolyte. The basic reduced measurement error for the molecular impurity in inert gases for measurements ranging from 0 to 5...50 and ...500 mln⁻¹ of oxygen totals 6, 3.8 and 2.8 % respectively. Similarly, measurement error totals respectively 8, 3 and 3.8 % for hydrogen, and respectively 6, 3 and 3 % for water molecules.

1. Introduction

Production of modern hardware components for micro- and nanoelectronics involves a wide range of high-efficiency electron-ion manufacturing processes, such as molecular beam epitaxy, ion implantation doping, laser annealing, plasma and ion beam etching, and applying vacuum coatings. These processes require particular purity of the used operating inert gas environments [1–4]. In this context it is extremely important to control such molecular components of operating gas impurities as humidity, oxygen and hydrogen to ensure the quality of the produced microelectronic devices. There are several methods of measuring the volume ration of oxygen and hydrogen in inert gases, e.g. using coulometric electrolysis and solid electrolyte cells [5–7]. A practical way to measure partial oxygen pressure in gases at high temperatures (above 600 °C) is by using a solid electrolyte cell [6, 7] designed as a tube made of solid electrolyte based on zirconium dioxide stabilized with oxides of calcium or yttrium. The most efficient way is to apply platinum electrodes in the form of spirals or pastes onto the external and internal surfaces of the tube [7]. Continuous simultaneous measurement of water, oxygen and hydrogen content is achieved by placing in the flow circuit of the studied gas a set of active electrolysis cells that simultaneously register the concentration of each impurity component.

2. Coulometric electrolysis cell

If this method is applied, the humidity is measured using a coulometric cell based on phosphoric anhydride film continuously absorbing moisture from a precisely regulated flow of the analyzed gas, with simultaneous electrolytic decomposition of the absorbed moisture into oxygen and hydrogen that are carried away by the flow of the analyzed gas. The amount of electricity spent on the electrolysis of the absorbed moisture (electrolysis current) indicates the concentration of moisture in the gas.



In accordance with Faraday's law, the moisture content is calculated as:

$$C_{H_2O} = \frac{I \cdot M_{H_2O}}{Q \cdot m \cdot F}, \quad (1)$$

where C_{H_2O} – moisture content, kg/m³; I – electrolysis current, A; M_{H_2O} – water molar mass, kg/mole; Q – gas flow through the coulometric cell, m³/sec; m – number of electron charges needed to decompose one water molecule; F – Faraday constant, C/mole.

3. Coulometric solid electrolyte cell

Oxygen can be measured with coulometric solid electrolyte cells (CSEC) that use direct current electrodes [8, 9]. CSEC is designed as a test tube made of high-temperature ceramics based on zirconium dioxide stabilized with yttrium dioxide that has selective oxygen-ionic conductivity. The cell has external and internal electrodes made of finely dispersed platinum [7]. Externally the cell is washed with atmospheric air due to the natural convection, and the analyzed gas is passed through the internal cavity of the cell. CSEC electrodes are powered (with specific polarity) from a direct current power source, under the effect of which oxygen is transferred through the solid electrolyte from the analyzed gas into the atmosphere.

If the analyzed gas flow is constant, the current through the CSEC can be used to measure the oxygen concentration in the environment (C_{O_2}), that according to Faraday's law is calculated as [7]:

$$C_{O_2} = \frac{I \cdot M_{O_2}}{Q \cdot n \cdot F}, \quad (2)$$

where C_{O_2} – oxygen concentration, kg/m³; I – current through the solid electrolyte, A; M_{O_2} – oxygen molar mass, kg/mole; Q – gas flow through CSEC, m³/sec; n – number of electron charges in the ionized oxygen molecule.

Physical and chemical properties of the solid electrolyte make it possible to use CSEC also for measuring hydrogen content in gases. The measurement is performed by means of electrolytic transfer of the amount of oxygen needed for hydrogen titration through the cell into the flow of the analyzed gas that contains hydrogen. In order to feed the titrant (oxygen) into the flow of the analyzed gas voltage is applied to the CSEC electrodes with polarity opposite to that of oxygen measurement. The signal indicating that the titration process is over is the steady transfer current and a sharp change of the cell electromotive force (EMF). EMF dependence on the titrant amount is typically for the titration curve characterized by the sharp voltage surge close to the equivalence point, i.e. the point in which the composition of the reactants corresponds with the stoichiometric proportion of the reaction products. At the moment of crossing the equivalence point the cell's EMF is changed by hundreds of millivolts. This not only indicates the end of the titration, but also makes it possible to use the cell in the automatic self-titration mode.

Figure 1 shows the CSEC flow chart for operation in the automatic self-titration mode.

CSEC consists of two chambers 1 and 2 divided by the solid electrolyte 3. Electrodes 4 are applied to the surface of the solid electrolyte. The electrodes are connected to the direct current source 5 via a current meter (milliammeter) 6. Chambers 1 and 2 correspondingly have an inlet and an outlet for the analyzed and the reference gas. The temperature of the cell is provided by an external electric heater and is sustained at a specified level by a temperature regulator.

It is known that in the stable conditions the cell's EMF depends on the oxygen partial pressure in chambers 1, 2, and is calculated by the Nernst formula [10]:

$$E = \frac{RT}{nF} \ln \frac{P'_{O_2}}{P_{O_2}}, \quad (3)$$

where E – EMF of the cell, B; $R = 8,314$, J/mole⁻¹·K⁻¹ – molar gas constant; T – absolute temperature, K; n – coefficient; $F = 96484$, A·c·mole⁻¹ – quantity of electricity needed for the electrochemical

transfer of one mole of oxygen; P'_{O_2} , P_{O_2} – partial oxygen pressure in the reference and analyzed environments respectively, Pa.

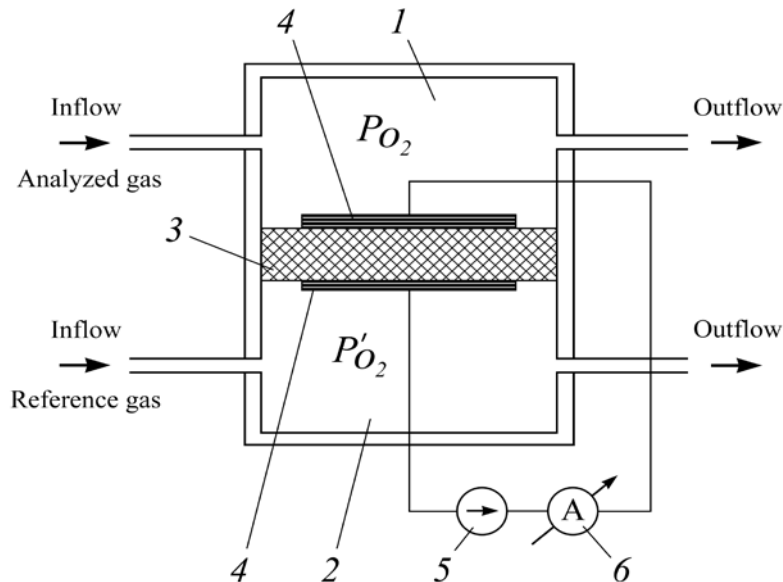


Figure 1. Coulometric solid electrolyte cell.

If the voltage of the direct current power supply is set to compensate the cell's EMF, the electrical equilibrium of the cell will not be changed. If some amount of hydrogen is put into the working chamber 1, it will react with oxygen and reduce the partial oxygen pressure and shift the equilibrium of the electrochemical reaction. The difference in the cell's EMF and the voltage of the direct current power supply will result in electric current in the external electric circuit, and oxygen will be transited from the reference environment into the working chamber through the solid electrolyte. When the ratio of the oxygen partial pressures in both chambers returns to the previous value, the system will return to equilibrium. The speed of equilibration is defined by the diffusion rate in the gas environment, the chemical reaction rate, the electric circuit resistance, and electrode polarization. Increase in cell's temperature, usage of low-polarizable electrodes and a power source with low internal resistance can significantly speed up the equilibration process.

4. Measuring method theory

In order to evaluate the dependence of hydrogen measurement error on the cell's operating conditions in the self-titration mode let's assume that all processes are reversible except for the process of mass-transfer through the solid electrolyte. Therefore, at any given moment the following Equation is true:

$$U + I \cdot r = \frac{RT}{nF} \ln \frac{P'_{O_2}}{P_{O_2}}, \quad (4)$$

where U – voltage of the direct current power supply, V; r – ohmic resistance of the solid electrolyte, Ohm.

If the inert gas with unknown hydrogen content is constantly passed through the working chamber, and the reference gas is characterized by constant oxygen partial pressure (i.e. atmospheric air), a certain electric current will be formed in the cell's electric circuit. According to the Faraday's law, this current will transfer oxygen from the reference environment into the working chamber. The relative amount of oxygen G_{O_2} that is transferred by the current per one volume of the analyzed gas will be calculated as follows:

$$G_{O_2} = \frac{Vm \cdot I \cdot \mathfrak{O}}{F \cdot M_{O_2} \cdot Q}, \quad (5)$$

where Vm – molar volume, m³/mole; \mathfrak{O} – oxygen electrochemical equivalent, kg/C.

Oxygen partial pressure in the cell's working chamber will be calculated according to equation (4). On the other hand the partial pressures of the mixture components in the cell can be calculated in accordance with the reversible reaction:



The reversible reaction proceeds in the working chamber taking into account the equilibrium constant K_p of this reaction:

$$K_p = \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{1/2}}. \quad (7)$$

Partial pressure of the reacting components (with the total pressure of one) relates to the hydrogen concentration C_{H_2} in the original analyzed as:

$$C_{H_2} = \frac{P_{H_2} + P_{H_2O}}{1 - P_{O_2}}, \quad (8)$$

Partial pressure of the reacting components relates to the relative amount of oxygen transferred through the solid electrolyte according to the Equation:

$$G_{O_2} = \frac{P_{O_2} + \frac{1}{2}P_{H_2O}}{1 - P_{O_2}}. \quad (9)$$

Simultaneous solution of the Equations (5), (7), (8) и (9) can be recorded as:

$$G_{O_2} = \frac{1}{2}C_{H_2} \cdot (1 - \delta), \text{ where} \quad (10)$$

$$\delta = \frac{2P_{O_2} \cdot (1 + K_p \cdot P_{O_2}^{1/2}) - C_{H_2} \cdot (1 - P_{O_2})}{2P_{O_2} \cdot (1 + K_p \cdot P_{O_2}^{1/2}) + C_{H_2} \cdot K_p \cdot P_{O_2}^{1/2} \cdot (1 - P_{O_2})}. \quad (11)$$

Equation (10) shows that the amount of oxygen transferred through the solid electrolyte per volume of the analyzed gas is stoichiometrically related in terms of reaction (6) to the amount of hydrogen in the analyzed gas with the inaccuracy of δ .

After reducing (11) provided that $P_{O_2} \ll 1$ и $K_p P_{O_2} \gg 1$:

$$\delta = \frac{2P_{O_2}}{C_{H_2}} - \frac{1}{K_p \cdot P_{O_2}^{1/2}}. \quad (12)$$

Simultaneous solution of the Equations (4), (10) and (12) give the following result:

$$\delta = \frac{2P'_{O_2}}{C_{H_2}} \exp \left[\left(U + \frac{C_{H_2} \cdot F \cdot M_{O_2} \cdot Q \cdot r}{44800 \mathfrak{O}} \right) \frac{nF}{RT} \right] - \frac{1}{K_p \cdot P_{O_2}^{1/2}} \exp \left[\left(U + \frac{C_{H_2} \cdot F \cdot M_{O_2} \cdot Q \cdot r}{44800 \mathfrak{O}} \right) \cdot \frac{nF}{RT} \right]. \quad (13)$$

Analysis of the Equation (13) shows that at certain conditions (gas flow Q , temperature T , ohmic resistance of the solid electrolyte r), it is possible to find such voltage U , when inaccuracy δ is changed relatively little within a wide range of measured concentrations. Calculations show that

under realistic conditions δ does not exceed 0.2 % within the range of measured concentrations from 1 to 500 mln^{-1} . This inaccuracy is significantly lower than inaccuracies connected with measuring and maintaining the flow of the analyzed inert gas. If inaccuracy δ is neglected, Equations (5) and (10) can be used to derive the following Equation for establishing the hydrogen concentration:

$$C_{H_2} = \frac{2Vm \cdot I \cdot \vartheta}{F \cdot M_{O_2} \cdot Q} \quad (14)$$

If the analyzed gas flow Q is constant, the hydrogen concentration can be calculated using the measured cell current. The described CSEC allows to measure the oxygen and hydrogen concentration with certain accuracy if the analyzed gas contains only one of these two components. If they are contained in the gas in commensurable quantities, they react with each other and consequently do not participate in the electrode reaction, which makes measurements indeterminate. This drawback is increasingly important taking into account that the inert gases used in industrial and laboratory practice usually contain both oxygen and hydrogen.

5. Experimental test

In order to implement the instrumental gas analysis system it is possible to use the principle of simultaneous measurement of oxygen and hydrogen microconcentrations that is demonstrated in Figure 2.

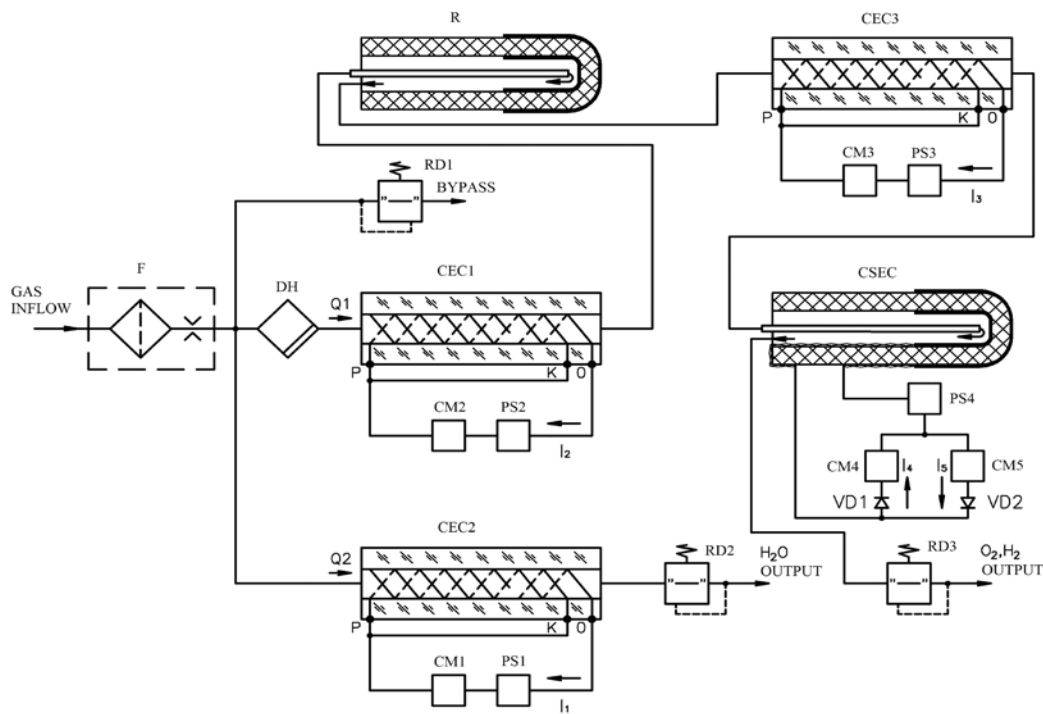


Figure 2. Flow chart of measuring oxygen, hydrogen and moisture microconcentrations in inert gas environment.

In this design the analyzed gas with constant flow Q_1 is successively passed through filter F , dehumidifier DH , coulometric cell $CEC1$, reactor R , coulometric cell $CEC3$ and further on through $CSEC$ and reducer $RD3$ is dumped into the atmosphere. Introduction of the dehumidifier DH into the design is conditioned by the need to reduce the error of measuring oxygen and hydrogen microconcentrations that occurs because of moisture presence in the gas. Phosphorous pentoxide is used as moisture absorber in the humidifier. In order to control the quality of moisture absorption in

the humidifier and simultaneously to correct the results of measuring residue moisture it is reasonable to introduce a coulometric cell CEC1 into the design.

The amount of moisture generated in the reactor R is measured with the coulometric cell CEC3. All cells including the CSEC are galvanically connected with each other, are powered by separate power sources PS1, PS 2, PS3 and are connected to the measurement circuit represented by diodes VD1, VD2 and current meter CM4, CM5 in such a way to ensure algebraic addition of the cells' signals to for the required functional changes of the latter. Basically, the measurement design is a bridge with diagonal connection of CSEC. If the analyzed gas contains excessive hydrogen (scenario $C_{H_2} > 0,5 C_{O_2}$), CSEC generates EMF that exceeds the compensating voltage from power source PS4. In this case CSEC circuit generates the oxygen ions transfer current I'_{O_2} that is proportional to the value ΔC_{H_2} . At the same time current flows through the current meter CM4; this current equals the sum of oxygen ions transfer current I'_{O_2} and the current of moisture electrolysis of the coulometric cell CSEC I'_{H_2O} . Simultaneously current flows through the current meter CM5; this current equals the difference of currents of CEC1 and CSEC (respectively I'_{H_2O} и I_{H_2O}).

In another case, when the analyzed gas contains excessive oxygen, (scenario $C_{O_2} > 2C_{H_2}$) CSEC generates EMF that is lower than the the compensating voltage. In this case the oxygen ions transfer current I_{O_2} that is proportional to the value ΔC_{O_2} will change its direction and will be one of the components of the current that flows through the current meter CM5.

Thus, the microconcentrations of oxygen and hydrogen in the analyzed gas can be analytically measured according to the following equations:

$$B_{O_2} = \frac{q}{2} \frac{(I_{O_2} + I_{H_2O} - I'_{H_2O}) \cdot (t + 273.15)}{Q_1 \cdot P}; \quad (15)$$

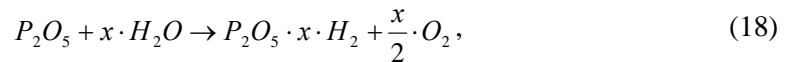
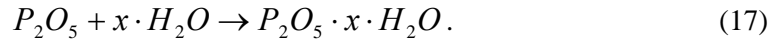
$$B_{H_2} = q \frac{(I'_{O_2} + I_{H_2O} - I'_{H_2O}) \cdot (t + 273.15)}{Q_1 \cdot P}, \quad (16)$$

where B_{O_2} – oxygen microconcentration in the analyzed gas, mln^{-1} ; B_{H_2} – hydrogen microconcentration in the analyzed gas, mln^{-1} ; I_{O_2} – oxygen ions transfer current if the analyzed gas contains excessive oxygen, μA ; I'_{O_2} – oxygen ions transfer current if the analyzed gas contains excessive hydrogen, μA ; I_{H_2O} and I'_{H_2O} – currents of moisture electrolysis in the coulometric cells installed in the gas flow beyond respectively reactor and dehumidifier, μA ; t – atmosphere air temperature, $^{\circ}\text{C}$; Q_1 – analyzed gas flow in the oxygen/hydrogen measurement channel (for measurement conditions), cm^3/min ; P – atmosphere pressure, kPa ; q – coefficient determined by the choice of measurement units, totals $2,582 \frac{\text{mln}^{-1} \cdot \text{cm}^3 \cdot \text{kPa}}{\text{min} \cdot \mu\text{A} \cdot \text{K}}$.

In the process of moisture microconcentrations measurement the analyzed gas is continuously passed through the coulometric cell CEC2 in the direction indicated by arrows. The analyzed gas flow Q_2 is maintained on a strictly constant level.

The cell's electrodes are connected to the direct current power supply PS1 with the applied voltage exceeding the moisture decomposition potential. This ensures the electrolysis of moisture simultaneously with its adsorption, which provides the conditions for uninterrupted electrolytic regeneration of phosphorus pentoxide.

The electrolysis current is measured by the microammeter AM1 installed into the current circuit. Following reactions occur as the result of the moisture sorption from the analyzed gas flow and its electrolysis in the sorbent foil:



where x – coefficient proportional to the amount of the abstracted moisture.

If the moisture microconcentrations in the analyzed gas are constant in stable conditions, balance is established between the processes (17) and (18). The Faraday's law describes the relation between the amount of substance generated on the electrodes in the electrolysis process and the quantity of electricity spend for it; according to this law, the current measured with the microammeter AM1 makes it possible to establish the moisture concentration in the analyzed gas. The following Equation describes the relation between the current and the moisture concentration:

$$B_{H_2O} = q \frac{I \cdot (t + 273,15)}{Q_2 \cdot P}, \quad (19)$$

where B_{H_2O} – moisture concentration in the analyzed gas, mln^{-1} ; I – electrolysis current, μA ; Q_2 – analyzed gas flow in the measurement channel (for measurement conditions), cm^3/min .

6. Measurement error

The basic reduced measurement error of the coulometric analysis method described in Figure 2 is defined by the volume ratio of the molecular impurity (oxygen, hydrogen or water) X_{II} and is calculated according to the following formula using control gas mixtures (CGM):

$$\gamma_{0X_{II}} = \frac{B_{I X_{II}} - B_{IIIC X_{II}}}{\Pi_{X_{II}}} \times 100, \quad (20)$$

where $\gamma_{0X_{II}}$ – basic reduced measurement error for the molecular impurity X_{II} , % ;

$B_{I X_{II}}$ – gas analyzer readings X_{II} , mln^{-1} ; $B_{IIIC X_{II}}$ – volume ratio of the molecular impurity X_{II} in the CGM, mln^{-1} ; $\Pi_{X_{II}}$ – measurement range for the molecular impurity type X_{II} , mln^{-1} .

Experiments show that the basic reduced measurement error for the molecular impurity X_{II} in inert gases for measurements ranging from 0 to 5, ...50 and ...500 mln^{-1} of oxygen totals 6, 3.8 and 2.8 % respectively. Similarly, measurement error totals respectively 8, 3 and 3.8 % for hydrogen, and respectively 6, 3 and 3 % for water.

7. Conclusion

Study of the coulometric method of measuring concentrations of oxygen, hydrogen and moisture molecular impurities in inert gas environment by passing the analyzed gas through several electrolyte cells demonstrates the technical possibility and high efficiency of registering the impurities. Technological improvement in the manufacture of the coulometric solid electrolyte cell results in wider measurement range of oxygen and hydrogen microconcentrations. The basic reduced measurement error of molecular impurities in inert gases for measurements ranging 0–5–50–500 mln^{-1} does not exceed 8–6–3 % respectively.

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