

OXYGEN MEASUREMENT IN NON – COMBUSTABLE GAS USING A MICRO – ELECTRIC CONDUCTIVITY CELL

by

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الطرق المتبعة لقياس ضغط الاوكسجين

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خلاصة المقالة

ان مشكلة التخلص من الاجزاء الاخيرة من الاوكسجين الموجودة في الغازات الخاملة يعد من المشاكل التي تواجه الصناعة ومراكز البحوث حيثما يتطلب الامر غازات نقية جدا .
وتقابلها من ناحية اخرى مشكلة قياس ضغط الاوكسجين النسبي في هذه الغازات وخاصة عند الضغوط المنخفضة جدا من الاوكسجين .
في هذا البحث حاولنا الاختصار ، قدر الامكان ، في تعداد الطرق المتبعة لقياس ضغط الاوكسجين ، مؤكداً في نفس الوقت على الطرق الحديثة في التحليل وخاصة الطريقة التي اتبعت في هذا البحث (والتي تعتمد على قياس التوصيل الكهربائي لسلك من اوكسيد الكوبلت).
والتي كان من ثمارها جهاز ذو حجم صغير ودقة اكثر حيث روعي التقليل من المشاكل التي كانت تحدث من فعالية الاجهزة السابقة .

ABSTRACT:

Presence of last traces of unwanted residual gases in gas mixtures as in environments have posed a considerable problem in many industries and research establishments (1); especially in applications where the system can combine with residual gases giving the adverse effects. This paper mainly deals with the detection of oxygen as residual gas when it is present in small quantity. Using a new modified instrument based on electrical conductivity measurements.

INTRODUCTION:

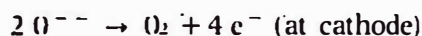
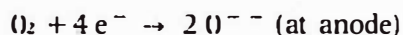
Methods available for oxygen measurement can be classified as macro-dosage methods, micro-dosage methods and other methods. (2-11) In macro-dosage methods, paramagnetic and diamagnetic properties of the gases have been made use of. Oxygen is well known as paramagnetic so its susceptibility can be measured as a function of temperature and later calibrated for oxygen content.

In micro-dosage methods, oxygen is absorbed in ammoniacal cupperous solution or sodium anthraquinon sulfate solution. The colour of the solution so changed is matched with standard solution to estimate the amount of gas absorbed.

In some cases oxygen is passed over heated carbon and amount of CO_2 evolved was calibrated for the amount of oxygen.

Other methods involve the use of certain properties of the gases like thermic effect of oxygen-hydrogen reaction, or the thermal conductivity of the gases. In a special case of oxygen-nitrogen mixture where the difference in thermal conductivity is small, special electrolyte cells have been used. In one case the electrolytic cell is termed by the authors as (oxytrode) and this consist of two electrodes of Pt /Pt-6% Rh separated by solid electrolyte of stabilised zircon. Gas to be analysed is passed around the anode and a reference gas (pure oxygen or air) is used around the cathode. When the whole cell is placed inside a furnace at about 900° , Oxygen mobility inside the crystalline lattice of zircon is increased and this results in sufficient ionic conductivity.

The reactions taking place can be put in the equation form as shown below.



E.M.F. of the cell is then given in volts by Nernst law (2)

$$\text{E.M.F.} = K.Q. \ln \frac{P_1}{P_0}$$

Where:

K = constant

Q = Absolute temperature

P_1 = Partial pressure of the gas to be analysed

P_0 = Partial of the reference gas

All these methods have limitations especially in their effective limit of oxygen traces detection, and their operation difficulties. These limitations are overcome in the newly developed electrolytic cell which is quicker and easier to operate.

EXPERIMENT AND RESULTS:

PRINCIPLE: It's based on the results obtained by F. MARION (1.12), using an oxymeter of cobalt oxide heated to 1000°C. According to the author, the resistance of such filament follows the following law:-

$$\log \frac{R(\text{CoO})}{R(\text{CoO})_0} = 0.266 \log P_{\text{O}_2} - 0.0042 \log P_{\text{H}_2}$$

Where:

$R(\text{CoO})_0$ is the resistance of CoO filament, for $P_{\text{O}_2} = 1$ atm.

This law is valuable only in the range of stability of CoO at 1000°C, i.e. for oxygen partial pressure between 1 atm. and 1.4×10^{-2} atm. this oxide shows a non-stoichiometry with cationic vacancies more or less ionized according to the temperature and pressure. It's therefore a semiconductor of type P, in which the electric conductivity is directly proportional to the quantity of oxygen in the surrounding gas. If we examine the process of current transfer under these conditions, we can see that the positive charges are transported by Co^{+3} ions of the lattice, the electrons which pass from one to the other provides charge transfer of a positive charge in an inverse direction. Current intensity (i) will therefore be equal to (after approximation) :-

$$i \sim N e (\text{Co}^{+3}) V_m = K(\text{Co}^{+3})$$

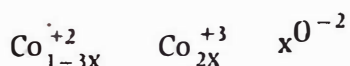
Where:

N is the Avogadro's Number.

e is the electron charge

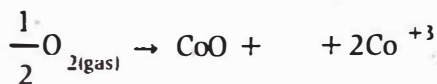
V_m is the average speed of electron passing from one Co^{+3} to other.

The electrostatic neutralisation of the lattice is then conserved only if the positive charge on the cations disappears and passes over a neighbouring cation which will therefore be of higher valence. The newly formed cations will therefore be qualified as positive vacancies. The representation formula of such oxide is written as follows:-



Where X represents the difference from stoichiometry.

The mass-action law at equilibrium will be written as follows:



$$K = (\quad) (\text{Co}^{+3})^2 P_{\text{O}_2}^{-1}$$

Since $2(\quad) = (\text{Co}^{+3})$

Therefore $(\text{Co}^{+3}) = K' \cdot P_{\text{O}_2}$

and $R = K'' \cdot P_{\text{O}_2}^{-1}$

The experimental isotherme ($\log R$ Vs $\log P_{O_2}$) determined by MARION, is in agreement with the precedent theory, where the slope is given by:

$$a = 0.266 - 0.10084 \log P_{O_2}$$

$$a = \frac{\log R}{\log P_{O_2}}$$

With one condition to be considered, that's the vacancies are incompletely ionised, i.e. $(\) = (Co^{+3})$, which implies a law of $P_{O_2}^{-1/2}$.

In the classical instrument based on this principle, the cobalt oxide filament was placed inside a tube furnace regulated automatically at 1000°C.

The filament was fixed over platinum wire supported on silica tube. After complete oxidation of the filament, the electric Resistance of the filament was measured using a wheatstone bridge associated with a potentiometric recorder (fig.1).

The gas to be analysed was circulating inside the interior tube, while the exterior envelope was of (Pythagoras).

NEW MODIFIED INSTRUMENT:

In this instrument which consist essentially of a micro furnace regulated with a rolled platinum wire surrounding the cobalt oxide filament, the micro furnace itself is placed inside a stainless-steel container of small volume (about 15 cm³) inside which the gas to be analysed is circulating (fig.2.) The furnace is heated by the rolled platinum wire, in which the resistance change with the temperature. This wire is in series with a nichrome Resistance, it constitutes one of the branches of a bridge, the other branch is constituted of a fixed resistance and a multiturn potentiometer (fig. 3).

The non-equilibrium amplified by an operational amplifier serve to command the furnace supply. It works thus at constant resistance, i.e. almost at a constant temperature. The measurement of the resistance of the cobalt oxide filament is affected by a conductimeter in alternative current.

The standardisation of the two apparatus was affected using air and then dilute mixtures of Nitrogen and Oxygen under a total pressure of 760 to a few millimeters of mercury.

The results were grouped and shown in fig.4. At very low oxygen pressure results have been extrapolated using MARION equation:

$$\log R_{CoO} = \log R_{(CoO)_0} - 0.266 \log P_{O_2} - 0.0042(\log P_{O_2})^2$$

Where:

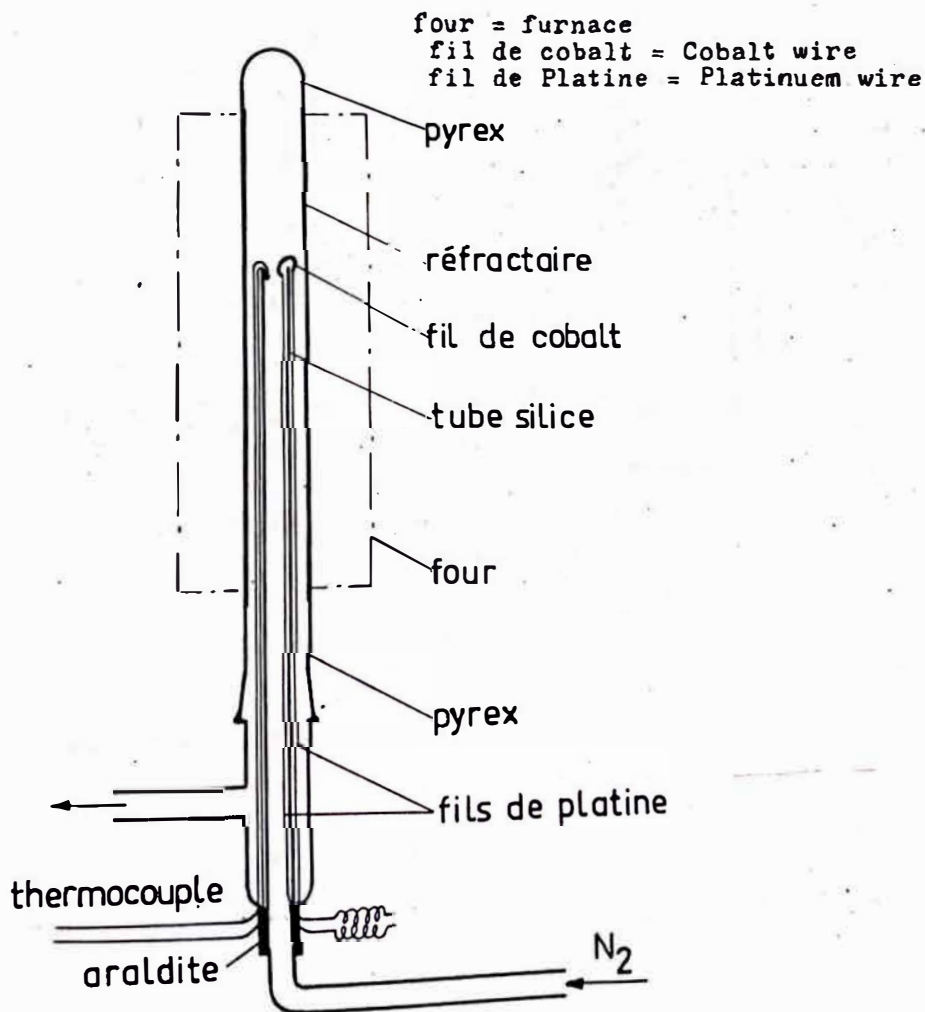
$$\log R_{(CoO)_0} = 1.87$$

CONCLUSION:

The development of control and regulation in industry had proposed many methods for oxygen analysing in a gas, or gas mixtures. Our method which is based on the conductivity of cobalt oxide had been used in a new original, tight, with very short response time, cell, with a wide limits (10⁻¹² atm. of oxygen).

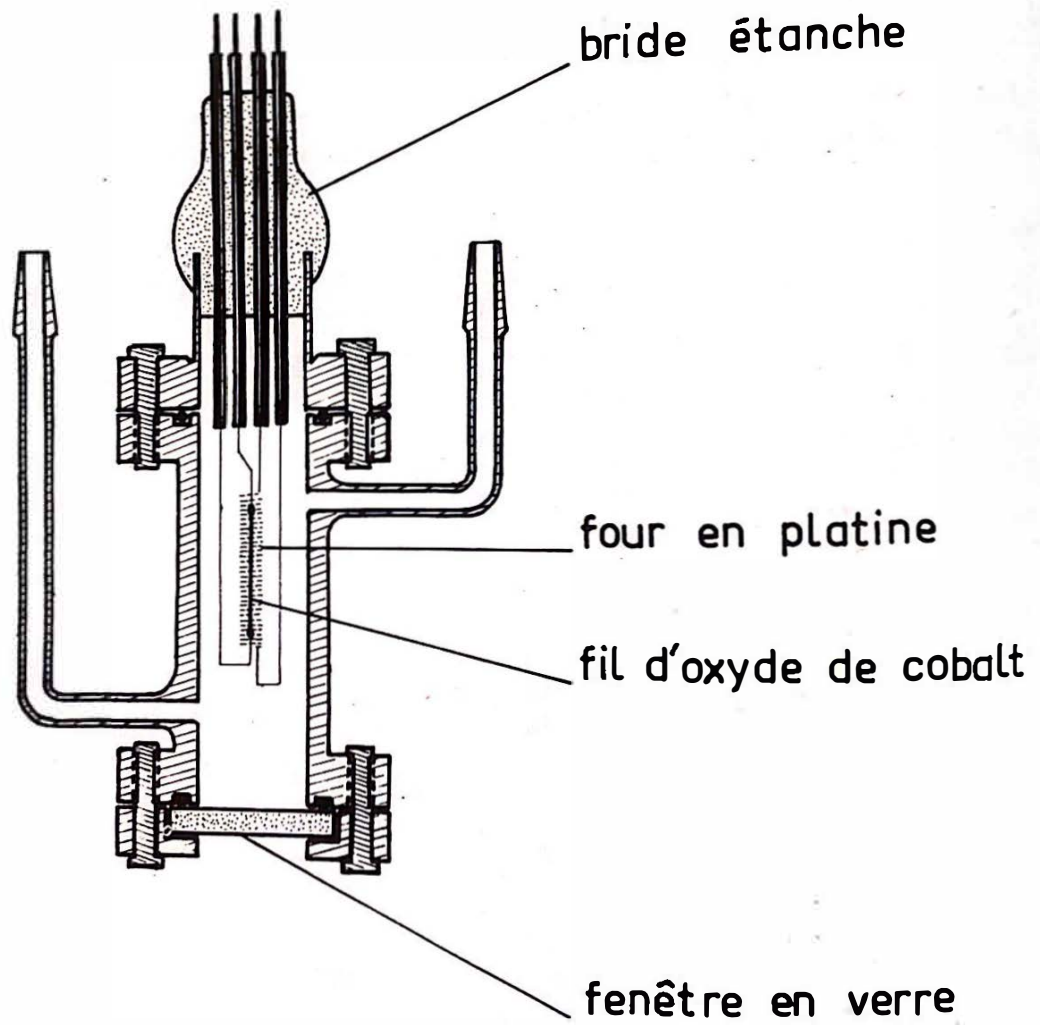
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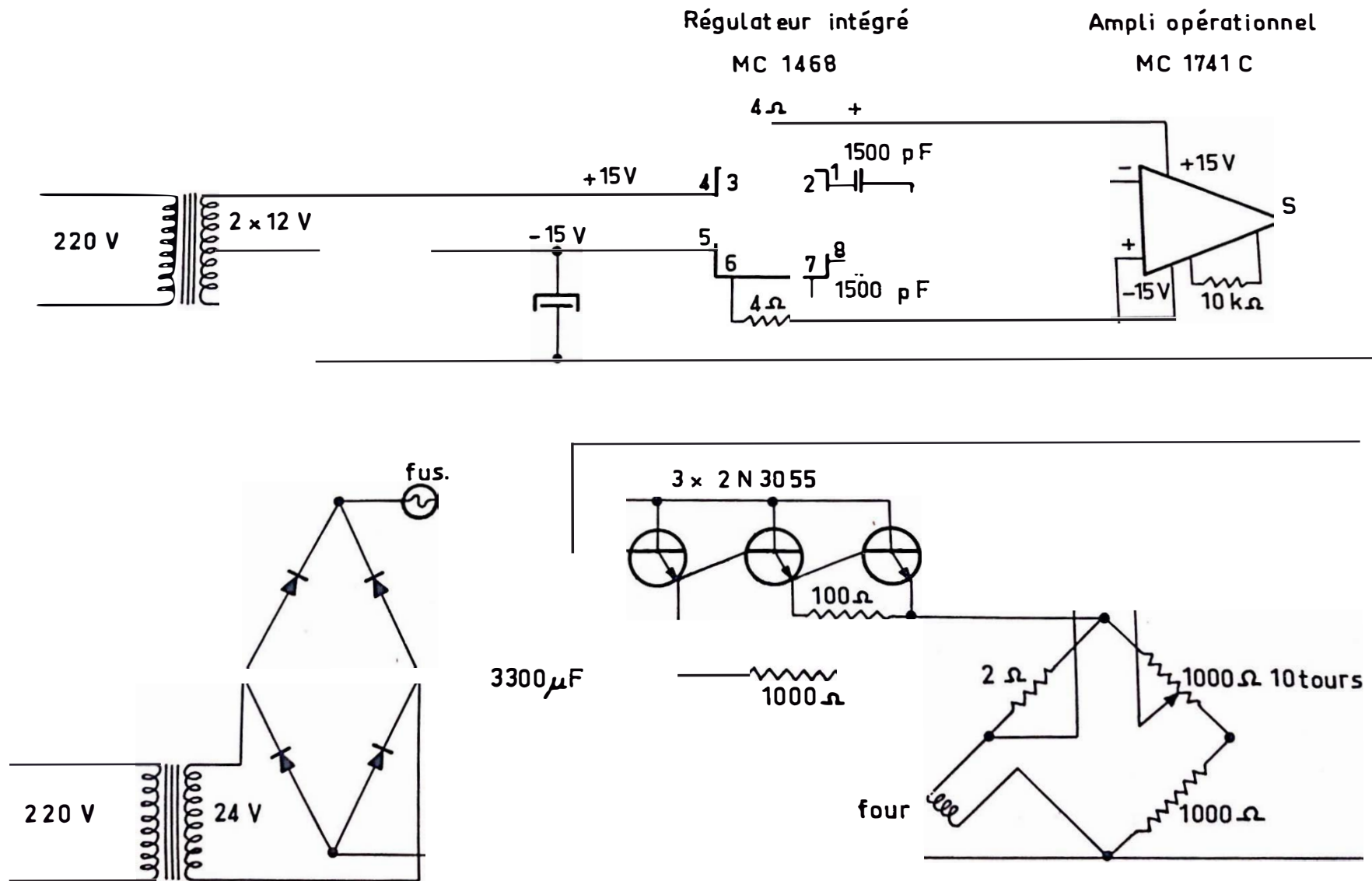


(Fig. 1) Classical measuring cell

fenêtre en verre = glass window
four en platine = platinum furnace



(Fig. 2) Platinuem furnace cell



(Fig.3) Electronic circuit for temperature regulation of the micro furnace

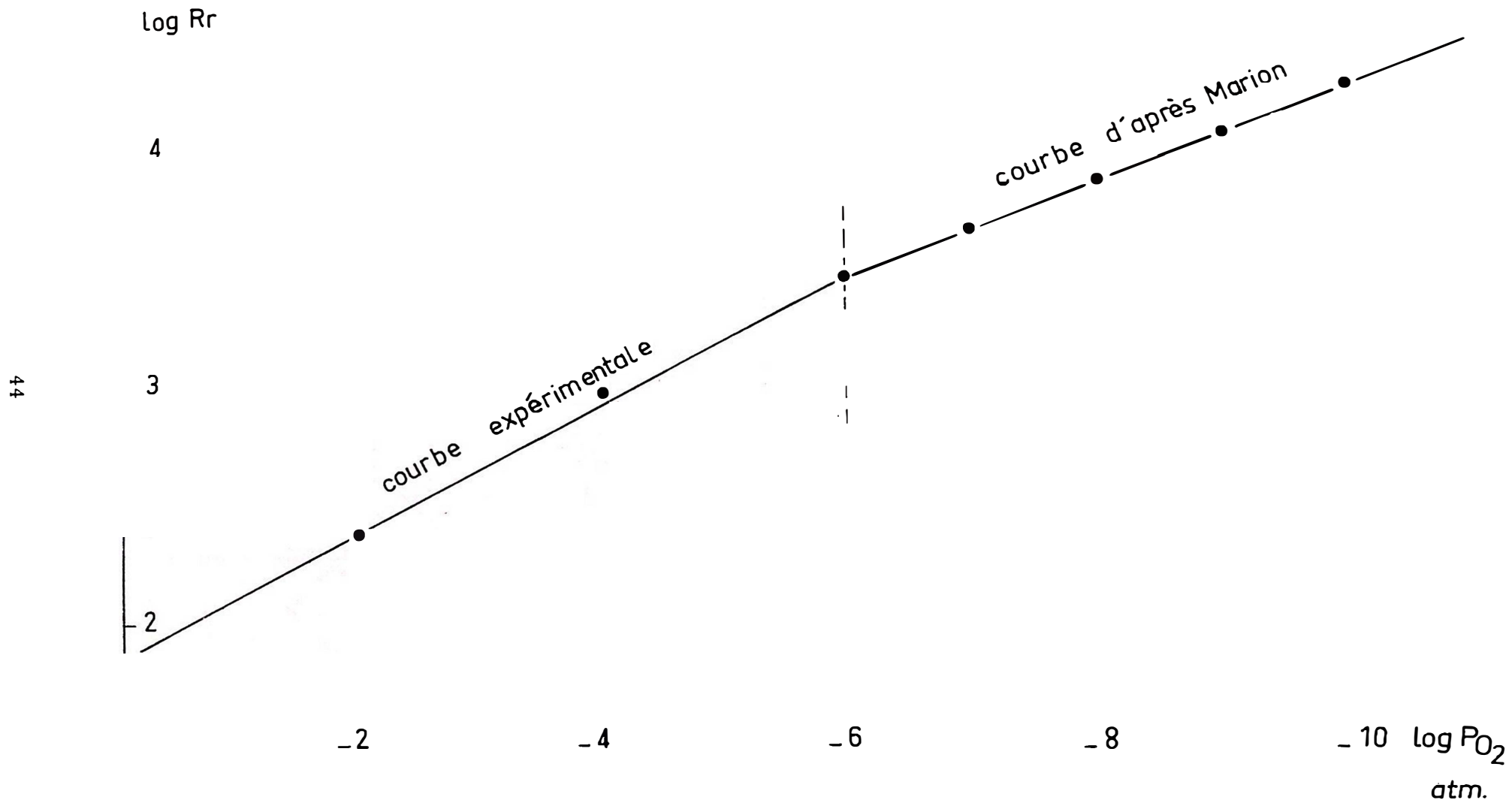


FIG.4 STANDARISATION CURVE(LOGR Vs LOG Po2 atm.)