

ガルバニセル型酸素分析計の設計と挙動

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Design and Performance of Improved Galvanic Cell Type Oxygen Analyser

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In order to measure the trace oxygen in gas continuously, a galvanic cell type oxygen analyser (Ag | 24 % KOH | Pb cell) was manufactured for trial. This analyser has a coil-type silver cathode which is separated from the lead anode, and an automatic water feeder having a specific device is applied so as to stabilize the sensibility and to simplify maintenance and handling. The value indicated by this analyser became independent of the rate of flow of gas over 300cc/min, showing reproducibility with standard deviation lower than 1.2%, and the response time to 90% response was in the range between 1.8 ~ 2.1min. After examination on the stability of various properties during continuous operation, it was found that this is suitable for use in industry.

1. Introduction

Of late analysis of trace oxygen (in concentrations in the order of ppm) in gas has been regarded as important in the field of semiconductor, gas, and organic chemistry, and continuous watching on the trace oxygen has become indispensable in the quality control. Formerly the authors made some fundamental experiments on a galvanic cell type oxygen analyser which was essentially selective for oxygen and disclosed its various features to establish the plan in designing. In case of continuous measurement in the manufacturing process, not to say of accuracy, but rather reproducibility and stability have been taken important from the nature of the aim. Therefore the authors manufactured tentatively an analyser for continuous measurement based on the previous paper and made a continuous test for quality for about two years. During the course of examination several improvements in the structure were repeated bringing about seemingly satisfactory results. In this paper the structure of the analyser finally obtained as well as its quality in continuous use is presented.

2. Construction and operation

The diagram illustrating the principle of the oxygen analyser is given in Fig.1. Valve 1 and 2 in Fig.1 are valves worked by hand and both are set at "Open" position during

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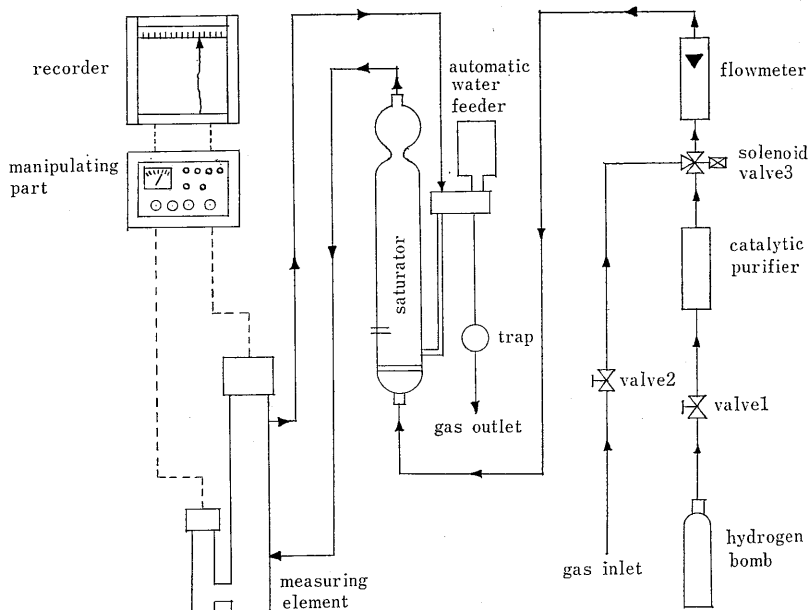


Fig.1 Schematic diagram of oxygen analyser

operation. On setting the selector switch of the manipulating part (described later) at "Meas." position, the three way solenoid valve 3 is de-energized leading a sample gas to the saturator via a flowmeter. The sample gas enters the measuring element after being saturated with water vapour. In the measuring element an electric current is generated corresponding to the concentration of oxygen in the sample gas, and consequently this current is passed through a definite load resistor, and the voltage-drop on the load resistor is recorded in the recorder. The sample gas coming out of the measuring element is dispersed in the pure water in the automatic water-feeder and discharged outward through the water trap. As the water in the saturator is brought out continuously by the sample gas, it is necessary to supply water to the saturator as much as the amount lost. A device equipped for this sake is the automatic water-feeder.

Then on setting the selector switch at "Zero" position, solenoid valve 3 is energized leading hydrogen gas to the flowmeter through a catalytic purifier. The catalytic purifier has the object to remove oxygen in the hydrogen gas. The hydrogen gas coming from the flowmeter passes through the saturator, measuring element, automatic water-feeder, and water trap in this order and is discharged outward. The zero point of the analyser is calibrated in this condition.

On setting the selector switch at "Cal." position, a definite electric current flows between a pair of platinum electrodes equipped in the saturator, where a definite amount of oxygen is generated and admixed into the hydrogen gas. Assuming the electrolytic current

at that time, the scale of the analyser is calibrated.

The working principle of this analyser is explained as follows. The measuring element is a kind of galvanic cell consisting of $\text{Pb} \mid 24\% \text{ KOH} \mid \text{Ag}$, and most of the silver protrudes in the gas phase. When oxygen flows over the surface of the silver in the cell of such constitution, an electrochemical reaction takes place at the three phase boundary²⁾ where the cathode, the electrolytic solution, and oxygen are mutually in contact giving rise to a current between silver and lead corresponding to the concentration of oxygen. Therefore by estimating the drop in the voltage between both terminals of the load resistor, which is caused by applying this electric current to a definite load resistor, the current, that is the concentration of oxygen, is made evident.

2.1 Detecting part

The detecting part consists of flowmeter, catalytic purifier, saturator, automatic water-feeder, measuring element, water trap, valves and a piping system connecting them as shown in Fig.1. The appearance in the interior of the detecting part is shown in Photo.1.

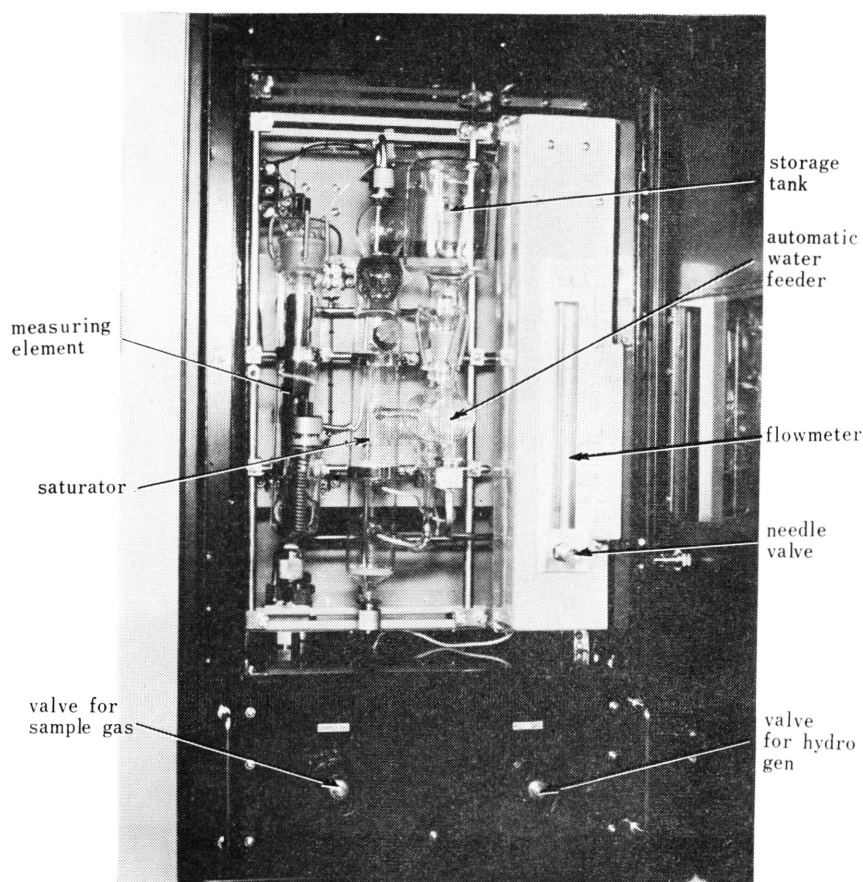


Photo.1 Interior of detecting part

2.1.1 Catalytic purifier

The catalytic purifier is provided with the object to remove the oxygen in the hydrogen gas at the time of calibration of the scale of analyser. The catalyser used at the normal temperature is the palladium metal precipitated on alumina carrier (made by Engelhardt Industries Inc.). By this catalyser the reaction, $2\text{H}_2(\text{gas}) + \text{O}_2(\text{gas}) \rightarrow 2\text{H}_2\text{O}(\text{gas})$, is promoted resulting in the elimination of oxygen, and such hydrogen gas as containing usually no more than 0.5~1 ppm oxygen, can be obtained.

2.1.2 Saturator and automatic water-feeder

In case of the galvanic cell type oxygen analyser, it is necessary to humidify the sample gas previously so that the water in the electrolytic solution in the measuring element may not be lost. For this purpose a saturator is equipped (In this part there are used entirely

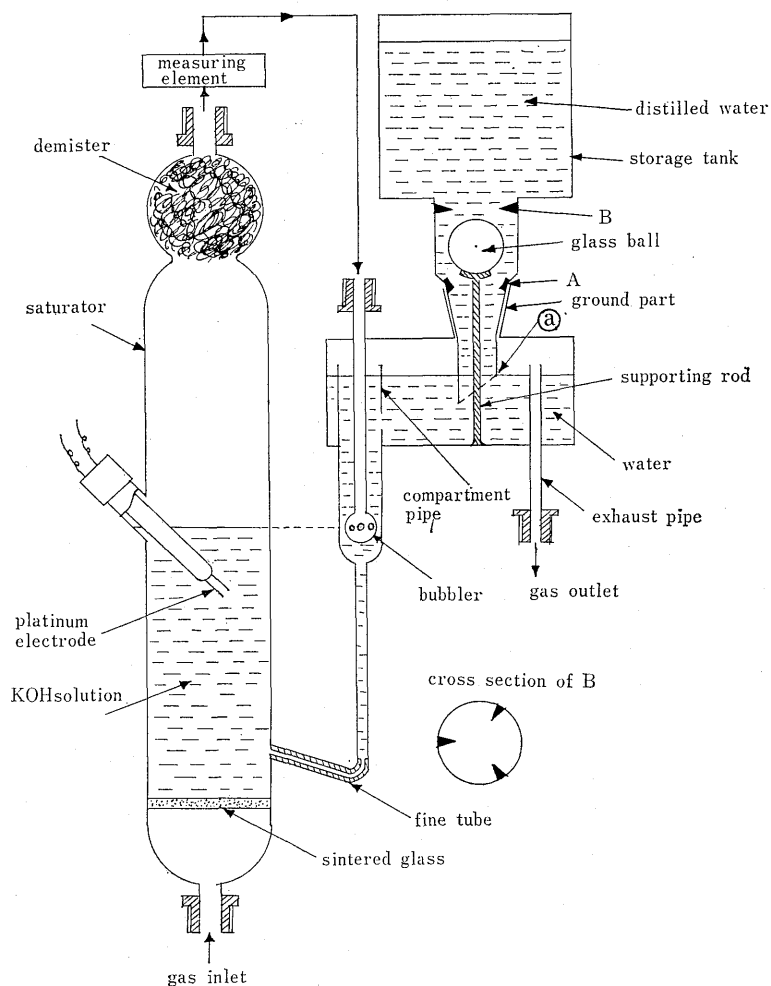


Fig. 2 Saturator and automatic water-feeder

no cocks, because during long usage troubles due to sticking of cocks often happened on account of the corrosion by the alkaline solution at the ground part of cocks). The outlined figure of the saturator is given in Fig.2.

Platinum electrodes in Fig.2 are used as the electrode for water electrolysis in calibrating the scale.

The sample gas is dispersed into 8% potassium hydroxide solution as fine bubbles by the use of sintered glass, during which time the sample gas is saturated with water vapour. Then the sample gas goes through a demister, wherein a nickel wire is wound at random (so as to prevent KOH mist from entering into the measuring element) and then through the measuring element and enters into the automatic water-feeder. Here the sample gas is deprived of dissolved oxygen in water in the compartment pipe by using a bubbler and then discharged outward from the exhaust pipe.

As the liquid level in the saturator drops, the liquid level in the automatic water-feeder also drops. When the liquid level of the automatic water-feeder drops below the upper cut end a of the glass tube having a slant cut end, the gas enters the storage tank, the water in the storage tank corresponding to the volume of gas is forced into the automatic water-feeder, and simultaneously the water in the compartment pipe (which has a hole on the side wall) goes through fine tubes into the saturator. When the liquid level in the saturator recovers to the original water level, the water level in the automatic water-feeder also rise to a , and the water supply from the storage tank ceases. In such a way, continuous supply of water is carried out, without need for the water supply by hand. The reason why the water passage from the compartment pipe to the saturator consists of fine tubes, is that the gas from the saturator may not enter into the compartment pipe, and the diffusion of potassium hydroxyde into the compartment pipe is made as small as possible. Since the capacity of the compartment pipe is not so large that the elimination of oxygen from the water to be supplied to the saturator is performed efficiently.

In the above method, it is highly advantageous that the water entering into the saturator is always in equilibrium with the sample gas. (On perfect removal of oxygen from the water supplied, the oxygen in the sample gas is dissolved in the water in the saturator. Namely it is disadvantageous because the oxygen in the sample gas is consumed. On the contrary if the water having been left in air is used intact, the oxygen dissolved in water is released into the sample gas which makes the indicated value a little higher).

In supplying water to the storage tank, the storage tank is lifted vertically to remove

from the apparatus. On this occasion a glass ball is separated from the supporting rod and adhere to the thick part A (this serves as a valve seat.) which permits no leakage of water. When the storage tank overturned in such condition, a glass ball is caught by three protrusions B. When water is poured from the above into the storage tank, water enters it through the clearance between a glass ball and the protrusions. If the storage tank is again overturned, a glass ball returns to a state close adhered to A preventing the leakage of water. The storage tank in this state is equipped to the automatic water-feeder. When the ground part is in close contact, a glass ball is uphold by the supporting rod, the water in the storage tank may easily fall down through the gap between a glass ball and A.

In order to facilitate cleaning of the platinum electrode, this is made possible of removal.

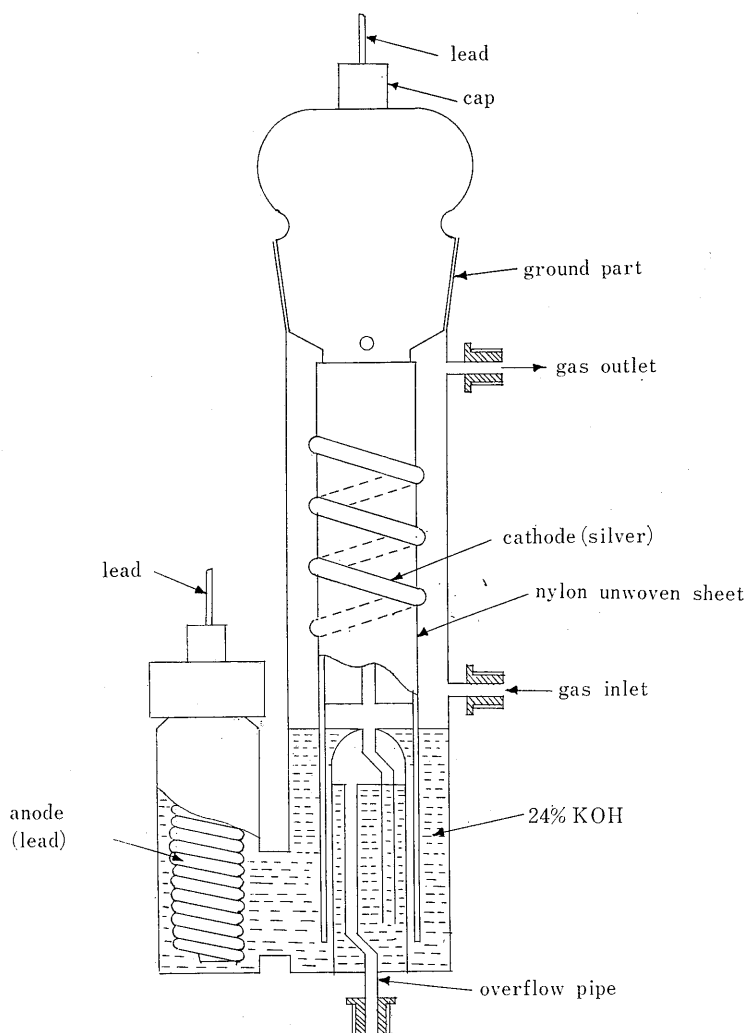


Fig. 3 Measuring element

2.1.3 Measuring element

The structure of the measuring element is illustrated in Fig.3. The silver cathode and lead anode are separated by nylon unwoven sheet. The anode is a lead wire rolled in a spiral and is so set that easy removal is possible for cleaning and other maintenance of the electrode. In the past ³⁾Hersch and ⁴⁾Baker et al. have informed an element of such a structure as having a cathode set over a porous vinyl chloride sheet covering directly around the cylindrical lead foil. But since this structure is defective because of its difficulty in cleaning and maintenance of the lead electrode, the lead anode was improved so as to simplify removal and exchange.

The cathode is a silver wire of 0.4 mm diameter rolled in a coil of 5 mm diameter which covers nylon unwoven sheet in a spiral. In the past ³⁾Hersch and ⁴⁾Baker et al. used an element in which a silver cathode net is set closely over a cylindrical porous vinyl chloride sheet impregnated with the electrolytic solution, and ³⁾Hersch used such a structure as having a cathode of silver plate bent in M type which is submerged in the electrolytic solution. But in case of the former it was difficult to bring the cathode uniformly in contact with the porous sheet, and especially immediately after assembling, large fluctuation of sensitivity occurred occasionally due to the change in the area of the cathode in contact. As for the latter, there is a possibility of change in the contact surface of the cathode due to the change of liquid level of the electrolytic solution according to the mechanical vibration. This is regarded as especially inadequate for use on the actual spot in the factory where mechanical vibration is frequent. Therefore in this analyser, the tension of silver coil is utilized to bring the silver cathode in uniform contact with the porous sheet.

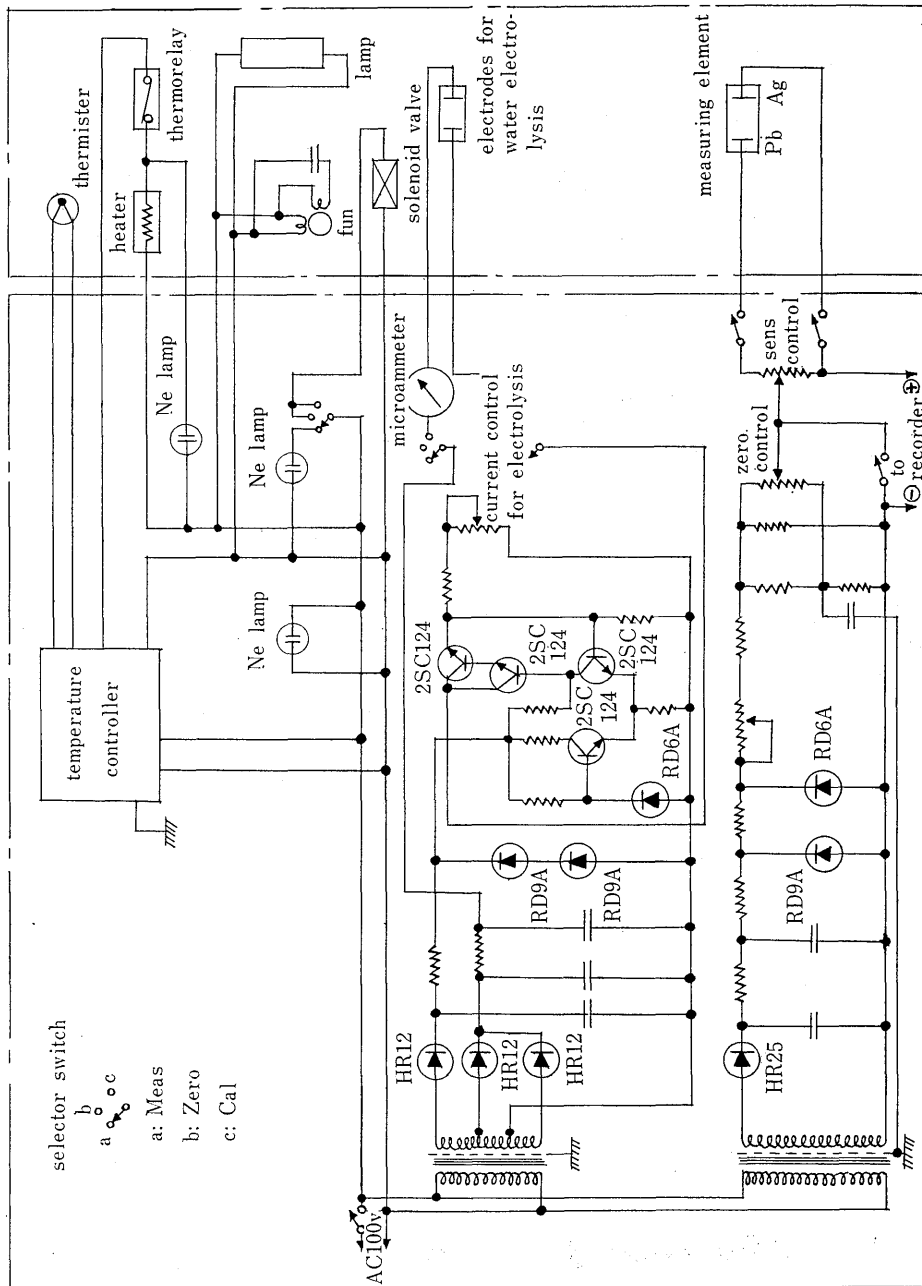
The lower part of nylon unwoven sheet is immersed in 24% potassium hydroxide solution which permeates through the unwoven sheet up to the top owing to the capillary phenomenon. Accordingly the cathode and anode are electrically connected each other by potassium hydroxide solution.

Both the area of cathode and the load resistance are selected suitably according to the range to be measured.¹⁾

During use for a long period it was observed that the liquid level in the measuring element rises gradually. This is considered to be due to the difference in the temperature gradient between the saturator and the measuring element and to the difference in the concentration of both electrolytic solutions (that is to say the difference in water vapour pressure). Therefore an overflow pipe as shown in Fig.3 is provided in order to keep the

liquid level of the electrolytic solution in the measuring element constant. As the overflow pipe is connected with the measuring element through the electrolytic solution, the air outside is entirely excluded from the element.

2.2 Manipulating part



part is illustrated in Fig.4. The load resistance is a 10-turn helipot suitably determined according to the measuring range. Both terminals of helipot are connected with the cathode and anode respectively, and the voltage between the anode terminal and the slider of helipot is used as the input for the recorder.

If oxygen is absent in the sample gas, the electric current should be theoretically zero, but practically there happens some current (Usually below 1~2 ppm calculated as the concentration of oxygen). This is caused by the dark current of the measuring element itself due to the impurity in the electrolytic solution and others and the leakage from the piping (all is made of copper). The zero point regulating circuit is provided so as to compensate the amount of current as above. This circuit is a kind of potentiometer (a 5-turn helipot is used and the output is ± 1 mV), which is inserted in series in the input side of the recorder.

The constant current circuit is provided to flow direct current through the platinum electrodes at the time of calibration of the scale. This circuit is used for avoiding the fluctuation of the indicated value. Because the oxygen generating at the platinum electrode appears as incontinuous bubbles, the electrolytic current fluctuates on using constant voltage source, resulting in variation in the indicated value. This variation had a tendency of increasing proportionally to the concentration of oxygen. The electrolytic current is so selected by 10-turn helipot as giving rise to an optional value between 0.2~1 mA (in the measuring range of 0~10 ppm) and 2~10 mA (in the measuring range of 0~100 ppm).

The temperature control circuit is an on-off control system using a thermister as the primary element, by which the temperature in the detecting part is kept constant ($\pm 0.1 \sim 0.2$ deg.) within the range of 40~45°C. When the temperature rises above 65°C owing to some failure, the heater becomes automatically off by the action of thermorelay.

Introduction of the sample gas, introduction of hydrogen gas at calibration of the scale and passage of the electrolytic current are all started automatically by only one selector switch. Namely when the selector switch is set at "Meas." position, the solenoid valve is opened introducing the sample gas into the measuring element, when set at "Zero" position, hydrogen gas is introduced automatically, and when set at "Cal." position, the electrolytic current is turned on permitting the calibration of the scale.

The frontal external appearance of the manipulating part is shown in Photo.2.

The output of this measuring element needs not be amplified and is directly connected with 0~5 mV recorder.

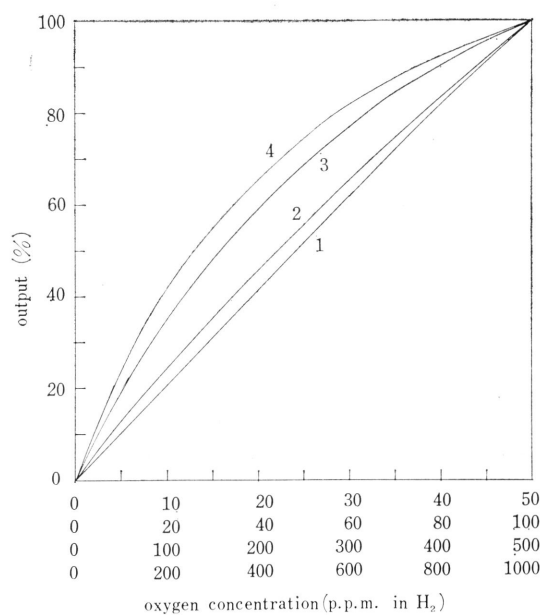
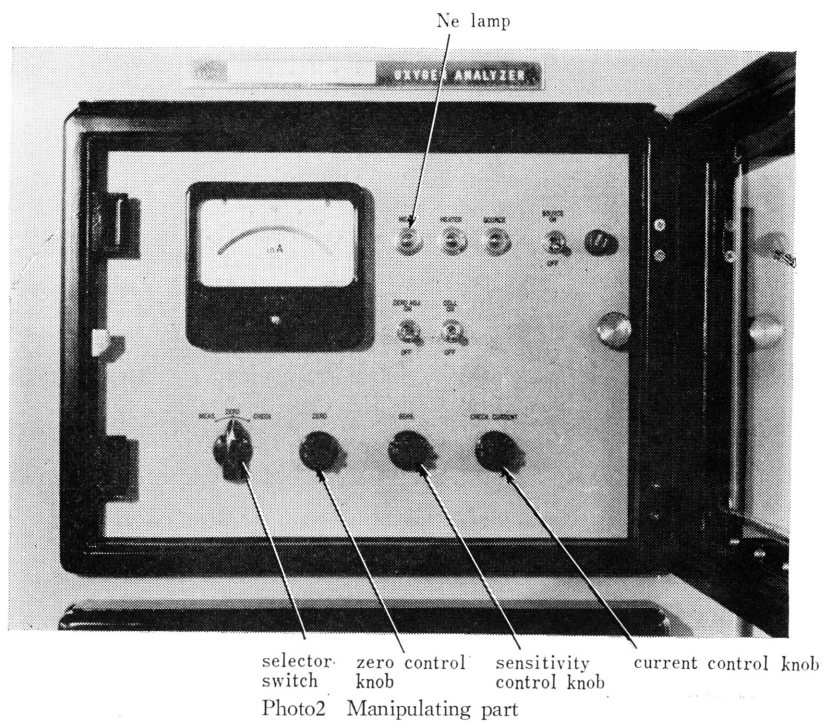


Fig. 5 Calibration curve

40°C; load resistor, 100Ω; Cathode, 3-turn,

1: measuring range~ 0~ 50 p. p. m.

2: " " 0~ 100 "

3: " " 0~ 500 "

4: " " 0~1000 "

3. Results

As the fundamental study has been reported¹⁾ already, some informations will be made here on the reproducibility and stability of above-mentioned analyser manufactured tentatively for continuous measurement when used for a long time.

3.1 Calibration curve

The calibration curve for constant area of cathode and various range are given in Fig. 5. As seen from Fig.5, in a condition that the area of cathode is fixed, the linearity of the curve becomes the lower, the larger the measuring range becomes. In the measuring range smaller than 30 ppm, almost perfect linearity was obtained. With the range larger than this, it was found that the linearity is somewhat improved by reducing the area of cathode.

3.2 Effect of flow rate

The effect of the flow rate of the sample gas is given in Fig.6. As seen from Fig.6, the indicated value is hardly influenced by the rate of flow if it exceeds 300cc/min.

Namely this analyser is markedly characteristic in that it is not influence by the rate of flow over a definite value. This may be said to be a large advantage as the industrial analyser seeing from the point of sampling. Then the change of effect by the rate of flow was estimated at intervals of one month. Namely the change of

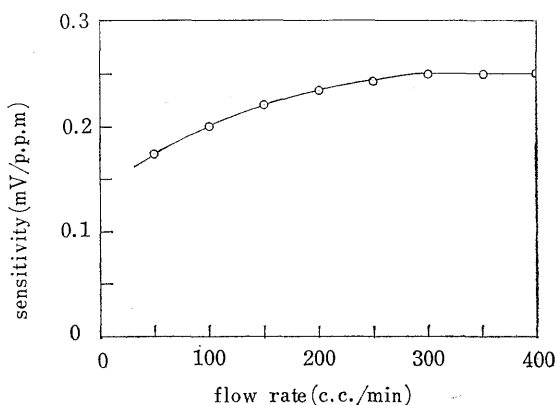


Fig.6 Effect of flow rate

Sensitivity was calculated from the range of 0~30 p.p.m.

indicated values for the rate of flow changing from 300 cc/min to 500 cc/min was estimated under a condition that nitrogen gas containing about 50 ppm oxygen is flowing. As the result, such change in values as 0.8, 1.2, 1.2, 0.7, 1.4, and 1.1 ppm was observed. From this it may be said that the effect of the rate of flow is small and this analyser manifests good stability in respect to the influence from the rate of flow.

3.3 Reproducibility

The reproducibility of indicated values (estimated three times repeatedly) was investigated at intervals of one month in case of flow of nitrogen gas containing about 20 ppm and 50 ppm. The rate of standard deviation against mean values(%) calculated from three estimations is given in the table below.

conc. of oxygen(p.p.m.)	May	June	July	Aug.	Sep.	Oct.
20	0.5	1.3	0.4	0.6	0.0	1.0
50	0.2	0.6	1.2	1.1	0.9	0.4

From this table the analyser seems to have a satisfactory reproducibility for industrial use.

3.4 Response time

In the test for six months the response time up to 90 % response was within the range of 1.8~2.1 min.

4. Portable type oxygen analyser

Based on the experience in the tentative assembling of continuous analyser described above, a portable type oxygen analyser for laboratory use was manufactured subsequently. As its principle as well as its characteristic in operation is identical with that mentioned above, merely the structure of the analyser made for trial will be presented here.

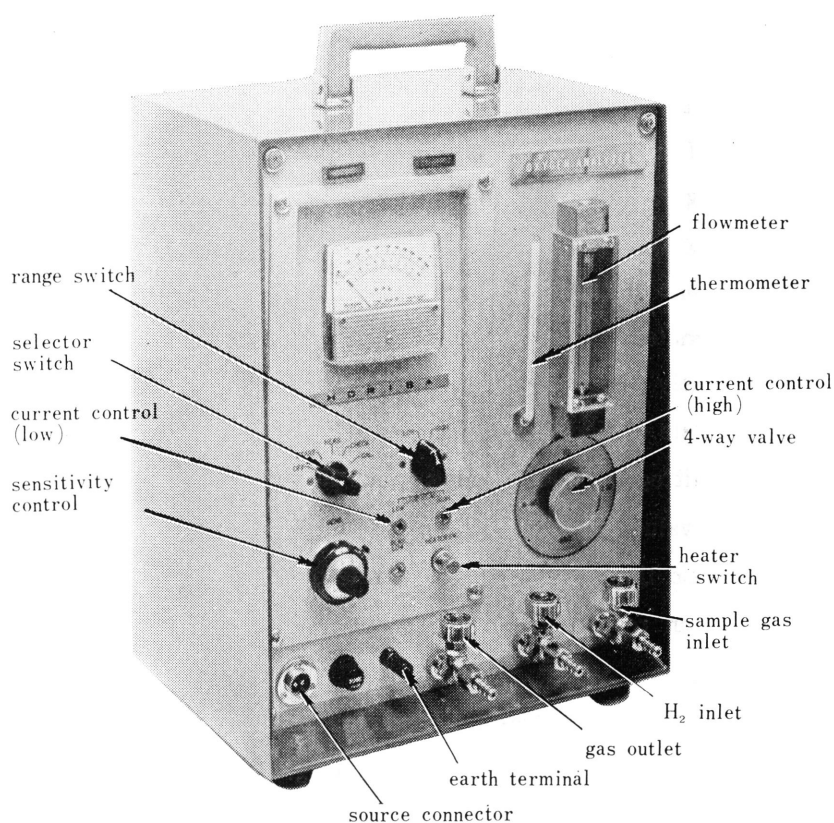


Photo 3 Portable type oxygen analyser

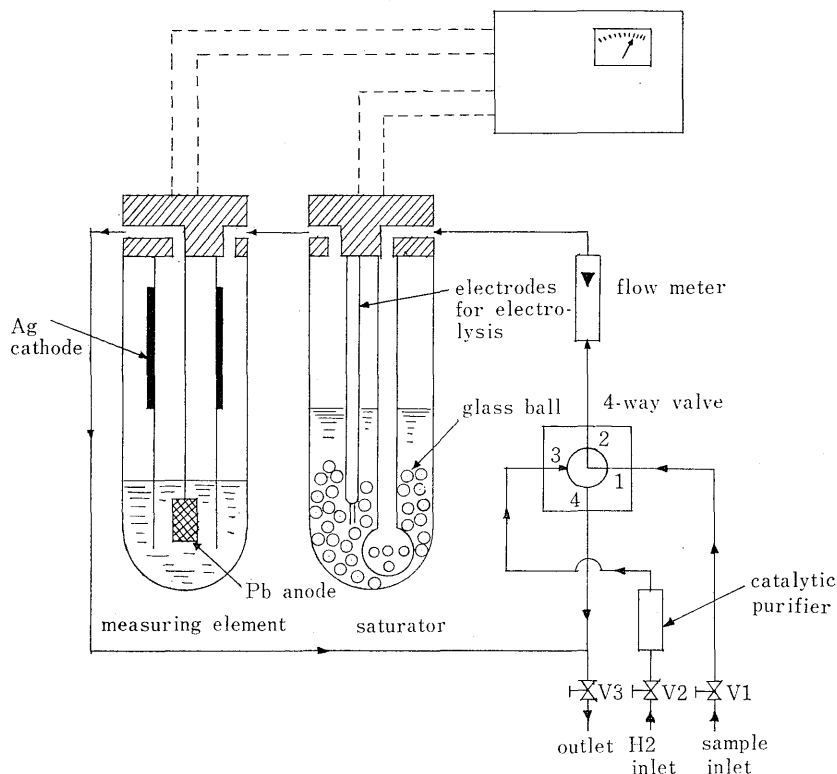


Fig.7 Schematic diagram of portable type oxygen analyser

The external appearance of the analyser is shown in Photo.3 and the shematic diagram is illustrated in Fig.7.

At the time of calibration of the scale the four way valve is set at position 2 and 3 as seen in Fig.7 and hydrogen is passed in the course of valve 2 $\rightarrow$ catalytic purifier $\rightarrow$ four way valve $\rightarrow$ flowmeter $\rightarrow$ saturator $\rightarrow$ measuring element $\rightarrow$ valve 3.

At measurement, the four way valve is set at position 1, 4; the sample gas is run fully between valve 1 and 3 to replace the gas in this passage with the sample gas completely, thereafter by setting four way valve at position 1, 2 the sample gas flows through the course valve 1 $\rightarrow$ four way valve $\rightarrow$ [from here on the same course as in case of hydrogen.]

When the analyser is not in use, the measuring element should be kept from entrance of air by setting the four way valve at position 2, 3 conducting hydrogen and then by changing the four way valve to position 3, 4 keeping the passage (flow meter $\rightarrow$ saturator $\rightarrow$ measuring element $\rightarrow$ 4 $\rightarrow$ 3 $\rightarrow$ catalytic purifier $\rightarrow$ valve 2) always full of hydrogen.

The output current from the measuring element can be read directly from the micro-

ammeter (doubly graduated in 0~10 together with in 0~100 ppm) and this meter is also used for measuring the electrolytic current (refer to Fig.8). In addition on-off control is carried out by a thermorelay near the measuring element.

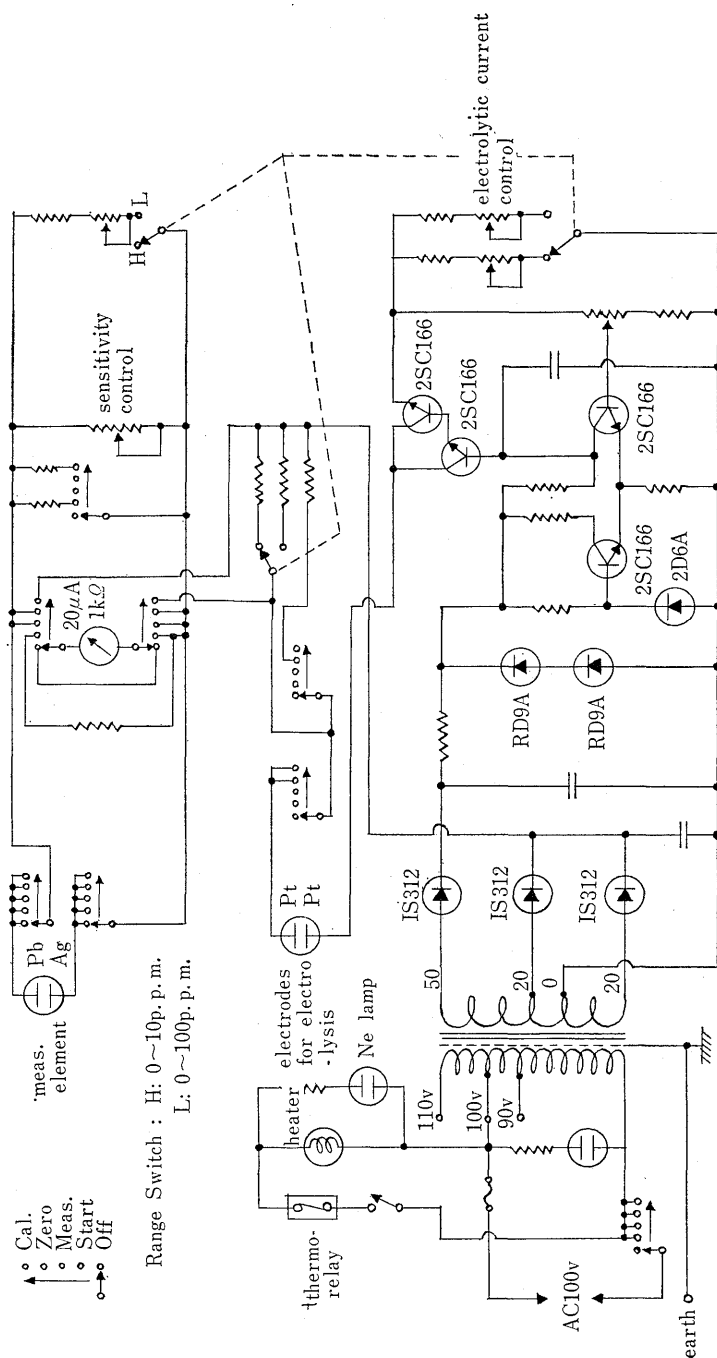


Fig. 8 Electric circuit for portable type oxygen analyser

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