

TRACE OXYGEN GAS ANALYZER

By Toshiyoshi Hamada

Toyoda Factory

I. PREFACE

Along with recent phenomenal development of the electronics industry and chemical manufacturing, demand for high purity gases (argon, nitrogen, and hydrogen for example) is increasing. Accordingly, for the improvement of purity and quality control of these gases, a continuous analysis of foreign material contained in these high purity gases has become an important subject. Often is the case where small amounts of oxygen contained in a non-pure gas become a problem (or when small amounts of oxygen are contained in plant gas at chemical plants) when high purity gas is desired. Also, the case where small amounts of oxygen of less than 10 ppm ($10^{-3}\%$) or sometimes less than 1 ppm can not be disregarded exists. A great demand has arisen for an oxygen gas analyzer which fully meets such requirements and performs with rapid and sensitive reaction.

Industrial instruments (oxygen gas analyzer) of various types have been developed for the use of analyzing small amounts of oxygen. *Table 1* shows the rough specifications of these instrument. Many of these analyzers have employed systems of using a chemical reaction for the measurement principle. In the case of the galvanic cell type analyzer (1), a sample gas is mixed with electrolyte and the oxygen in the sample gas is allowed to be absorbed in the electrolyte for the purpose of analyzing small amounts

of oxygen contained in the sample gas. The amount of oxygen which is absorbed in the electrolyte is in proportion to the partial pressure (density) of oxygen in the sample gas under a constant temperature and pressure.

For the detection section, a type of galvanic battery is provided. This consists of a non-active anode (silver is mainly used) and an active cathode (primarily lead, cadmium is used) in the solution. The battery generates current only in proportion to the amount of oxygen which is absorbed in the electrolyte, due to depolarization of the non-active anode to the oxygen. The current can be measured to obtain the density of the oxygen contained in the sample gas.

In the combustion reaction method (2), small amounts of oxygen in the sample gas and a sufficient amount of hydrogen (separate hydrogen is added when hydrogen is not contained in the sample gas) to react with oxygen are applied for reaction through a special catalyzer called "Deoxo". In this case, heat is created. The heat is measured to obtain the temperature rise.

The ion current method (3) is based on the principle used in a mass spectrometer. The sample gas is fed into an ionization chamber and the small amount of oxygen is ionized by a α -ray from a RI ray source (α -ray source) so that an ion current flows across two polarities of high potential difference. This ion current is measured. However, this method is not applicable for cases where a gas mixture is contained which turns into negative ions by the α -ray.

The colorimetric method (4) is used to discolor a special type of sample chemical by the oxidizing effect of small amounts of oxygen contained in the sample gas. The discoloration is measured by a colorimeter, so that the density of oxygen can be obtained.

The oxygen analyzer equipment, as shown in *Table 1*, limits the measurement range within 10 to 100 ppm, or more. The equipment requires a longer time for response due to application of chemical reaction and construction of the equipment itself, where 20 or 30

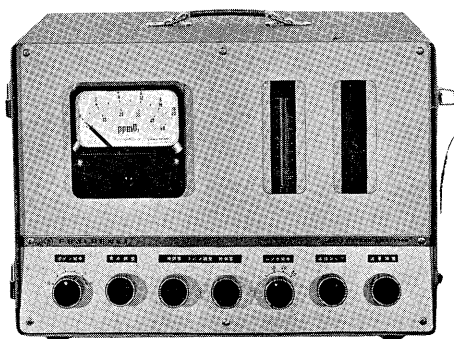


Fig. 1 Oxygen gas analyzer

Table 1 Comparison List of Oxygen Gas Analyzers made by Other Manufacturers

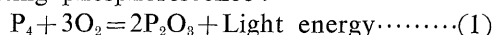
No.	Measurement Principle	Name of Analyzer	Name of Manufacturer	Measurement Range (ppm)	Accuracy (%)	Sample Gas Flow Rate l/hr	90% Response Time (sec)	Power Required
(1)	Method using a galvanic cell (Phase equilibrium method)	Elco Flux Analyzer	Dr. Thiedig & Co. (Germany)	0~20 0~1000	± 5	2.5 ± 5	120	220 V 200 W
		Minoxo Analyzer	Baker & Co. (USA)	1~10 0~100	± 5	22.1 ± 0.3	150	110 V 150 W
		A.S.C. Trace Oxygen Analyzer	Analytic Systems Co.	0~10 0~10,000	± 2	10 ~ 20	60	115 V 200 W
		Beckman Trace Oxygen Analyzer	Beckman Instrument Co. (USA)	0~5 0~10,000	± 5	6 ± 0.6	120	115 V 200 W
		MOM-1 type Trace Oxygen Measurement Instrument (Portable type)	Horiba Seisakusho (Japan)	0~10 0~100	± 5	18 ~ 30	180	100 V 110 W
		Model AE-301 Trace Oxygen Analyzer	Horiba Seisakusho (Japan)	0~10 0~50 0~100	± 2	24 ~ 42	60	100 V 300 W
(2)	Method using a catalyzer (Combustion method)	Super High Sensitivity Deoxo Analyzer	Baker & Co. (USA)	0~200 0~2500	± 2	114	180	110 V 500 W
(3)	Method using ionization of gas (Ion current method)	MSA Trace Gas Analyzer	Mine Safety Appliances Co. (USA)	Unknown	Unknown	100	Unknown	Unknown
(4)	Method using oxidization (Colorimetric method)	DEE Trace Oxygen Analyzer	Davis Emergency Equipment Co. (USA)	0~50 0~1000	± 2	15 ~ 30	120~180	115 V

minutes are usually required for a 100% indication. In addition, the equipment is complicated in construction. In this paper, an introduction and explanation are given hereunder regarding an advanced type of oxygen gas analyzer based on a principle of the luminescent phenomenon of yellow phosphorus. The system was first developed by Nippon Sanso Co. and has been designed anew and manufactured by Fuji Electric under the patent of Nippon Sanso #412260. It is well known that vapor of yellow phosphorus will display an oxidizing reaction with ambient oxygen gas, radiating light energy. However, no oxygen analyzer has utilized this luminescent phenomenon. Entirely different from any of the methods previously mentioned, this system permits oxygen analyzing of extremely small amounts with a full scale of 1 ppm O₂.

Due to the principle which the method employs, the response speed has increased: 1/6 to 1/18 for 90%, and 1/100 to one over several hundreds for 100% response.

II. MEASUREMENT PRINCIPLE

When balanced under ordinary temperature and atmospheric pressure, yellow phosphorus discharges vapor of approximately 33 ppm in the form of P₄. This yellow phosphorus vapor, when small amounts of oxygen exist, displays the following oxidizing reaction, radiating phosphorescence:



In this case, 3 molecules of oxygen for 1 P₄ molecule are applied to the reaction, so that the amount

of oxygen which produces perfect reaction under normal temperature and atmospheric pressure is approximately 100 ppm. This method accordingly is applicable to the analysis of oxygen of less than approximately 100 ppm. For the oxygen of less than 100 ppm in the sample gas shown in formula (1), the radiated light energy is proportionate to the amount of oxygen which reacts. The radiated light energy is extremely small, so that it is photoelectrically converted through a highly sensitive photomultiplier.

The construction of the analyzer is illustrated in Fig. 2. The analyzer is used mostly for measuring

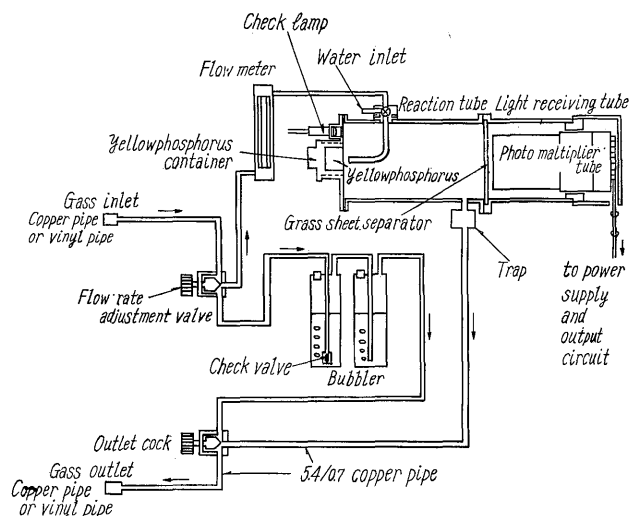


Fig. 2 Composition of oxygen gas analyzer

gas of plus pressure, with the sample gas previously adjusted to approximately 1 liter/min and applied to the gas inlet. Upon measurement, the sample gas is divided at the inlet valve, one part limited (flow rate adjustment) to the determined flow rate at the inlet valve (needle valve), and flows through the flow meter to the reaction tube.

The residual gas flows through the bypass where a bubbler is provided, joins (at the outlet valve) the gas which is discharged from the reaction tube, and is discharged from the gas outlet to outside the analyzer. This bypass for disposal of residual gas after the gas flow rate is adjusted also plays a role for completely purging air (containing approximately 21% O_2) existing in a pipe between the gas inlet and inlet valve prior to the start of measurement. Ahead of the operation start, the inlet valve and outlet valve are fully closed and the interior of the reaction tube is sealed from outside air. However, in the pipe which runs between the gas inlet and inlet valve, some outside air exists, so that the air must be purged upon commencement of measurement.

Sample gas is adjusted to the determined flow and fed into the reaction tube. This is blown against the face of yellow phosphorus inside the reaction tube, where sample gas is dispersed together with yellow phosphorus vapor. The trace oxygen gas reacts with the phosphorus vapor until the vapor reaches the exhaust outlet of the reaction tube and radiates light. Most of the radiated light is reflected against the tube wall which is treated to produce a mirror-like surface, passes through the separating glass sheet, and enters the photomultiplier for current conversion.

III. OUTPUT CHARACTERISTICS

1. Output Characteristics by Sample Gas

The amount of light which is produced by luminescent reaction is, as shown in formula (1), proportionate to the absolute amount of oxygen which

exists in the sample gas fed into the reaction tube. When the sample gas flow rate into the reaction tube is constant, the output is in proportion to the sample gas density. When the sample gas density is constant, output can be obtained in proportion to the flow rate.

1) Output characteristics relative to gas density

Fig. 3 shows an example of output regarding gas density under a constant flow rate.

It is also possible to make the full scale 1 ppm O_2 by increasing the voltage (by means of the gain selector switch shown in *Fig. 10*) to be applied to the photomultiplier tube under a constant flow rate, thus raising the amplification sensitivity of the photomultiplier. *Fig. 4* shows actually measured data at full scale (1 ppm O_2).

2) Flow amount characteristics

Fig. 5 illustrates one example of output versus gas flow rate under a constant density of the sample gas. When the gas flow rate is changed as needed, the sensitivity of the analyzer can be varied. For instance, in measuring gas of high density (near 50 ppm) and when such measurement is made with the standard flow rate, a large current flows through the photomultiplier tube to cause a drift phenomenon (of which detailed information is given in later pages) or to promote contamination of the interior wall of

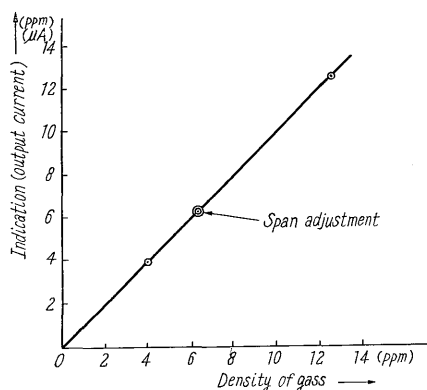


Fig. 3 Relation of oxygen content versus output characteristics

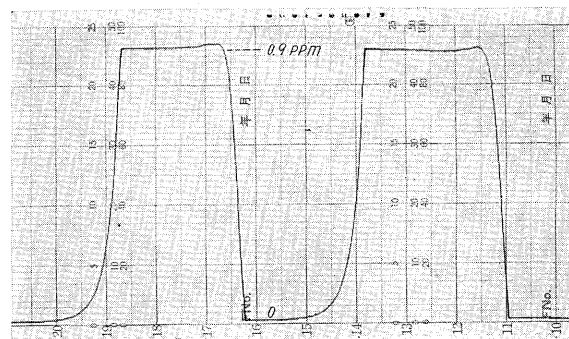


Fig. 4 Data of full scale at 1 ppm

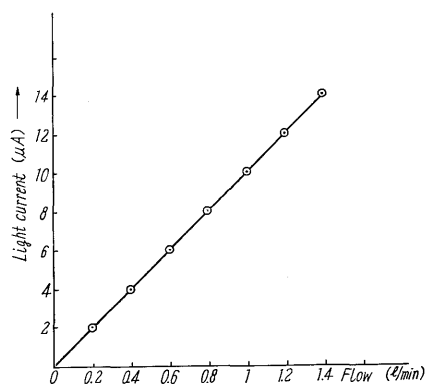


Fig. 5 Relation of gas flow versus output characteristics

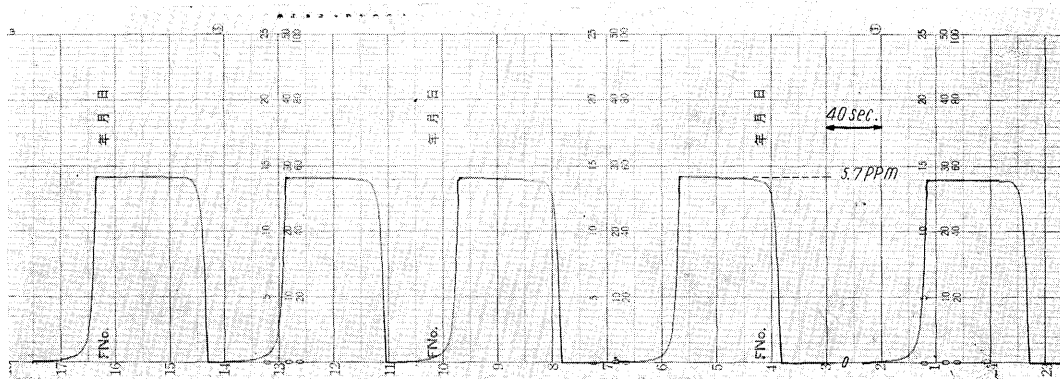


Fig. 6 Response data characteristics (at full scale 10 ppm O_2)

the reaction tube. Accordingly, a method can be used where the sample gas flow rate is reduced and the indication scales are read by compensating for the reduction of sample gas flow rate.

3) Response speed

Fig. 6 illustrates an actual measurement example of the response characteristics.

The figure includes data of response characteristics by the inlet valve opening and closing, where 8 to 9 seconds is required for 90% response.

2. Zero Point Check

Assuming that the inlet valve and the outlet valve are fully closed to stop the feeding of sample gas into the reaction tube, oxygen which remains in the reaction tube is gradually consumed. When no oxygen remains in the reaction tube, light radiation stops and the indicator points to zero.

Usually, it is difficult to produce standard gas completely free from oxygen. Hence, it is necessary to feed hydrogen (as a zero point gas) which is treated with the previously mentioned Deoxo catalyzer. When the sample gas feed is completely stopped in this analyzer, the zero point can be automatically obtained. (Refer to data of the response characteristics in Fig. 6). Should there be any small leak in an ordinary conduit, joint, or packing, oxygen of the atmosphere penetrates and adversely affects proper operation of the indication. However, when a leak exists along the path after the inlet valve, it should be checked by such a method that the gas is stopped and the zero point stability is observed. This provides for easy and simple inspecting.

3. Span Check

The analyzer is provided with a convenient check device (check lamp) in addition to a span check by standard gas.

As illustrated in Fig. 2, a neon lamp is installed facing inside in parallel with the yellow phosphorus container inside the reaction tube.

When the outlet and inlet valves are fully closed to allow the indicator to point to zero and when the

neon lamp is turned on, output current corresponding to the light amount of the lamp flows in the photomultiplier. In this case, a certain constant value is indicated. A linearity relationship as shown in Fig. 7 between current through the lamp and the light current (output) which is derived from the photomultiplier exists. Accordingly, the scale of the instrument may be adjusted as was previously done with standard gas and the lamp current-output current relationship is checked, next time the span check can be done for case by operating switch and variable resistor. The current value which flows through the lamp and the output current value of the photomultiplier (when the lamp lights) can be read on the indicator (microampere meter) located in the front of the analyzer and scaled according to the gas density (when operating the attached switch). The lamp current is adjustable.

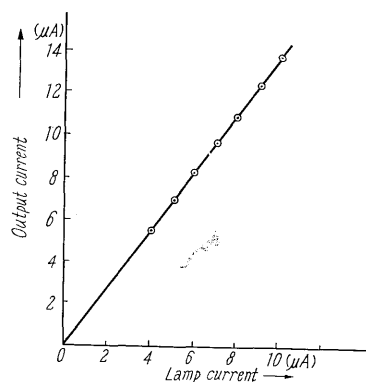


Fig. 7 Relation between lamp current and output

IV. CONSTRUCTION OF EACH COMPONENT

Construction of major components is as shown in Fig. 2.

Construction diagrams are detailed under :

1. Reaction Tube

The reaction tube is 53 mm ϕ in inside diameter and 200 mm in length. It is made of yellow copper with the interior surface coated with 2 μ of gold and 2 μ of rhodium for providing a mirror-like finish. The gold coating protects the inside wall from corrosion by phosphoric acid when reaction is made. In the center part of the cover of the reaction tube, yellow phosphorus is located as contained in a detachable container, 16 mm ϕ in diameter and 11 mm in depth. The sample gas is fed through the blow tube and blown against the surface of yellow phosphorus. A check lamp in parallel with the yellow phosphorus container and water inlet (in common with blow tube) are provided in the reaction tube. The water inlet is used when maintenance or change of the yellow phosphorus is made, where water is applied through the inlet for making the yellow phosphorus wet for safety purposes. Since yellow phosphorus, when completely dried, bursts into flames upon exposure to air, extreme care should be taken.

2. Light Receiving Tube

Light produced in the reaction tube passes into the light receiving tube separated from the reaction tube chamber by a separating glass sheet and is photoelectrically converted by a photoelectric multiplier installed in the chamber. The light receiving tube chamber is a pipe made of vinyl chloride and phenol resin and is designed with full consideration against penetration of outside light into the photomultiplier tube.

The photomultiplier tube is a head-on 10-stage type having an antimony cesium photoelectric cathode and a wide amplification range. The tube used is a #7696 which is sensitive to wavelengths of 3000 \AA to 6500 \AA .

General ratings of the tube are as shown in the following:

1) General ratings

Photoelectric cathode	Semi-transparent antimony cesium
Spectral sensitivity characteristic	E1AS 11
Wavelength at maximum sensitivity	4400 \AA
Position of incident light flux	Head section
Connector	Di-heptal, 14 pin (B14-38)
Position used	As desired
External dimensions	Total length: 143 \pm 5 (mm)
	Valve diameter 53 ϕ max.
	Maximum diameter: 59 ϕ max.
	Effective size of photoelectric cathode 40 ϕ min.

2) Maximum ratings

Anode supply voltage	1500 v
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Between anode and 10th dinode	250 v
1st dinode	300 v
Focusing electrode voltage	300 v
Anode current	750 μ a
Ambient temperature	50°C

3) Typical operation

Anode supply voltage	1250 v	900 v
Between anode and 10th dinode	1/12E _{bb}	1/12E _{bb}
Between dinodes	1/6E _{bb}	1/6E _{bb}
Focusing electrode voltage	1/12E _{bb}	1/12E _{bb}
Cathode sensitivity	85 μ a/1 m	85 μ a/1 m
Anode sensitivity	50 μ a/ μ lm	5 μ a/ μ lm
Amplification ratio (approx.)	6×10^5	0.6×10^5
Dark current (maximum)	0.05 μ a	0.05 μ a

The analyzer is used particularly to measure extremely small amounts of light. Hence, more than 6×10^5 amplification ratio is selected and used. Although the photomultiplier provides a remarkably large amplification ratio, it produces a unique attenuation phenomenon. Such attenuation is caused by fatigue of the photoelectric cathode.

This increases when more light is applied and more current is picked up. This phenomenon is particularly noticeable with a newer multiplier. In actual operation, it should be used in such a manner that minimum current flows in the photomultiplier. This provides for stable amplification.

When using a new photomultiplier, such attenuation phenomenon is inevitable. It is recommended that the multiplier be aged as much as possible before it is used for measurement. The span check circuit is of use for aging the photomultiplier.

3. Gas Circuit

1) Inlet valve

For the inlet valve, a needle type is used. The needle valve also serves as a stop cock. When opening the inlet valve and when the sample gas is applied to the reaction tube, remaining air in the valve enters the reaction tube and produces a large current in the photomultiplier. Such a large current may damage the reaction tube or the indicating meter.

It is mandatory that any air in the valve be purged (including pipes before the valve) prior to measurement operation. To minimize the change of remaining air, efforts should be made to eliminate pockets in the valve and to minimize the size. Fig. 8 shows construction of the inlet valve.

2) Bubbler

Two bubblers, each made of glass with an inside diameter of 40 ϕ and a length of 210 mm and 180 mm are arranged in series. These are used to produce sufficient pressure for forcing sample gas into the reaction tube when the inlet valve is adjusted. The inside part of the bubbler is half filled with trans-

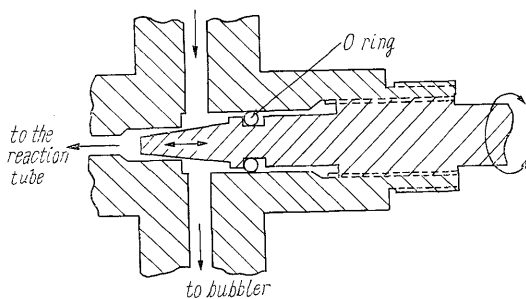


Fig. 8 Construction of inlet valve

former oil. A check valve is provided to prevent reverse flow of the oil.

3) Flow meter

A float type flow meter is used, with triple scales for argon, nitrogen, and hydrogen. Scales are available for flow amount of 1.5 liters/min. For the measurement of small amounts of oxygen contained in other gases, a flow amount correction is necessary.

4) Piping

Metal pipe is used for the piping system through which sample gas flows.

For the measurement of this extent of oxygen, rubber and vinyl pipes can not be used because of adherence of oxygen.

Use of rubber packings for the joint sections are avoided when possible and an air tight system by a tangential line connection directly between the metals is employed. For the bypass circuit between the gas intake and the reaction tube, a copper pipe of 3.8 ϕ

outside diameter and 0.6 mm thickness is used. For the piping running from the outlet of the reaction tube to the gas outlet, a copper of 5.4 ϕ outside diameter and 0.7 mm thickness is used.

4. Electrical Circuit

The electrical circuit of the analyzer is illustrated in Fig. 9.

1) Power supply of photomultiplier tube

A layer-built dry cell with a total voltage of 1440 v is used for the power supply of the photomultiplier tube. The cell has an intermediate tap which supplies voltage to the intermediate dinode of the photomultiplier tube.

The amplification characteristics of the photomultiplier tube are largely affected by the power supply voltage, so that high voltage stability is required.

When a dry cell is used, a stable power supply is obtained and the analyzer becomes transportable.

For voltage drop caused by battery consumption (mostly by discharging of the battery itself), a certain extent of correction can be made through switching of SW_1 and E_3 terminals as shown in Fig. 9.

2) O point correction circuit

When the power is supplied, a current (dark current) is produced through the photomultiplier tube even with no light exists on the light receiving surface. This current is varied depending on the voltage supplied. As long as this dark current exists, a correct O point can not be obtained. Accordingly, a reverse current is supplied to the output circuit

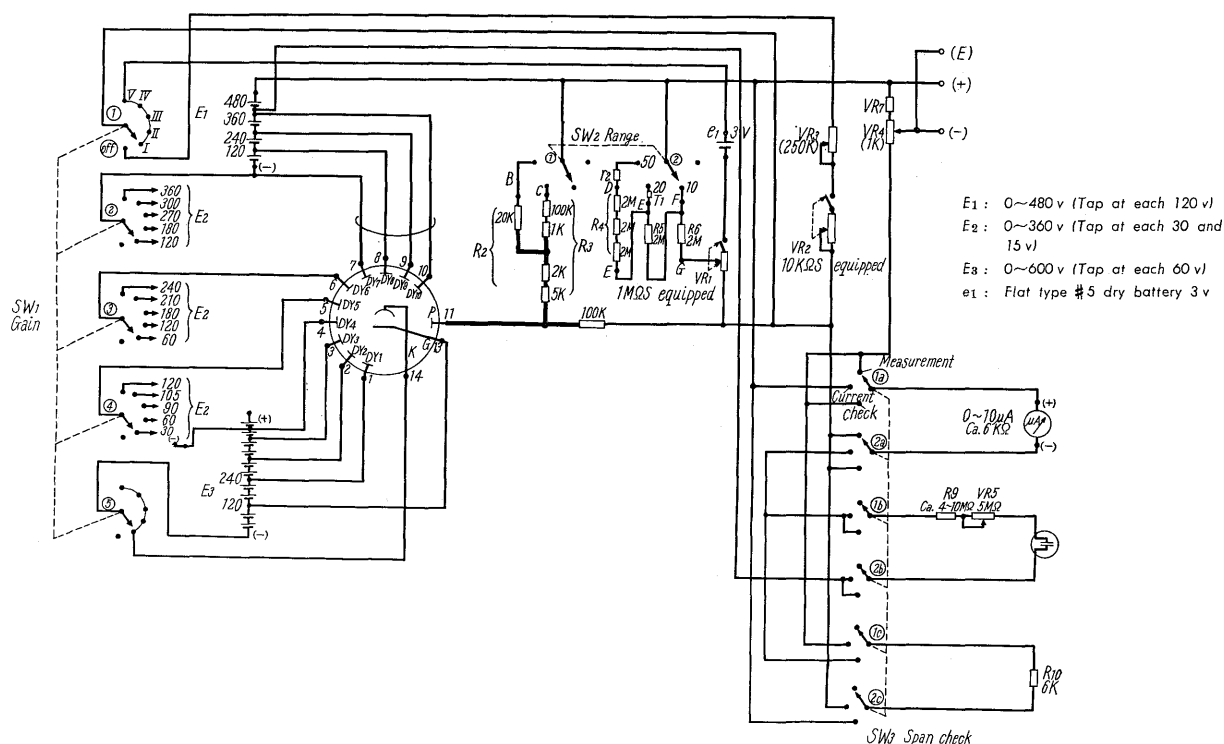


Fig. 9 Electrical circuit

to cancel the dark current. This dark current is very small and is not necessarily adjusted for a normal measurement operation. However, when such adjustment is necessary and performed, the inlet valve and the outlet valve should be fully closed to eliminate oxygen in the reaction tube. Verification is made that the indication is stabilized when the analyzer is allowed to sit and that no air penetrates through both the valves, the pipe between the valves, and the packing of the reaction tube.

3) Span check circuit

The circuit consists of a check lamp, a variable resistor VR_5 for lamp current adjustment, and a selector switch SW_3 . The circuit is used by operating the selector switch to produce a reading (full scale, $10 \mu a$ meter) from the output current of the photomultiplier tube during measurement and the output current of the photomultiplier tube when the check lamp lights.

5. Indicating Meter

A Fuji indicating meter model SM3b with full scale of $10 \mu a$ is used. As well known, this meter is a span band supporting type. This meter eliminates friction often produced in pivot type meters and obtains good results.

6. Connection Receiving Instrument

An output terminal is provided for remote transmission of the output. Since the analyzer output current from the photomultiplier is small and limited to 0 to $10 \mu a$, the receiving instrument is limited to have the fully high internal impedance. The transmitting output into variable resistor $1 k\Omega$ provides a maximum of 10 mv.

V. REMARKS ON HANDLING

Upon handling the analyzer, careful attention should be directed to the following points:

- 1) Measurement is concerned with an extremely small amount (1 ppm).

Much attention must be given to the piping and instruments along the gas passage in order to prevent gas adherence prior to entering the analyzer.

For the piping, for instance, vinyl or rubber tubes can not be used because of external oxygen adherence and penetration, except for a few points in a piping joint part. Most of the parts should be made from metal piping. The interior of the pipe should be cleaned with acid. The use of a pressure-reducing valve is undesirable. When any plastic material is contained in the diaphragm of the pressure-reducing valve, oxygen from the atmospheric adheres and elimination is difficult.

When it becomes necessary to use a pressure-reducing valve due to variation of the original pressure, such a valve should be fully purged by using high purity nitrogen or argon, taking the above

into consideration.

- 2) The photomultiplier tube is very sensitive to even the slightest amount of light.

When the photomultiplier tube is accidentally exposed to external light with voltage supplied, the tube often becomes defective. Accordingly, it is important to verify that no voltage is supplied during maintenance of the reaction tube, such as a change of yellow phosphorus or cleaning of the reaction tube.

As mentioned in Paragraph 2 of Chapter IV, when the slightest amount of high density oxygen is allowed to flow in the reaction tube during measurement, the photomultiplier tube produces an attenuation phenomenon and variation of amplification may result. Care should be taken.

- 3) Yellow phosphorus is harmful to the human body and dry yellow phosphorus bursts into flames when exposed to sufficient air.

Careful attention should be directed to such charac-

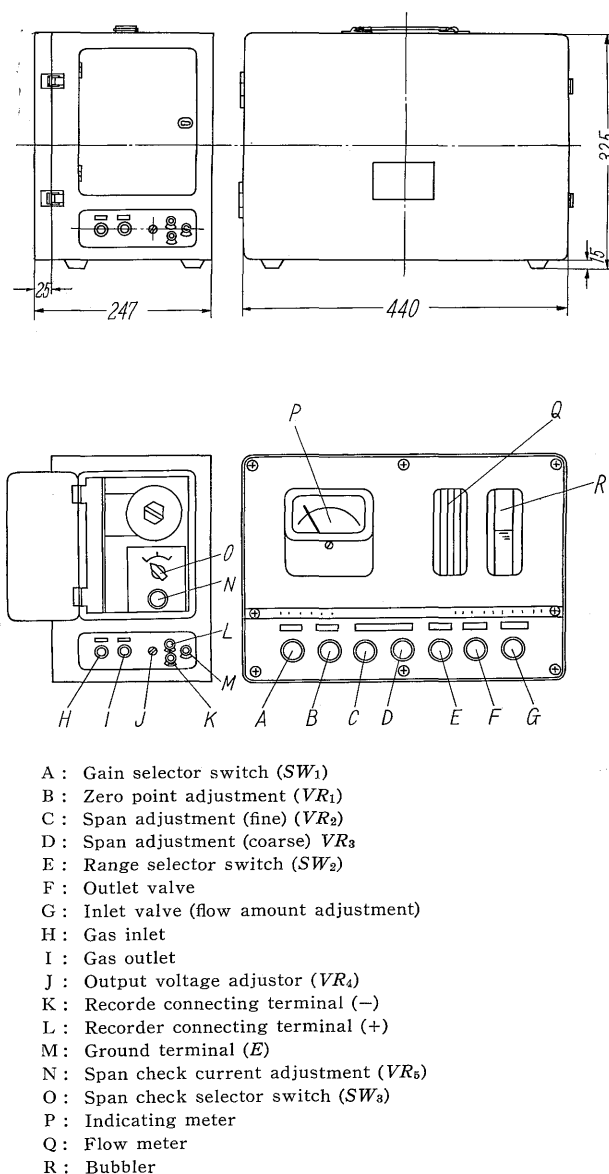


Fig. 10 External view

teristics of yellow phosphorus. In the exhaust gas following the completion of measurement, non-reacted yellow phosphorus is contained. Accordingly, such exhaust gas should be disposed of (by means of a vinyl pipe) in a safe location.

VI. SPECIFICATIONS

Measurement

principle : Luminescent type

Measurement gas : N_2 , H_2 and O_2 in argon (for the measurement of O_2 contained in other gases, flow amount correction is necessary)

Measurement range : 0 to 1, 0 to 10, 0 to 20, 0 to 50 ppm (Indicating meter is scaled at 10, 20, and 50 ppm)

Measurement gas

flow rate : Reaction tube 0.8 liters/min., standard

Bypass Approx. 0.2 liters/min. $\pm 2\%$

Accuracy :

Ambient

temperature : 0 to 40°C

Power supply : 1440v (3 v dry cells contained)

Connecting pipe : Copper or vinyl pipe (outside diameter of 6 ϕ mm, provided that the vinyl pipe as a joint is 6 ϕ mm inside diameter of the intake, less than about 1 cm in length, and 8 ϕ mm inside diameter of outlet).

Output : 0 to 10 mv (0 to 10 μ a indicating meter)

Weight : Approximately 18 kg, portable

The outside dimensions and parts location are shown in *Fig. 10*.

