A CONTINUOUS METHOD FOR MEASURING O₂ AND CO₂ IN EXPIRED GAS.

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In physiological and clinical studies on gas exchange in the lung it is absolutely necessary to measure O₂ and CO₂ in expired gas continuously. In 1957, FOWLER and HUGH-JONES¹⁾ attempted to measure O₂ and CO₂ concentration in a gas sample simultaneously by modifying a mass spectrometer. Recently, ELLIOTT and others²⁾ demonstrated continuous recordings of both the respiratory gases by use of a galvanic cell³⁾, sensitive to O₂ and an infrared CO₂ analyser. Hitherto, several methods of measuring either one of O₂ and CO₂ such as an infrared CO₂ analyser or an O₂ analyser utilizing heat conductivity in a magnetic field have widely been used. However, with the exception of the mass spectrometer, simultaneous measurements of O₂ and CO₂ are not possible as yet.

Over the past several years^{4,5)}, the authors have investigated the application of electric currents produced by the glow discharge of gases in a vacuum tube for gas analysis. As a result of the investigation, it was demonstrated that ions and electrons produced in a glow field are distributed asymmetrically with respect to the field, in the presence of a gas flow in the discharge tube. It was noted that positive charges are distributed more densely at the distal part of the glow field than at the proximal part and vice versa.

Hence, when two electrodes, tentatively called "collector electrodes" are inserted into the tube at points 5-7 cm respectively from the glow field in both proximal and distal directions, the electric current observed through the collector electrodes was approximately proportional to the distribution of the charges which is asymmetrical with respect to the glow field. In other words, the current was proportional to the density of the produced electric charges as well as the flow rate of the sample gas. Especially, it varied with the type and the concentration of the gases measured. For instance, when a sample gas containing O₂ and CO₂ was added to the air, the current showed a deflection, proportional to the CO₂ concentration alone, from the air level,

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but was not so sensitive to O_2 . When the sample gas was mixed with a mixture of pure N_2 and 0.3% CO_2 , the current was sensitive to O_2 alone and not to CO_2 . Therefore, when two vacuum tubes were prepared and the air and the mixture of N_2 and CO_2 were forced to flow respectively through the tubes, O_2 and CO_2 in the expired air could be measured simultaneously. Since the response of the current to the concentration change was very rapid, the analyses could also be made continuously.

APPARATUS

The experimental apparatus is illustrated schematically in FIG. 1, where two discharge tubes are arranged for the analyses of O_2 and CO_2 . A glass tube with an outer diameter of about 6 mm was used for the discharge tube. The tube was shielded with a brass tube which had a large leeway of $7 \times 7 \times 7 \text{ cm}^3$ around the glow field to minimize undesirable stray capacity. This shielding cylinder was connected at the leeway with the mount of an oscillator through a brass tube of 3 cm in diameter. The temperature of the apparatus was generally kept at 45° to 50°C .

The discharge electrode was made of a Pt wire and at its tip a small ball of about 1 mm in diameter was attached. The tips were buried in the glass wall of the tube and not exposed to the inner side of it, facing each other across the path of gas flow. The discharge voltage with a frequency ranging from 20 kc to several 100 kc was supplied from a stabilized oscillator. The voltage was about 2,000 volts from peak to peak.

The electrodes for measuring the current, the collector electrodes, consisted of Pt wire were sealed inside the discharge tube. These were placed in symmetrical order to the glow field at points at a distance of 3–7 cm from the field. In the preliminary experiments, however, 6 electrodes were sealed at 7.5, 10.0 and 12.5 cm distances from the glow field in both the proximal and distal directions. In most cases, the distal collector electrode was grounded directly and the proximal end was led to a DC amplifier with a high input resistance through which the electrode was grounded. The amplifiers had sufficient sensitivity to detect currents of 10^{-12} A.

The vacuum tube had a length of 30 cm and its distal end was connected to a vacuum pump. The proximal end was separated into two prongs: one was an inlet of the sample gas and the other was for the carrier gas. The sample and carrier gases were mixed together at the junction of these prongs at a ratio of about 1:100 in volume. The ratio was adjusted by nozzles placed at the inlets. The vacuum pressure was monitored by a Pyrani-type vacuum meter placed at the junction of the distal ends. The flow rate of the carrier gas was measured by a floater type flow meter and it was maintained at about $300 \text{ ml} \cdot \text{min}^{-1}$ in most cases. In the actual measurements of O_2 and CO_2 , a mixture of 99.7% N_2 and 0.3% CO_2 and room air were used as the carrier gases, respectively.

RESULTS

1) *Relationship between the current through the collector electrodes and the flow rate.* When there was no gas flow, the current observed through the collector electrodes varied mainly with changes of the vacuum pressure and of the applied discharge voltage. At constant pressure and constant voltage, however, the current was fairly constant. When the gas flow was introduced,

FIG. 1. Schematic illustration of the entire apparatus.

FIG. 2. Relationship between the flow rate of gas and the current obtained through two collector electrodes at 5 cm distance from the discharge field. The vacuum pressure was 4 mmHg.

the resulting current of the order of 10^{-11} A was observed in the direction from the distal electrode to the proximal, and it increased linearly with the increase of flow rate of the gas in a flow rate range of 0 to 300 ml · min⁻¹. The relationship between the current and the flow rate is shown in FIG. 2, where the current was obtained in N₂ gas through two collector electrodes placed symmetrically to the glow field at a distance of 5 cm. The vacuum pressure was kept constant at 4 mmHg. The increase rate of the current was about 0.9×10^{-11} A versus the flow rate increase of 100 ml · min⁻¹.

2. *Dependency of the type of gas on the current.* The current observed through the collector electrodes varied with the composition of the gas tested. The currents obtained in media of O₂, N₂, CO₂ and various gas mixtures are shown in FIG. 3, where the flow rate was kept at 300 ml · min⁻¹ and the vacuum

FIG. 3. The currents observed when CO₂, O₂, N₂, air and three gas mixtures were made to flow.

pressure, at 4 mmHg. The highest current was observed in air, and the lowest, in pure CO₂ gas. The current level in air was higher than that in the mixture of O₂ and N₂, in other words, when O₂ and N₂ were mixed, the current of the mixture became higher than that of the respective constituent gas.

On the other hand, when CO₂ was mixed with air, the current level in air lowered at a rate proportional to the CO₂ concentration.

3. *Relationship between the current and the position of the collector electrodes.* The current through the collector electrodes is believed to correlate strongly with the quantity of electrons or ions arriving at both the collector electrodes, which may depend on the flow rate and the diffusion velocity as well as the elimination rate of charge due to recombination. This is well recognized from the experimental results which showed a reduction of the current along the travelling direction of the tube. For instance, when one electrode was close to the glow field and the other was at a considerable distance from it, the current was limited rather by the quantity of ions or electrons arriving at the distant electrode than by that arriving at the closer electrode. In TABLE 1 are shown

TABLE 1.

Currents measured in air through one collector grounded electrode and one of five other electrodes: The six electrodes were placed in symmetrical order to the glow field at 7.5, 10.0 and 12.5 cm distances from the glow field in both the distal and the proximal directions. The negative sign of the current indicates that the direction of current flowing outside of the glass tube is from distal to proximal side. The current in the opposite direction is positive.

Current: $\times 10^{-11}$ Amp.

Electrode No.	1	2	3	4	5	6
Distance between collector electrode & glow field: cm	Proximal			Distal		
	12.5	10.0	7.5	7.5	10.0	12.5
Experiment No. 1	-1.86	-4.74	-11.00	-4.83	-2.16	earth
2	-2.00	-5.34	-17.30	-7.00	earth	2.36
3	-2.00	-5.34	-18.33	earth	7.67	6.00
4	-1.33	-3.33	earth	17.66	16.66	10.33
5	-1.00	earth	1.67	5.33	4.83	4.66
6	earth	0.13	0.00	1.66	0.83	0.16

the currents which were measured in air through six electrodes which were arranged symmetrically with respect to the glow field at 7.5, 10.0 and 12.5 cm distances respectively. The vacuum pressure was 3.9 mmHg. The flow rate was $150 \text{ ml} \cdot \text{min}^{-1}$. As shown in TABLE 1, the direction of the current was always contrary to that of the gas flow, namely, the distal part was always the source of the electric current.

In experiments No. 1 and 6 shown in TABLE 1 the distal and proximal electrodes of 12.5 cm distance were led to the earth, respectively. Namely, the earth point was symmetrical to the glow field in those two cases. As shown at the top and bottom lines of the table the currents measured between the No. 6 electrode which was grounded and each one of the other five electrodes were constantly higher than those measured between the No. 1 electrode

and each one of the other five. Hence, the number of effective negative charges colliding with the grounded No. 1 electrode seems to be less than that of the positive charges colliding with the grounded No. 6 electrode.

On the other hand, in experiments No. 3 and 4, both the distal and proximal electrodes of 7.5 cm distance were grounded and, since they were fairly close to the glow field, they should be supplied with a large amount of positive or negative charges. Consequently, the currents observed through the grounded electrode and each one of the other electrodes which is located at a farther distance should be limited by the quantities of the effective charges colliding with the latter electrodes. As shown in TABLE 1 the absolute magnitude of current measured between the grounded No. 4 electrode and the respective electrode of No. 1 and 2 was less than that obtained between the grounded

FIG. 4. Chromatograph patterns, when 0.3 ml of gas mixtures of 16.0% O₂+4.4%CO₂ and 29.3% O₂+6.1%CO₂ were given respectively to the carrier gas through an activated charcoal column. The carrier gas was air at 45°C.

No. 3 electrode and the No. 5 and 6 respectively. This fact seems to suggest that the quantity of the effective positive charge on the distal electrodes was higher than that of the negative charge on the proximal electrodes at the same distance.

FIG. 5. Chromatograph patterns obtained when 0.3 ml gas mixtures of 16.0% O₂+4.4%CO₂ and 29.3% O₂+6.1%CO₂ were added respectively to the carrier gas. The carrier gas was a mixture of 99.7%N₂+0.3%CO₂.

4. *The changes in current due to mixing of various kinds of gas.* When O₂, N₂ and CO₂ were mixed with each other, the current showed characteristic changes, as already described in FIG. 3, where it was demonstrated that 1) the current in N₂ was increased by mixing O₂, while it was not changed by mixing CO₂ and 2) the current in air was markedly decreased by mixing CO₂, while it was not changed markedly by mixing O₂. Such quantitative changes were demonstrated in gas chromatographic patterns shown in FIGS. 4 and 5. 0.3 ml of two gas mixtures, i.e., 16.0%O₂+4.4% CO₂ and 29.3%O₂+6.1%CO₂ were added into the carrier gas flowing at a rate of 50 ml · min⁻¹ and were made to flow through a column of activated charcoal at 45°C. The carrier gases were air and a mixture of 99.7%N₂+0.3%CO₂ in the cases of

FIG. 6. CO₂ and O₂ patterns obtained when 5 different gas mixtures with known compositions were blown into the inlet of the sampling nozzle.

FIGS. 4 and 5 respectively.

In FIG. 4 a small peak of O_2 appeared prior to the main peak of CO_2 : The ratio of the peak of O_2 to that of CO_2 was about 1:100. In the pattern shown in FIG. 5, however, the peak of CO_2 disappeared entirely and only the peak of O_2 appeared as the main peak. In both cases the areas of the main peak were linearly proportional to the concentrations of CO_2 and O_2 respectively.

5. *Continuous recordings of O_2 and CO_2 .* In the above measurements it was clarified that O_2 and CO_2 contained in a sample gas could be measured individually, when the sample was led separately into two discharge tubes whose

FIG. 7. O_2 and CO_2 patterns showing the response time, when a gas mixture of 16.0% O_2 and 4.4% CO_2 was blown into the inlet of the sampling nozzle abruptly.

carrier gases were a mixture of N₂ with CO₂ and air respectively. This fact suggested the possibility of measuring O₂ and CO₂ simultaneously.

When the sample gas was constantly mixed with the carrier gas at a constant mixing ratio by the apparatus shown in FIG. 1, the changes of O₂ and CO₂ concentrations could be obtained continuously. In FIG. 6 are shown the actual curves, recording changes of O₂ and CO₂ concentration, which were caused by blowing sample gases with known compositions via the sample nozzles from bombs into the carrier gases. In the figure, the base line represents the level of air, that is, the base line of CO₂ curve represents a concentration of 0.03%CO₂ and that of O₂ curve, 20.93%O₂. As shown in FIG. 6, the height of deflection was strongly dependent on the concentration of O₂ and CO₂, respectively. Moreover, the response time was very short.

As the response time of the recorder used in the experiment of FIG. 6, was 0.3 sec for a deflection of 25 cm, it was difficult to obtain the accurate response time within 0.1 sec with this recorder. Thus, for obtaining the response time, another galvanometer with a flat frequency response from 0 to 70 cps was used. In FIG. 7 are shown the response curves measured by blowing a gas mixture of 16.0%O₂ and 4.4%CO₂ into the air. The middle line shows the "on" and "off" marks of the sample gas. Because it was difficult to blow the sample gas at a given certain time into the sampling nozzle, the transition time was longer at the "on" time than at the "off" time. The transition time at the "off" time was about 0.1 sec and 90% response time

FIG. 8. Simultaneous records of O₂ and CO₂ in expired gas.

was about 0.1 sec.

6. *Continuous measurements of O_2 and CO_2 in expired gas.* In a similar manner to the curve in FIG. 6, when expired gas was added into the discharge tubes, the changes of O_2 and CO_2 in the airway appeared on the records. Unlike dry gases from bombs, expired gas contains moisture which often causes a fluctuation in the curves of O_2 and CO_2 . Such an influence, however, was easily excluded by placing blocks of silica gel in the passage between the nozzle for the sampling and the discharge tube. The size of the silica gel block must be sufficiently large, otherwise the response time is prolonged.

In FIG. 8 is shown an example of simultaneous recordings of O_2 and CO_2 obtained with expired air from a normal human subject. The calibration curve before and after the breathing was identical within an error of 2%.

DISCUSSION

In a previous paper MOCHIZUKI and KAWAKAMI used a single collector electrode as a detector for gas chromatography. In their paper, the discharge tube had a length of 25 cm, and the distance between the glow field and a metal nozzle which was grounded was about 10 cm. Lately, however, when authors attempted to study the distribution of the effective charges around the glow field by use of a discharge tube of 60 cm in length, it became apparent that the current through a single collector electrode converged on zero after a long period of observation. And it became absolutely necessary to insert two electrodes into the discharge tube to attain a stable current due to moving charges. Thus, the current was measured through a closed circuit formed by these two collector electrodes as shown in FIG. 1. Furthermore, it was clarified that the distribution of the effective charges produced in a glow field was shifted by a gas flow, and that the amount of the charges arriving at the collector electrodes was influenced by the composition of gas.

The current through the collector electrodes should depend on the diffusion and the convection of the effective charges arriving at both electrodes. As shown in TABLE 1 and FIG. 2, in the presence of a gas flow, the quantity of positive charges increased at the distal part and that of negative charges or electron showed a relative increase at the proximal. On the other hand, when several collector electrodes were arranged symmetrically with respect to the glow field as shown in TABLE 1, the currents through a distal grounded electrode and other proximal electrodes were generally larger than those through a proximal grounded electrode and other distal electrodes respectively both the distal and the proximal electrodes being at the same distance from the glow field. This, in turn, may suggest that the amount of effective positive charges arriving at the distal electrode was higher than the negative charges

arriving at the proximal. In other words, the distribution of positive ions was shifted more easily by the gas flow in a distal direction than that of the negative charges. Thus, the occurrence of the current measured in a flowing medium may be ascribed to the fact that the motion of the positive ions is apt to be influenced by the gas flow because of their heavier mass and lesser diffusibility, whereas the motion of the electron receives none or only a slight influence of the gas flow.

As shown in FIG 3 the current in air was far larger than that of pure O₂ and N₂. This fact suggests apparently that the ionization potential of air was lower than that of N₂ and O₂. It is well known⁶⁻¹⁰⁾ that O₂ and N₂ in air combine in the glow field to produce NO. According to the table¹¹⁾ on the ionization potentials of various kinds of gas, the ionization potential of NO and NO₂ are much lower than those of O₂ and N₂. Therefore, the above experimental fact may suggest the production of NO and NO₂ by a combination of O₂ with N₂ in air by the glow discharge. As for the influence of CO₂ on the ionization of air it may be stated that the energy used for the combination of O₂ and N₂ is consumed by CO₂, namely, by the excitation of CO₂ molecules. However, inasmuch as no methods for the measurement of the concentration of CO₂ in the excited state are available, this problem remains unsolved.

The quantities of electrons or ions may diminish due to recombination along the travelling course. Thus, the electrodes placed at a far removed place from the glow field receives only a small amount of electrons or ions. Actually, as shown in TABLE 1, the current observed through two asymmetrical electrodes was limited mainly by the quantities of charges arriving at the distant electrodes. Thus, in order to increase the current, both the electrodes should be brought closer to the glow field. However, when the electrode was placed too close to the glow, the signal to noise ratio markedly decreased. Consequently, usual electrodes were placed symmetrically to the glow field and within a range of 3-5 cm from it.

Under this experimental condition the current change corresponding to a change of 1% CO₂ was about 10⁻¹² A and that corresponding to a 1% O₂ change was 0.5×10⁻¹² A. For measurements of such small currents, the amplifiers used had an input impedance of 0.5×10⁹ ohms or thereabouts, and in order to minimize undesirable noises, capacitors of about 10⁻¹⁰ F were added at the input circuit in parallel with the resistor. These input circuits had a time constant of about 0.1 sec. Therefore, the response time shown in FIG. 7 seemed to depend chiefly on the time constant of the input circuit, although the structure of the sampling nozzle was certainly very important.

The temperature dependency of the current was further tested by varying the temperature of the thermoregulator. No serious change was observed in a range of 25° to 50°C. The influence of water vapor could not be removed

by increasing the temperature alone.

SUMMARY

A new method of measuring O_2 and CO_2 in expired gas by leading the sample to a glow discharge field in a vacuum tube was reported. When a gas is made to flow and is luminously discharged, an asymmetrical distribution of plus and minus charges occurs in the discharge field. Thus, when two electrodes were set in the flow path at some points proximal and distal to the discharge field the current caused by the asymmetric distribution of the charges could be measured through them. As the quantity of discharged molecules depended on the kind of gas, the current also depended on the composition of gas. Thus, the current was used to determine the concentration of the sample gas. When expired gas was introduced with air into the vacuum tube, the current was sensitive only to CO_2 , while, when the sample gas was mixed with a mixture of 99.7% N_2 and 0.3% CO_2 , it was sensitive to O_2 alone. When the mixing ratio of expired gas to the carrier gas was about 1:100, a linear relation was observed between the current and the concentrations of O_2 and CO_2 in the sample gas respectively.

By use of this apparatus a simultaneous and continuous recording of O_2 and CO_2 in expired gas was made possible.

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