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## A STUDY OF PHYSICAL METHODS FOR THE DETERMINATION OF THE TENSION OF ETHER VAPOR IN AIR-ETHER MIXTURES \* † ‡

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### INTRODUCTION

MANY approaches have been made to the problem of determining the ether tension in anesthetic gas mixtures. Most of these have depended on individual samples taken at widely spaced intervals and as a result the observations have been of limited value (1, 2, 3, 4, 5, 6, 7, 8, 9). In the work presented herein an effort has been made to develop a method for the continuous determination of the ether tension of an unknown mixture of gas. It was hoped that any time lag inherent in the method could be kept to a minimum and that a method highly selective for ether vapor could be found.

Many physical properties of the gases encountered in anesthesia were investigated, including velocity of light, diffusion through tubes and orifices, thermal conductivity, dielectric constants and velocity of sound. While some of these properties have been exploited or suggested in attempts to analyze gas (10, 11, 12, 13, 14, 15, 16), the most promising avenue of approach seemed to lie with the velocity of sound.

Attempts to utilize differences in velocity of sound in an unknown mixture of gas for the determination of ether tension were based on work previously done by Geberth (14), Dublin, Boothby, Brown and

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Williams (10, 11, 12) and by Faulconer, Clarke and Osterberg (13). If a source of sound of fixed frequency is placed at one end of a gas-filled, closed tube, the tube will resonate when the length of the tube is one half the wave length of the sound applied. Since the wave length is a function of velocity of sound ( $V = f\lambda$ , where  $V$  = velocity,  $f$  = frequency,  $\lambda$  = wave length), the length of the tube under the conditions described will be proportional to the velocity of sound propagated in the gas confined in the tube.

By utilization of the principle just set forth, an apparatus was constructed (fig. 1) by which mixtures of two gases, in which the velocities of sound were considerably different, could be analyzed. The operation of this instrument depended on the application of a fixed frequency (1,024 cycles per second) to one end of the brass tube and a measurement of the intensity of the sound induced. The intensity of the sound was measured in terms of an electric current set up in a microphone placed at one end of the tube. This current was indicated on a milliammeter after being suitably amplified by a vacuum tube amplifier. By adjustment of the length of the tube with a piston, the point of resonance (maximal intensity of sound) was detectable on the milliammeter. Then, by application of the formula  $V = f\lambda$ ,  $V$  could be determined. If there was a linear relationship between the velocity of sound in a mixture of two gases and the composition of the mixture, the percentage composition of varying mixtures of the two gases could be determined in terms of the length of the tube at the resonant point. Such a calibration was made and found to be roughly correct when checked against known mixtures.

The primary disadvantages of this device were three: 1. Continual manual adjustment of the length of the tube was decidedly inconvenient when it was necessary to follow rapidly changing mixtures of gases. 2. Accuracy was limited by the fact that a rather broad "end point" limited the exactness of the results to within  $\pm 2$  percentage points of mixtures of nitrous oxide and oxygen. 3. The amount of sample necessary for a single analysis was 150 to 250 cc. which required either an excessive flow, for continuous sampling, or the introduction of a considerable lag in the time that the determinations were made.

Many ideas were considered in an attempt to eliminate these disadvantages. These fell into the following categories. The device described might be improved by using a source which gave a sound of higher frequency. Thereby the length and volume of the tube needed would be reduced. It seemed possible that the manual adjustment of the length of the tube could be eliminated by making the adjustment mechanical and causing it to be driven by an electric finder circuit. In this manner the length of the tube would be maintained continually at the point of resonance for the gas contained in the tube. This method was abandoned as presenting too many difficulties in mechanical and electrical design.

A second principle considered required that the length of the tube be fixed and that there be a continuous variation in the frequency of the sound applied to it through a practical range. If this were done, the intensity of the sound would be dominant at one range of frequency compatible with the formula  $V = f\lambda$ . Various means are available for

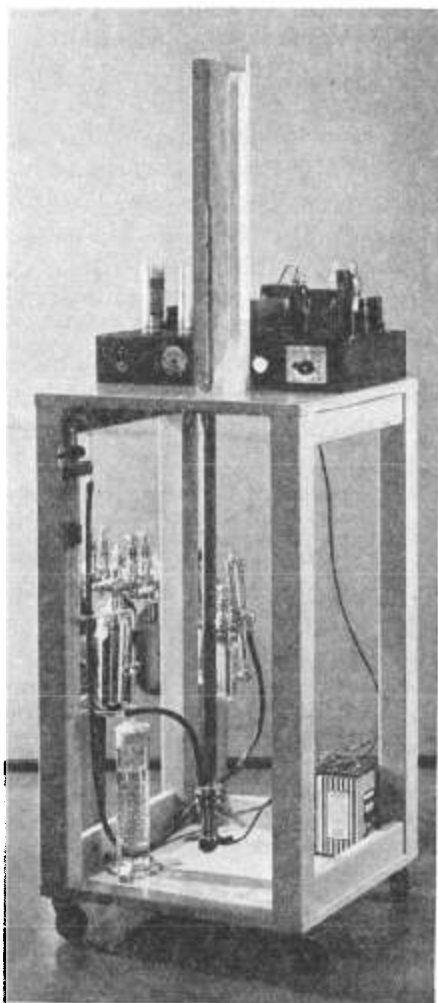


FIG. 1. Original model of sound tube and piston type of acoustic gas analyzer.

the electronic selection and indication of the dominant frequency, which indication could be calibrated in terms of the percentage composition of a two-gas mixture. Designed on this principle, a device could be made to have a very small "dead space" and continuous observations might be made. This principle was not developed further, however, because of the technical complications involved in electronic design.

The third approach considered involved a variety of means by which the gas itself governed the establishment of a characteristic single frequency. The possibility of activating a whistle by the unknown gas mixture was considered and some experiments were done to test this approach. If the dimensions of a whistle are kept constant, then the frequency of the sound generated in activating the whistle with the gas is a function of the velocity of sound produced in that gas. In order to eliminate the annoyance of a loud, audible sound and to reduce to a minimum the gas required for its activation, a Galton whistle, which had a frequency range of about 20,000 cycles per second, was used. It was demonstrated quickly that different pure gases applied to this whistle would produce frequencies which were functions of the velocity of sound in those particular gases. However, grave disadvantages were immediately apparent in this method. When analyzed on a cathode-ray oscilloscope, the wave form of the sound generated was found to be very impure; this rendered the selection of a dominant frequency from a number of harmonics difficult. Also, a considerable difference in the frequency generated was found when the velocity of the flow of gas through the whistle was not maintained constantly. These difficulties led to the abandonment of the method.

The principle of allowing the gas to establish its own single frequency was utilized again when consideration was given to the possibility of initiating in a tube a series of single sound pulses which would traverse the gas in the tube in a period of time depending on the velocity of sound in that gas. When the sound reached the opposite end of the tube, the sound pulse would activate an electronic switch which would start another sound pulse from the sound source. The frequency of repetition of these individual sound pulses would depend on the length of the tube and on the velocity of sound in the gas contained in the tube. This frequency could be measured by a variety of well-established electronic methods and calibrated in terms of percentage of gas present. Further investigation of this method was abandoned when promising results were obtained by utilizing the principle to be outlined next.

#### ETHER METER

The circuit to be described was developed as a result of experiments with measurement of the specific acoustic impedance of the gases to be dealt with. It was found that the application of two microphones to opposite ends of a small brass tube which contained gas, as in the circuit indicated in figures 2 and 3, would complete the circuit of an amplifier-oscillator in which a frequency characteristic of the particular gas contained in the tube would be generated.

In this amplifier the input originates in one of two microphones. The output is carried to the other microphone. The voltage amplifica-

tion of the circuit is 1,000. The two microphones close the ends of a small brass tube provided with a gas inlet and outlet.

If an electric impulse originates at the input microphone, it is instantly amplified and applied to the output microphone where the energy is delivered into the gas-filled tube as a sound wave. An interval of time dependent on the velocity of sound characteristic of the gas contained in the tube elapses before the energy of the sound wave is re-established as an electric impulse at the input microphone and the

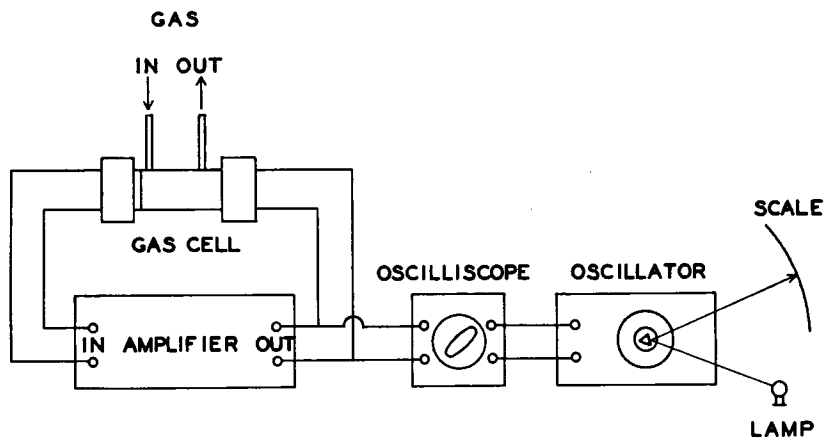


FIG. 2. Schematic layout of oscillator type of acoustic gas analyzer.

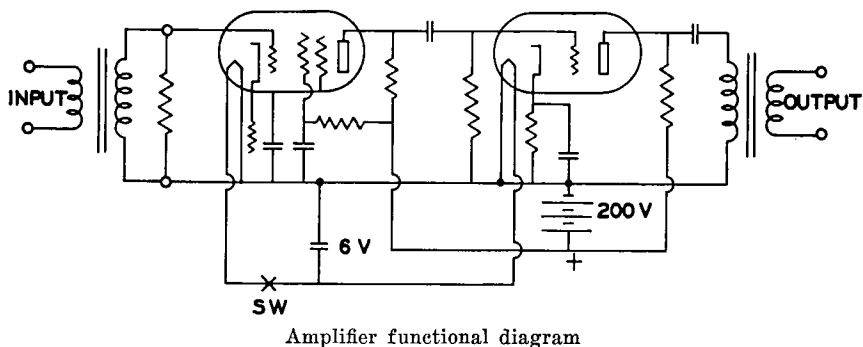


FIG. 3. Functional diagram of the oscillator circuit of the oscillator type of acoustic gas analyzer.

cycle is renewed. Under these conditions the circuit functions as an oscillator, and the frequency of oscillation is a function of the velocity of sound in the gas contained in the brass tube. As the tube was small (about 10 cc. capacity), the problem of "dead space" was minimized. Inasmuch as only a single frequency of oscillation was generated, the definition of an "end point" depended on how accurately this frequency might be measured. Since it was known that a measurement of frequency could be made continuously and automatically, this method

seemed to abolish most of the disadvantages presented in the original piston-tube instrument, and, therefore, attention was devoted entirely to its development.

For the purposes of investigating the method, the following method of determining frequency was used (figs. 2 and 3). The frequency of the amplifier-oscillator circuit was applied to the y-axis of a cathode-ray oscilloscope while the output of a known variable oscillator was applied to the x-axis of the oscilloscope. In this manner, when the two frequencies were in any whole number ratio to one another a Lissajou's figure appeared on the screen of the oscilloscope. From this figure and the knowledge of the frequency output of the oscillator, the frequency of the acoustic circuit could be determined. With my equipment, it was soon found that the easiest figure to establish was a 2:1 figure in which the frequency output of the acoustic circuit was exactly double that of the oscillator. This provided an extremely delicate end point.

Because of the total range of frequency of the variable oscillator, the range in which I was particularly interested was too small to allow sufficiently fine discrimination in reading directly from the dial. To correct this shortcoming, the scale was expanded by reflecting a light beam from a small concave mirror fixed to the center of the dial knob. The beam originates from a fixed source and is reflected to a scale 50 cm. from the knob center (fig. 4).

In operation, the gas mixture to be tested is drawn by suction at a rate of about 100 cc. per minute through the sound tube where it governs

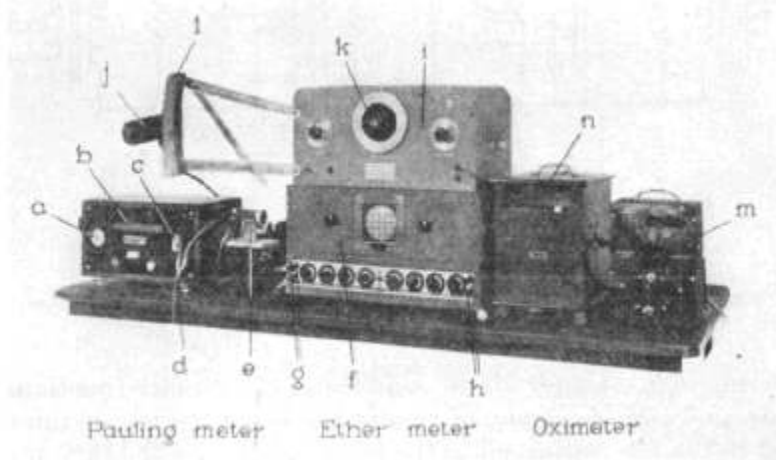


FIG. 4. Apparatus as assembled for clinical observations: *a*, thermometer on Pauling meter; *b*, Pauling meter scale; *c*, sample line flow meter; *d*, gas sample line to Pauling meter and ether meter; *e*, sound tube of ether meter; *f*, oscilloscope; *g*, x-axis leads from sound tube oscillator circuit; *h*, y-axis leads from variable oscillator; *i*, variable oscillator; *j*, light source; *k*, concave mirror; *l*, ether meter scale; *m*, control box of Millikan oximeter; *n*, oximeter galvanometer scale.

the establishment of a characteristic frequency. The dial on the oscillator is adjusted manually until the typical 2:1 Lissajou's figure appears on the screen of the oscilloscope and is brought to as nearly a stationary position as is possible. Then the position of the light beam on the scale is noted.

### CALIBRATION OF ETHER METER

In pilot tests, it was found that mixtures of ether vapor and air containing widely different proportions of ether produced significantly divergent readings when run through the ether meter. The definition of these points in terms of partial pressure of ether vapor was accomplished as follows:

A source of ether vapor in air was set up providing for an inlet of dry room air which passed successively over the surface of liquid ether contained in two bottles, thence through an aluminum condenser spiral to a large test tube containing loose cotton batting and a thermometer. This entire system was placed in an ice water bath where the temperature could be controlled, within  $\pm 0.5$  C., at the desired level. From the test tube containing the thermometer, the air-ether mixture was passed to a carefully calibrated weighing bulb which had glass stopcocks at its inlet and outlet. From the outlet of the weighing bulb the mixture proceeded directly to the sound tube of the ether meter, the outlet of which was connected to a flow meter. The gas in the entire system was moved by suction applied to a flow meter.

The air-ether mixture thus established was allowed to flow until a stable point was indicated on the scale of the ether meter. It then was assumed that a state of equilibrium had been reached, the bulb was closed, removed from the circuit and weighed on an analytical balance.

When concentration of ether vapor of higher ranges was used, it was difficult to control the temperature adequately in this vaporizing system. Hence a vaporizer was improvised which allowed varying dilution of air in an air-ether mixture, saturated at room temperature. Equilibrium was established in the same manner as before by allowing the reading on the scale to become constant, after which the bulb was weighed.

The volume of the weighing bulb was determined by weight when filled with water and also when filled with air, nitrogen and nitrous oxide at known temperature and pressure. The capacity of the bulb was found to be 111.93 cc. at average room conditions. Corrections for buoyancy were unnecessary inasmuch as the same bulb and the same weights (Bureau of Standards calibration) were used throughout this study. The balance used had a sensitivity of 0.05 mg.

The weight of the bulb filled with air at room conditions was determined and from this figure was subtracted the weight of 111.93 cc. (volume of the bulb) of air at the same conditions, giving a figure which

was the tare weight of the bulb. When the bulb had been filled with the unknown mixture of air and ether, it was again weighed and the tare weight of the bulb subtracted from this figure. In this manner the weight of 111.93 cc. of the unknown air-ether vapor mixture contained in the bulb was determined for each of thirty different samples and recorded with the simultaneous reading on the scale of the ether meter for each of these observations (table 1).

TABLE 1  
COMPILATION OF ETHER METER CALIBRATION DATA

Series	Date, 1947	Temperature, Degrees C.	Barometric Pressure, mm. Hg	Weight of Air and Ether in Bulb, Gm.		Partial Pressure of Ether*	Scale Reading, mm.
				Observed	Corrected to 25° and 730 mm.		
	1-22 a.m.	25	736	0.1742	0.1728	150	129
	1-22 a.m.	25	736	0.1732	0.1718	147	137
	1-22 a.m.	25	736	0.1720	0.1706	143	137
	1-22 a.m.	25	736	0.1744	0.1730	151	133
	1-22 a.m.	25	736	0.1749	0.1735	152	133
A	1-22 p.m.	26.5	740	0.1512	0.1484	70	80
A	1-22 p.m.	26.5	740	0.1425	0.1399	42	49
A	1-22 p.m.	26.5	740	0.1336	0.1311	13	26
B	1-23	24	724	0.1629	0.1648	124	118
B	1-23	24	724	0.1635	0.1654	126	114
B	1-23	24	724	0.1620	0.1639	121	122
B	1-23	24	724	0.1635	0.1654	126	120
C	1-24	26.5	723	0.2006	0.2014	244	215
C	1-24	26.5	723	0.2001	0.2010	243	210
D	1-27	26	723	0.1722	0.1733	152	140
D	1-27	26	723	0.1673	0.1684	135	135
D	1-27	26	723	0.1432	0.1441	55	65
D	1-27	26	723	0.1293	0.1301	9	15
D	1-27	26	723	0.1295	0.1303	10	15
D	1-27	26	723	0.1357	0.1366	31	39
D	1-27	26	723	0.1662	0.1672	131	105
D	1-27	26	723	0.1544	0.1554	93	103
D	1-27	26	723	0.1806	0.1817	179	167
E	1-28	26	735	0.1526	0.1511	78	75
E	1-28	26	735	0.1515	0.1500	75	84
E	1-28	26	735	0.1578	0.1562	95	100
E	1-28	26	733	0.1758	0.1745	156	151
E	1-28	26	733	0.1329	0.1319	15	25
E	1-28	26	733	0.1290	0.1280	2	8.5
E	1-28	26	733	0.1308	0.1299	9	12

\*  $pE = 3294.5 (ae - 0.1273)$ .

The data obtained as outlined were used and calibration curves were made by two different processes of reasoning.

*First Method of Calibration.*—The limits of possible weights of mixtures of air and ether vapor contained in the bulb were determined under the pressure and temperature conditions of each observation,



that is, the weight of pure air in the bulb and the weight of pure ether in the bulb. Inasmuch as it was impossible to make an actual observation of the weight of 100 per cent ether vapor at room conditions, this point was calculated as follows: The density of 100 per cent ether vapor at 34.6 C. and 760 mm. of mercury is 0.00311 Gm. per cubic centimeter. By application of the gas laws, this density was calculated in terms of grams per 111.93 cc. (volume of bulb) at the conditions of the observation.

As the weight of a bulb full of pure ether vapor, pure air and an unknown mixture of the two was known, it was possible to calculate the percentage of ether in the mixture as a function of the volume. \*

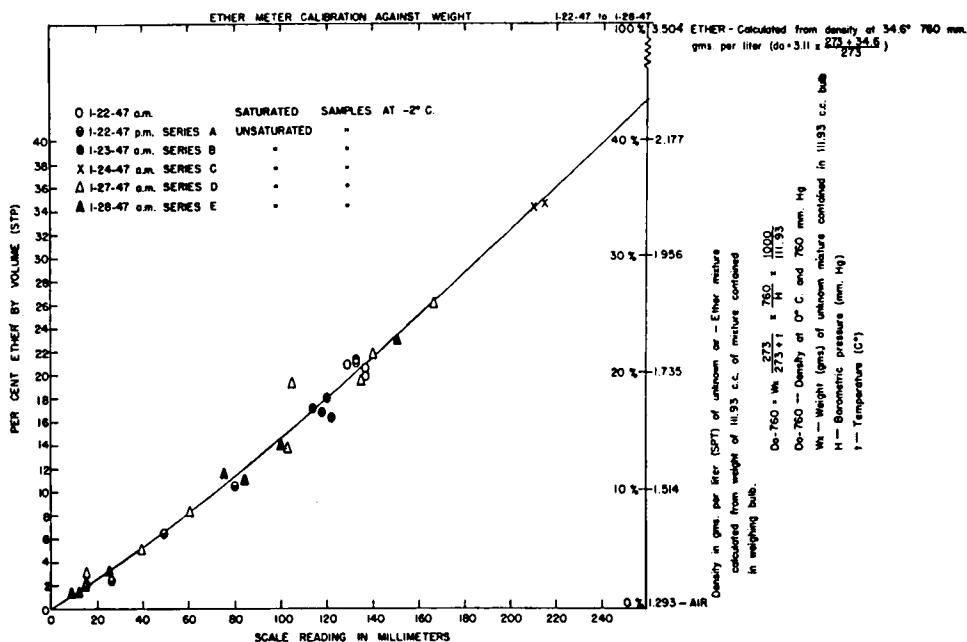


FIG. 5. Calibration of ether meter: first method.

The percentage of ether thus determined in the 30 observed mixtures was plotted on the ordinate of a graph (fig. 5) and the reading on the ether meter scale for each observation on the abscissa. These points describe a gentle curve.

*Second Calibration Method.*—To eliminate the necessity of basing calculations of the weight of ether vapor, under hypothetical (and impossible) conditions, on the assumption that it behaves in accordance with the gas laws, the following method was used:

$$* \text{ Ether per cent} = \frac{ae - a}{e - a} \times 100$$

where: *ae* = weight of bulb volume of air-ether vapor mixture  
*a* = weight of bulb volume of air  
*e* = weight of bulb volume of ether,

and: All weights have been corrected to the same conditions of temperature and pressure.

During the course of these investigations average room conditions of temperature and barometric pressure were 25 C. and 730 mm. of mercury, respectively. All data were corrected to these conditions to minimize any errors inherent in application of correction factors.

From the classical work by Ramsey and Young (17), the following data are taken:

Vapor pressure of ether at 25 C. = 537 mm. of mercury.

Density of saturated ether vapor at 25 C. = 0.002293 Gm. per cubic centimeter. By use of these data, the weight of ether vapor alone in a saturated air-ether vapor mixture contained in the bulb at 25 C. and 730 mm. of mercury is seen to be  $111.93 \times 0.002293 = 0.2567$  Gm.

The density of air at the same conditions is 0.001137. And the partial pressure of air in a saturated ether vapor mixture is  $730 - 537 = 193$  mm. of mercury, or, in terms of volume at 25 C. and barometric pressure of 730 mm. of mercury, the air alone would occupy  $111.93 \times 193/730 = 29.59$  cc. Therefore the weight of air alone in the specified mixture is  $29.59 \times 0.001137 = 0.0336$  Gm.

Hence, the total weight of the saturated ether vapor-air mixture at 25 C. and 730 mm. is  $0.0336 + 0.2567 = 0.2903$  Gm.

By taking the partial pressure of ether vapor in any air-ether vapor mixture as  $pE$  and the weight of the bulb contents of the mixture as  $W$  when corrected to 25 C. and barometric pressure of 730 mm. of mercury, the following algebraic expressions may be made:

$$\text{when } pE = 537, \quad W = 0.2903$$

$$\text{when } pE = 0, \quad W = 0.1273 \quad \text{or} \quad 0.001137 \times 111.93$$

$$\text{therefore} \quad \frac{pE - 0}{537 - 0} = \frac{W - 0.1273}{0.2903 - 0.1273}$$

$$\text{or} \quad \frac{pE}{537} = \frac{W - 0.1273}{0.1630}$$

$$\text{or} \quad pE = \frac{537(W - 0.1273)}{0.1630}$$

$$\text{so} \quad pE = 3294.5(W - 0.1273).$$

The weights of the bulb contents of all the observations made have been corrected to 25 C. and pressure of 730 mm. of mercury and applied to this equation (table 1). In this manner the partial pressure of ether in each of the mixtures was determined and plotted on a graph against a simultaneous reading in millimeters on the ether meter (fig. 6).

The second method has been accepted as the more valid of the two, and from the calibration curve determined a scale reading of the partial pressure of ether vapor has been made in millimeters of mercury and applied to the ether meter.

## Ether meter calibration

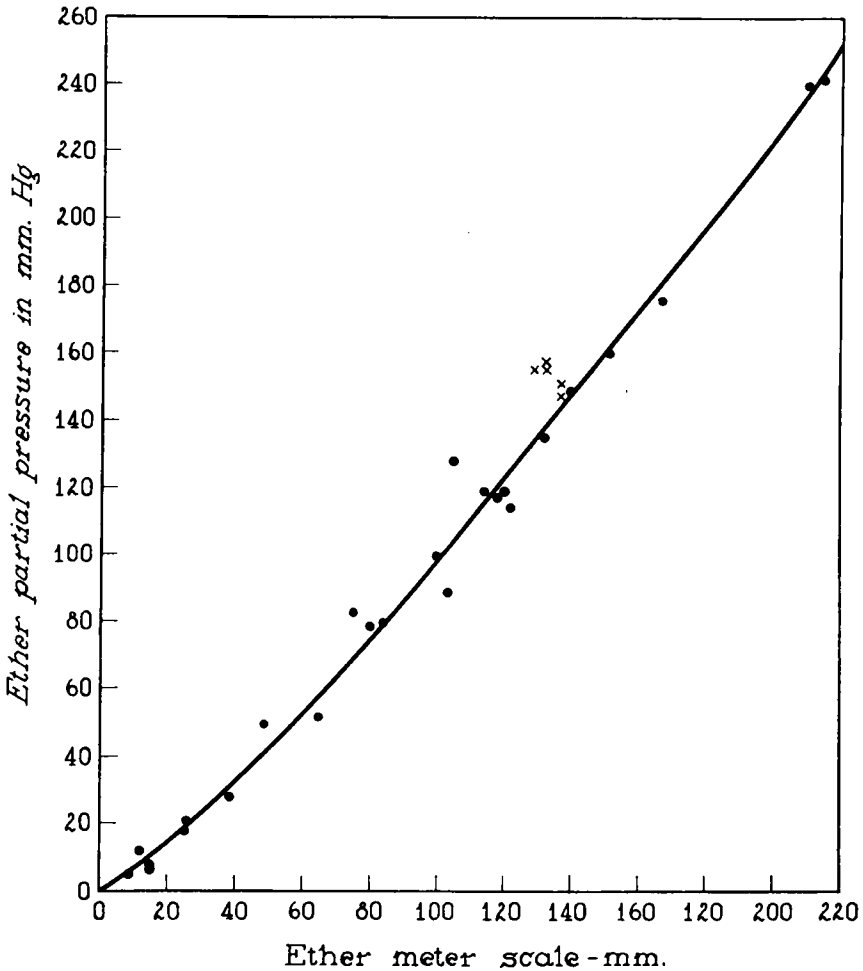


FIG. 6. Calibration of ether meter: second method.

## COMMENT

A further check on the validity of these calibration curves is the fact that the points determined as indicated on the first calibration graph (fig. 5) under the date "1-22-47 a.m." and on the second calibration graph (fig. 6) as "X's" were obtained from mixtures of air saturated with ether at constant and known temperature. Thus, from a standard vapor pressure curve of ether, it is possible to predict the approximate partial pressure of ether present in these mixtures. The temperature of the vapor generation system for the observations mentioned was held at  $-2.5 \pm 0.5$  C. The vapor pressure of ether at this temperature is about 160 mm. of mercury. The observations referred

to fall on the first calibration curve at about 21 per cent ether. The barometric pressure on that date was 736 mm. of mercury, giving a figure of 154 mm. of mercury partial pressure of ether, in close agreement with the partial pressure predicted from the vapor pressure curve. On the second calibration curve the "X's" are seen to fall in the same general range of partial pressure.

Still more evidence supporting the validity of the calibration curve was provided when unknown air-ether mixtures were drawn simultaneously through the Pauling meter and the ether meter. The partial pressure of ether was determined directly by reading on the scale of the ether meter simultaneously with an observation of the oxygen tension revealed by the Pauling meter. The reduction in the oxygen tension below that observed for room air by the diluting effect of ether vapor was found to be in close agreement with the value calculated when accepting the ether meter reading as valid (fig. 7).

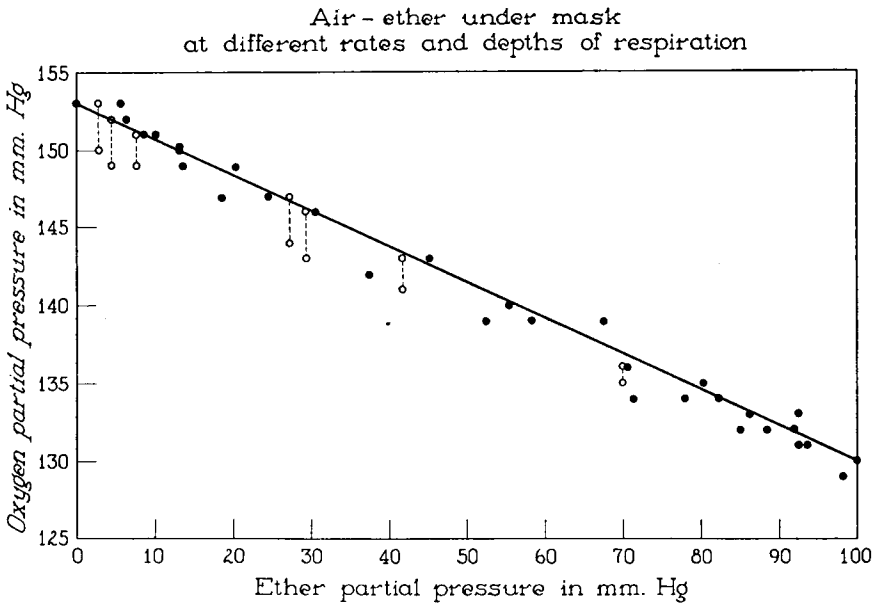


FIG. 7. Oxygen diluting effect of ether vapor. Solid black line represents calculated dilution of ether vapor with oxygen. Dots are observations.

At the present time accuracy of the readings on the ether meter is probably within  $\pm 5$  mm. of partial pressure for partial pressure of ether vapor within the range of from 0 to 200 mm.

The accuracy in clinical use may be somewhat less as a result of variations in percentages of oxygen, nitrogen, carbon dioxide and water vapor in the gas mixtures. However, experience has shown errors from this source to cause deviations of less than 6 mm. of partial pressure in the readings from the scale. This is the maximal

variation in the scale reading between room air and expired air free of ether vapor.

Experiments and developments now in progress indicate that a fully automatic device based on the principles outlined in this paper will soon be available for use. This device will allow for direct and continuous indication of the tension of ether vapor in most of the normally used anesthetic gas mixtures. It will be constructed to allow for photographic recording of changes in the tension of ether vapor in a wide variety of circumstances.

### SUMMARY

Various physical means for the estimation of the tension of ether vapor in air were investigated together with the principles underlying the development of an acoustic air-ether vapor analyzer. Then an air-ether vapor analyzer was designed and constructed.

Calibration of the instrument was undertaken by two methods which are reviewed in detail. From these observations the accuracy of the instrument described under conditions of continuous estimations of air-ether vapor mixtures was found to be within  $\pm 5$  mm. of the partial pressure of ether vapor over the range of from 0 to 200 mm.

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