ANESTHESIOLOGY

The Journal of

THE AMERICAN SOCIETY OF ANESTHESIOLOGISTS, INC.

Volume 11	MAY, 1950	Number 3

CONTINUOUS QUANTITATIVE ANALYSIS OF MIXTURES OF
OXYGEN, NITROUS OXIDE AND ETHER WITH
AND WITHOUT NITROGEN

I. THE ACOUSTIC GAS ANALYZER FOR MIXTURES
OF FIRST THREE GASES

II. THE ACOUSTIC GAS ANALYZER AND THE BECKMAN
OXYGEN ANALYZER FOR MIXTURES
OF THE FOUR GASES *

ALBERT FAULCONER, JR., M.D.,† AND ROGER W. RIDLEY, M.D.†

Mayo Clinic, Rochester, Minnesota

INTRODUCTION

MANY methods have been devised for analysis of mixtures of two gases
for use in anesthesia (1–17).

The analysis of a mixture of three gases presents many difficulties.
Quantitative measurements by selective absorption are limited in that
there are no suitable selective absorbents available for certain anes-
thetic gases or vapors. This method also has the disadvantage that
it usually must be done by an intermittent sampling technic. During
anesthesia concentrations may change suddenly and it is of great value
to have available a continuous analysis. The purpose of this paper
is to describe an acoustic gas analyzer which will measure continu-
ously and simultaneously three gases and further to describe a method
for the determination of nitrogen when present with these three gases.
For the determination of the amount of nitrogen present a Beckman
oxygen analyzer is employed in addition to the acoustic gas analyzer.
This latter instrument developed by Faulconer and Jones was the
natural outcome of a device previously reported for measuring a two

* The apparatus described in this paper was designed and built with the aid of the Sec-
tion on Engineering of the Mayo Clinic.
† Section on Anesthesiology.

gas mixture by utilizing the principle of measuring the velocity of sound through the mixture (18, 19). The calibration of this acoustic tri-gas analyzer also is presented.

The method of quantitative analysis of gas in the acoustic gas analyzer depends on three facts: (1) the gases to be analyzed must be known; (2) velocity of sound which is propagated in the gases to be analyzed must differ significantly and (3) the gas with the lowest velocity of sound must be subjected to complete selective and continuous absorption. These requirements are satisfied when this method is utilized for the continuous quantitative analysis of oxygen, nitrous oxide and ether.

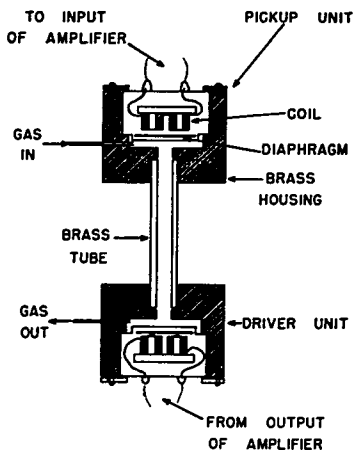## DETERMINATION OF NITROUS OXIDE AND OXYGEN

The speeds of sound through certain gases are given in table 1. It is seen that the rates of 317.2 m. per second for oxygen, 261.8 m. per second for nitrous oxide and 179.2 m. per second for ether vapor provide a considerable spread. Thus when a small amount of oxygen is added to a sample containing only nitrous oxide, a measurable difference in the velocity of sound propagated in this sample will ensue.

TABLE 1

VELOCITY OF SOUND

Gas	Meters per second
Nitrogen	337.8
Air	331.7
Oxygen	317.2
Nitrous oxide	261.8
Carbon dioxide	258.0
Ether vapor	179.2
Water vapor	404.8

By the formula, $V = f(n, \Lambda)$, when V = velocity of sound, f = function, n = frequency, and Λ = wavelength, if the wavelength is kept constant, changes in velocity will be reflected by changes in frequency.

We will consider first analysis of a two-gas mixture, namely, oxygen and nitrous oxide. Samples of the mixture to be analyzed are continuously passed through a small test cell or chamber (fig. 1). A transducer is placed at each end of this chamber or cell. If a sound impulse arises at the lower transducer, this impulse will travel through the mixture of gases in the test cell to the upper transducer. Here it is translated into electrical energy, carried to an amplifier, amplified approximately a thousand times and returned to the lower transducer where it sets up another sound impulse (fig. 2). The time that it takes the impulse to travel from the upper transducer through the amplifier to the lower transducer is infinitesimal compared to the time it takes the impulse to travel through the test cell. The time spent in traveling through the test cell is determined by the velocity of sound propaga-

TO INPUT
OF AMPLIFIER

PICKUP UNIT

COIL

GAS
IN

DIAPHRAGM

BRASS
HOUSING

BRASS
TUBE

GAS
OUT

DRIVER UNIT

FROM OUTPUT
OF AMPLIFIER

GAS CELL DETAIL
(CROSS SECTION)

FIG. 1. Gas cell detail.

tion in the medium contained in that cell. Hence the frequency at
which this circuit oscillates is a function of the velocity of sound in the
substance present in the test cell.

By direct measurement of frequencies in the acoustic gas analyzer,
it has been found that when only oxygen is present in the test cell,
the circuit oscillates at 3180 cycles per second, and when only nitrous

INPUT AMPLIFIER OUTPUT
TO FREQUENCY
MEASURING CIRCUITS

GAS

GAS CELL
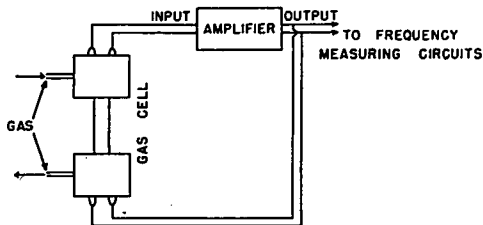
BASIC OSCILLATOR CIRCUIT

FIG. 2. Basic oscillator circuit.

oxide is present, the frequency is 2750 cycles per second. Hence as oxygen is added to nitrous oxide in the mixture, there will be an increase in frequency until all the nitrous oxide is displaced, and the system oscillates 3180 cycles per second.

The oscillatory circuit is tapped and the impulses are carried to a frequency-measuring electronic circuit. This circuit consists of a square wave generator, a filter and a meter. The square wave generator converts the sine waves or oscillatory impulses into square waves of equal size both with regard to width and height. The sum of the
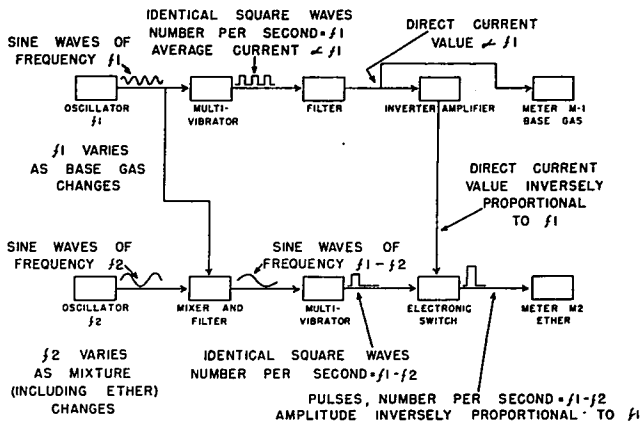
ELECTRONIC CIRCUIT

Fig. 3. Electronic circuit.

square waves gives a direct current which is directly proportional to the frequency, and this current activates meter number one (M1 in fig. 3). This meter is also referred to as the base gas meter (fig. 3).

DETERMINATIONS OF NITROUS OXIDE, OXYGEN AND ETHER

The device described will continuously indicate the ratio of oxygen to nitrous oxide when only these two gases are present. However, to study concentrations of ether as well, it became necessary to develop a much more complicated apparatus. The sample from the ternary mixture (nitrous oxide, oxygen and ether) to be analyzed is divided into two parts. One part passes through an ether absorber containing sulfuric acid (fig. 4), which removes all of the ether in the sample without

affecting the ratio of nitrous oxide to oxygen. This part of the sample is then carried to the base gas cell which activates the base gas meter as described (fig. 5). The other part of the sample goes directly to a second identical test chamber. This is part of another oscillatory circuit which functions in the same manner as that described for the base gas cell. This second test chamber is called the "plus ether cell." In normal operation the gas mixtures contained in the two cells at any moment are parts of the same sample and are identical except that there is no ether vapor in the base gas cell.

An inspection of the velocity of sound table (table 1) reveals that the velocity of sound in ether (179.2 m. per second) is much lower than that for nitrous oxide (261.8 m. per second) or for oxygen (317.2 m. per second). Hence when ether is present in the plus ether cell that system
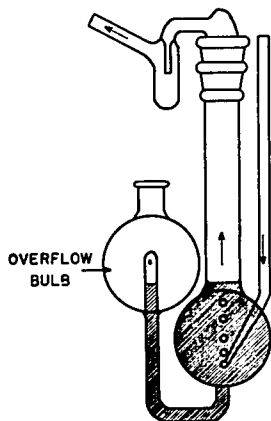

FIG. 4. Ether absorber.

will oscillate at a lower frequency than the base gas system. The difference in frequencies of the two systems is due to the presence of ether in the plus ether cell. The electronic measurement of this difference in frequency activates an ether meter (M2 in fig. 3).

The functioning of the ether meter may be explained as follows: The difference in the frequencies of the base gas and plus ether circuits is a function of the concentration of ether in the sample. The frequency of the plus ether circuit is subtracted from the frequency of the base gas circuit by electronic means.

Now let us assume that the original sample is composed of oxygen plus 20 per cent ether. On reference to figure 6, it is apparent that a

difference in frequency of 320 cycles per second could be made to indicate on the ether meter (M2). If the frequency of the base gas circuit were constant as when only oxygen is present, then the frequency difference between the two circuits would be solely a function of the percentage of ether present. However, when the frequency of the base gas circuit varies as when nitrous oxide is added to the mixture, the difference in frequency is no longer a function of the amount of ether present only. For example, it has been seen that when oxygen is in the base gas cell, a difference in frequency of 320 indicates the presence of 20 per cent ether in the original sample whereas when nitrous oxide is in the base gas cell a difference in frequency of 230 indicates the
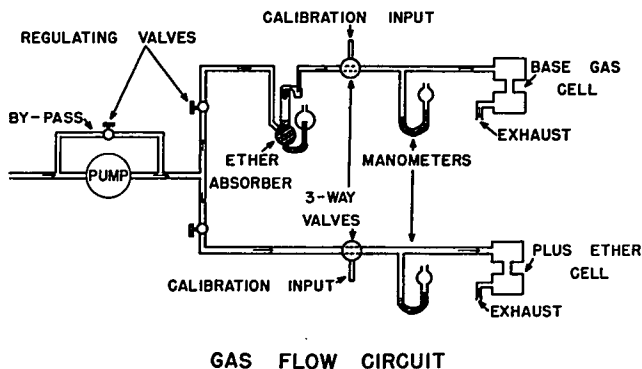

GAS FLOW CIRCUIT

Fig. 5. Gas flow circuit.

presence of 20 per cent ether in the original sample (fig. 6). Hence, if the apparatus were set in a manner that ether meter M2 would read 20 per cent ether with oxygen in the base gas cell, it would only register approximately 14 per cent when nitrous oxide was in the base gas cell. Conversely if set to read 20 per cent ether with nitrous oxide, it would register about 28 per cent with oxygen in the base gas cell. Therefore, some adjustment must be made in order to register the same amount of ether regardless of the ratio of oxygen to nitrous oxide in the mixture. This is done by means of a compression circuit.

The difference in frequency between the two oscillator systems is determined electronically (fig. 3). In each cycle this difference in frequency activates an electronic switch which passes an increment of current, the amount of which is in inverse proportion to the frequency of oscillation in base gas cell. The sum of these increments activates the ether meter, M2. Thus when only oxygen is present in the base gas cell in normal operation, and 20 per cent ether is present in the mixture

a difference in freqency of 320 will be indicated on meter M2 in terms of current output of exactly the same value as when nitrous oxide is present in the base gas cell and there is a frequency difference of 230. This compensation is accomplished by the compression circuit (fig. 7).

In summary then the current indicated on meter, M2, is the function of two values: (1) it is related directly to the difference in frequency between the base gas and plus ether circuits and (2) it is related inversely to the frequency of the base gas circuit.
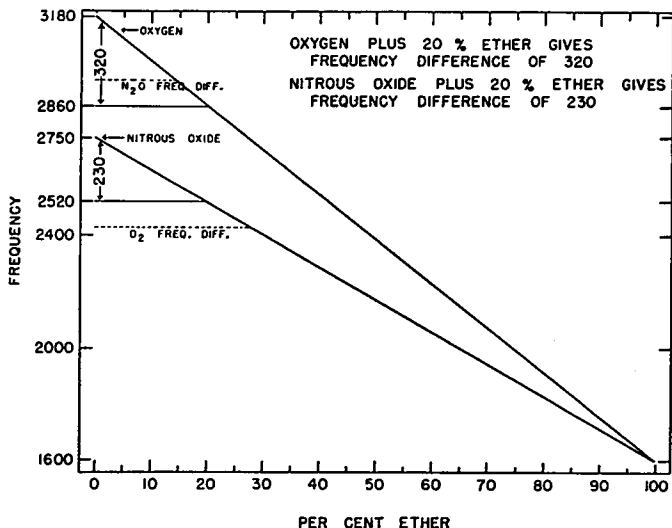

FIG. 6. The effect of changes in the mixture of base gas on the difference in frequency between the base gas oscillator and plus ether oscillator when the concentration of ether remains the same.

Figure 4 is a diagram of the ether absorber. The reaction between the ether and the concentrated sulfuric acid in the absorber is as follows: $H_2SO_4 + (C_2H_5)_2O \rightarrow (C_2H_5)_2SO_4 + H_2O$. The gas flow is passed through the sulfuric acid.

A diagram of the gas channels of the analyzer may be found in figure 5. The pump is of a propulsion type so that the sample of gas is pushed through the cells. This was necessary in order to have the sample arrive at each cell nearly simultaneously. The gas which must flow through the ether absorber and then to the base gas cell must be under a greater pressure in order to offset the flow impedance of the
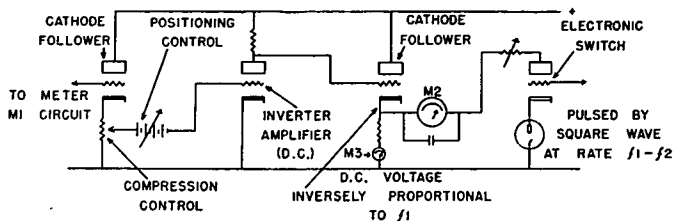
DETAILS OF COMPRESSION CIRCUIT

FIG. 7. Details of the compression circuit.

absorber and thus allow simultaneous arrival of the samples at their respective sound cells. It is important that the two parts of the sample which has been divided arrive at their respective cells simultaneously. The reason for this is shown in the following example: When the analyzer contains oxygen and then the sample is changed to nitrous oxide if the nitrous oxide arrives at one cell sooner than it arrives at the other, there will be a difference in frequency of the two oscillatory systems. This difference will register as ether, thereby making an artifact in the ether reading. Although it is difficult to remove this artifact entirely, it is possible to minimize it to a great extent.
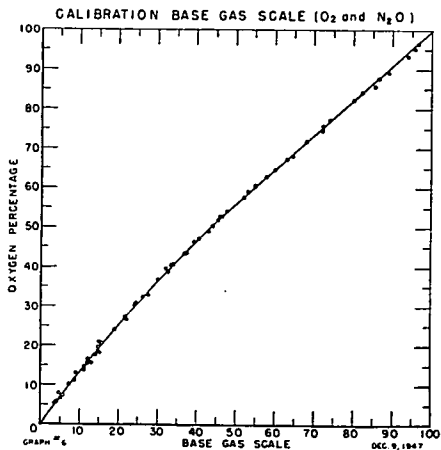

FIG. 8. Calibration of base gas scale.

CALIBRATION

Base Gas Meter.—The first step in the calibration of this instrument was accomplished by weighing different mixtures of oxygen and nitrous oxide and plotting these weights against scale reading of the base gas meter. A glass bulb having a capacity of exactly 112 cc. was used. The bulb was weighed on a balance sensitive to 0.05 mg. However, depending on variations in ambient pressure and temperature, 112 cc. of nitrous oxide weighs only 53 to 57 mg. more than 112 cc. of oxygen. A small error as that introduced by a speck of dust or a small electrostatic charge will cause a substantial error in the calculation of the percentage of oxygen of such a mixture.

The second step in the calibration of the base gas meter was made with the aid of a Beckman oxygen analyzer (Model C). This method of calibration was much more accurate and satisfactory than the weight method. A sample to be analyzed was divided into two parts: one part was carried to the Beckman oxygen analyzer while the other part was drawn simultaneously into the acoustic gas analyzer. The calibration line obtained from this method is shown in figure 8. Of the sixty-two values obtained the scatter is well within ± 1 percentage point with the exception of five values which were within ± 1.5 percentage point. A scatter of the values obtained by weight in twenty-four observations was ± 1 to 6 percentage points.

The acoustic gas analyzer (fig. 9) has two large meters, (fig. 9g) the base gas meter (fig 9i) on the left and the ether meter (fig. 9j) on the right and a third smaller meter (fig. 9o) which appears as M3 in figure 7. Both the base gas meter and the ether meter have scales which are arbitrarily divided into 100 parts. Thus, it is possible to construct a calibration curve for these meters. The percentage of oxygen in the mixture determined by the Beckman oxygen analyzer is placed on the ordinate of a graph and the reading of the base gas scale of the acoustic gas analyzer is placed on the abscissa. Sixty-two points were obtained and a curve drawn (fig. 8). The base gas meter (M1) scale in terms of percentage of oxygen in nitrous oxide was constructed from this information.

Ether Meter.—In calibrating the ether meter scale (M2) it was necessary to add varying quantities of ether vapor to different mixtures of nitrous oxide and oxygen. These "base gas" mixtures of nitrous oxide and oxygen were prepared in cylinders and carefully analyzed to determine their oxygen content in terms of volumes per cent. Thus, when the base gas mixtures to which ether vapor in varying amounts had been added were analyzed on a Beckman oxygen analyzer the percentage reduction in the oxygen content of the total mixture represented the volumes per cent of ether vapor which the total mixture contained. By using this method it was possible to make accurate determinations of the per cent of ether vapor in mixtures with
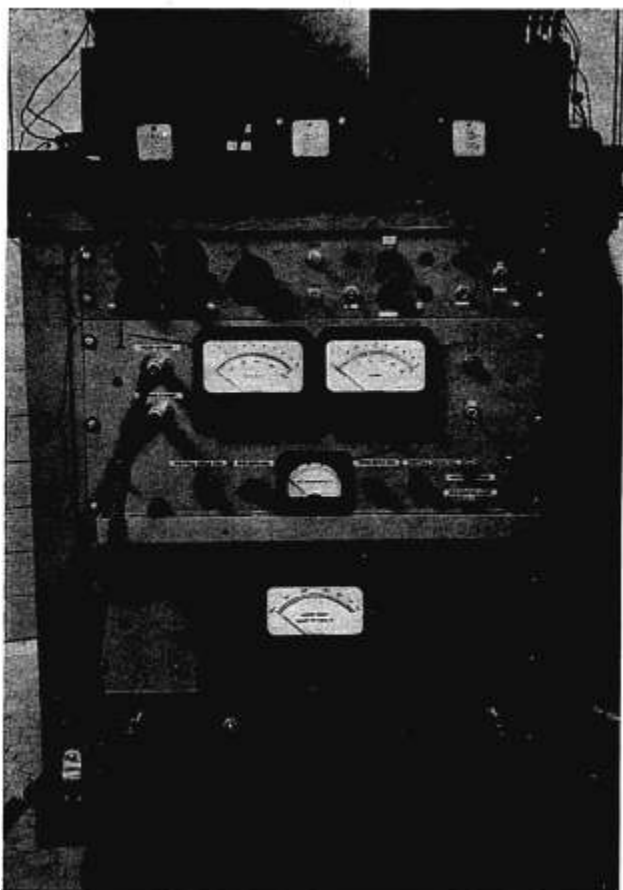
Fig. 9. Face of gas analyzer and recording unit: *f*, main control panel; *g*, acoustic gas analyzer; *h*, cardiotachometer; *i*, base gas meter; *j*, ether meter; *o*, M3.

known ratios of nitrous oxide and oxygen. By drawing a sample simultaneously through the Beckman oxygen analyzer and the acoustic gas analyzer, it was possible to relate varying percentages of ether in different mixtures of nitrous oxide and oxygen to known readings of

ether meter. From these data appropriate adjustment of the compression circuit was made. Following this adjustment the ether meter was calibrated with several mixtures of the three gases concerned. Figure 10 represents the consolidated calibration of the ether meter scale. This graph reveals that with the base gas mixtures from 34 to 100 per cent oxygen there is a very small deviation of the reading on the ether meter scale for any given concentration of ether. Ether added to mixtures of 15 per cent oxygen and 85 per cent nitrous oxide causes a slightly smaller deflection on the ether meter scale than is correct. For 10 per cent concentrations of ether depending on the base gas reading
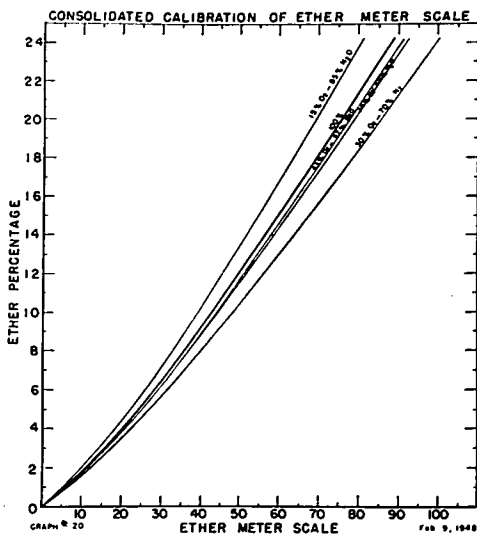

Fig. 10. Consolidated calibration of the ether meter scale.

it is found that the ether scale reading may vary ± 1 percentage point, a discrepancy of 10 per cent. The actual ether meter scale registering concentration of ether in volumes per cent was constructed from the calibration curve obtained with 100 per cent oxygen in the base gas cell. When 100 per cent oxygen is in the base gas cell, the reading of the ether meter is accurate (fig. 11). Of the thirty-nine values obtained to make up this curve thirty-one fall within a scatter range of ± 0.2 percentage point. Thirty-seven fall within ± 0.4 percentage point and thirty-nine fall within ± 0.8 percentage point throughout the range of concentration of ether vapor from 0 to 27 per cent.

DETERMINATION OF NITROGEN IN MIXTURES OF NITROUS OXIDE, OXYGEN, NITROGEN AND ETHER

By calculation it is possible to make a determination of the percentage of nitrogen present in mixtures of nitrous oxide, oxygen, ether and nitrogen, if the Beckman oxygen analyzer is used in conjunction with the acoustic gas analyzer.

The absolute percentage of oxygen in the mixture is determined by direct reading of the scale of the Beckman oxygen analyzer. The
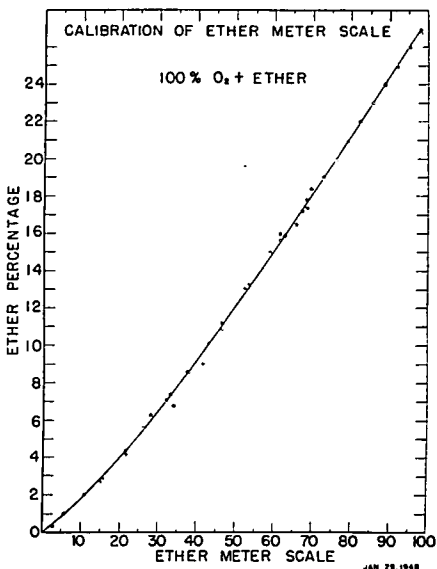

FIG. 11.   Calibration of ether meter scale with 100 per cent oxygen in the base gas cell.

absolute volumes per cent of ether vapor present is determined by direct reading of the scale of the ether meter on the acoustic gas analyzer.   If no nitrogen is present in the gas mixture, the amount of nitrous oxide present is determined by subtracting the sum of the percentage of oxygen and percentage of ether vapor from 100.   If nitrogen is present in the mixture of the gases mentioned, a discrepancy between the percentage of oxygen read on the base gas meter (M1) of the acoustic gas analyzer and the percentage of oxygen indicated by the Beckman oxygen analyzer will become apparent.   This discrepancy is

indicated by a falsely high oxygen percentage indicated on the acoustic gas analyzer base gas meter. The reason for this discrepancy is that velocity of sound through nitrogen is greater than that through oxygen. Knowing accurately the amount of oxygen present as determined by the Beckman oxygen analyzer and knowing further the discrepancy introduced by the amount of nitrogen present as indicated on the base gas meter when compared with the Beckman oxygen analyzer reading, it is possible to calculate the amount of nitrogen present in the four-gas mixture. This calculation is made by use of the following equation:

$$N = 0.73 \left(BG - \left[\frac{100 \times 0}{100 - E} \right] \right). \text{*}$$

When N equals the per cent by volume of nitrogen in the mixture, BG equals the per cent by volume of oxygen indicated on the base gas meter (M1), 0 equals per cent by volume of oxygen indicated on the Beckman oxygen analyzer, and E equals the per cent by volume of ether indicated on ether meter (M2).

Following the calculation of the amount of nitrogen in the four-gas mixture the sum of this per cent, the per cent of oxygen, and the per cent of ether is subtracted from 100 leaving the per cent of nitrous oxide in the total mixture.

Summary

A device is described for measuring quantitatively the components of a three-gas mixture. It is emphasized that this apparatus will measure these three components simultaneously and continuously. Furthermore, with the addition of a Beckman oxygen analyzer, it is possible to measure the components of a four-gas mixture when that four-gas mixture contains oxygen, nitrous oxide, nitrogen and ether.

This acoustic gas analyzer also may be used for the quantitative determination of certain other gas mixtures of interest to the anesthesiologist.

* This equation is derived as follows:

1. 0.73 equals the ratio of the velocity of sound in oxygen minus the velocity of sound in nitrous oxide to the velocity of sound in nitrogen minus the velocity of sound in nitrous oxide.

$$0.73 = \frac{317.2 - 261.8}{337.8 - 261.8}.$$

2. $N = 0.73$ (Base gas reading—Beckman oxygen analyzer reading) $= 0.73 \ (BG - 0)$.

3. With ether present in the sample, a correction must be made to what the Beckman oxygen analyzer reading would be were no ether present.

$$\text{Corrected Beckman } 0 = \frac{100 \times \text{actual reading in } 0}{100 - E}.$$

4. Hence equation is:

$$N = 0.73 \left[BG - \left(\frac{100 \times 0}{100 - E} \right) \right].$$

The validity of this equation has been checked by actual measurement of known mixtures of nitrogen in nitrous oxide and oxygen.

REFERENCES

1. Boothby, W. M., and Sandiford, Irene: The Analysis of Nitrous Oxide for Physiological Work, Am. J. Physiol. 37: 371–377 (May) 1915.
2. Chaney, A. L.: Purity of Nitrous Oxide With Especial Reference to Nitrogen Content, Anesth. & Analg. 12: 42–44 (Jan.–Feb.) 1933.
3. Chaney, A. L., and Lombard, C. F.: Analysis of Nitrous Oxide by Solubility in Water, Indust. & Engin. Chem. (Analyt. Ed.) 4: 185–187 (Apr. 15) 1932.
4. Crouthamel, C. E., and Diehl, Harvey: Gas Analysis Apparatus Employing the Velocity of Sound, Analytical Chemistry 20: 515–520 (June) 1948.
5. Crowley, J. H.; Faulconer, Albert, Jr., and Lundy, J. S.: Certain Factors Influencing the Percentage of Oxygen in Mixtures of Nitrous Oxide and Oxygen, Anesth. & Analg. 27: 255–261 (Sept.–Oct.) 1948.
6. Dublin, W. B.; Boothby, W. M., and Williams, M. M. D.: Determination of the Velocity of Sound in a Gas. Application to Analysis of Mixtures of Oxygen, Helium, and Nitrogen, Proc. Staff Meet., Mayo Clin. 14: 588–592 (Sept. 13) 1939.
7. Dublin, W. B.; Boothby, W. M., and Williams, M. M. D.: Determination of the Velocity of Sound in a Gas. Application to Analysis of Mixtures of Helium, Oxygen and Nitrogen, Science, n.s. 90: 399–400 (Oct. 27) 1939.
8. Dublin, W. B.; Boothby, W. M.; Brown, H. A., and Williams, M. M. D.: Analysis of Mixtures of Helium, Oxygen and Nitrogen by Means of Determination of the Velocity of Sound: Further Observations, Proc. Staff Meet., Mayo Clin. 15: 412–416 (June 26) 1940.
9. Faulconer, Albert, Jr., and Latterell, K. E.: Tensions of Oxygen and Ether Vapor During Use of the Semi-open, Air-ether Method of Anesthesia, Anesthesiology 10: 247–259 (May) 1949.
10. Geberth, Rudolph: A New Method of Gas Analysis, Indust. & Engin. Chem. 15: 1277–1278 (Dec.) 1923.
11. Griffiths, Ezer: A Gas Analysis Instrument Based on Sound Velocity Measurement, Physical Society of London, Proceedings 39: 300–303, 1926–27.
12. Haber, F.: Über Schlagwetteranzeige, Chem.-Ztg. 37: 1329–1330 (Oct. 30) 1913.
13. Hardy, E.: Sur l'analyse acoustique des mélanges de deux gaz de densités différentes, Compt. rend. Acad. d. sc. 121: 1116–1117, 1895.
14. Hurwitz, Engen: The Estimation of Hydrogen by an Acoustic Method, Zetschr. Tech Physik. 6: 113–116, 1925.
15. Mikelson, W.: Apparatus (Having a Hollow Cylindrical Resonator for Sound Waves) for Measuring the Density of Gases as in Determining Air in Admixture With Hydrogen. United States Patent, No. 2,283,750. (May 19) 1942.
16. Pauling, Linus; Wood, R. E., and Sturdivant, J. H.: An Instrument for Determining the Partial Pressure of Oxygen in a Gas, Am. Chem J. 68: 795–798 (May) 1946.
17. Fowle, F. E.: Smithsonian Physical Tables, Washington, D. C., Smithsonian Institution. 1934, p. 191.
18. Faulconer, Albert, Jr.; Clarke, F. C., and Osterberg, A. E.: An Apparatus for the Clinical Determination of Percentage Constituents of Anesthetic Gas Mixtures, Proc. Staff Meet., Mayo Clin. 18: 89–93 (Mar. 24) 1943.
19. Faulconer, Albert, Jr.: A Study of Physical Methods for the Determination of the Tension of Ether Vapor in Air-Ether Mixtures, Anesthesiology 10: 1–14 (Jan.) 1949.