THE RICE INSTITUTE

A RAPIDLY RESPONDING NARROW BAND INFRARED
GASEOUS CO₂ ANALYZER FOR PHYSIOLOGICAL STUDIES

By

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FOREWORD:

The importance of CO₂ analysis in respiratory physiology is well recognized. A number of commercial industrial gas analyzers have been used in this work, and commercial and laboratory equipments have been constructed explicitly for physiological studies. Many of these instruments, however, leave something to be desired in regard to size, response time, convenience, and overall reliability. Also, in view of the continued increase in biological instrumentation, there is increasing need for small, simple, efficient, and trouble-free transducers of all sorts so that the preponderance of instruments used does not confuse or restrict the information one hopes to gather. It was with the goal of developing a small, efficient, rapidly responding, and reliable CO₂ analyzer that work was begun in the Biophysics Laboratory of the Baylor University College of Medicine, under the direction of Dr. L. A. Geddes.

This work is written more from the chronological viewpoint than the logical. A logical presentation is more pleasing esthetically, but generally fails to report the sequence of steps and procedures actually followed.

THE PROBLEM:

Respiratory studies involve not only measurement of the CO₂ content of expired air, but also determinations of N₂, O₂, and the total inspired and expired air volume. It is preferable that these analyses be

on a breath by breath basis. A sampling technique currently employed is that of aspirating a small portion of the expired air from the main stream through the analyzers, after which it is passed on to a collecting tank or exhausted into the atmosphere. The fact that the CO₂ analyzer represents only one system component must be given as much consideration as possible in the matter of overall design, but this work had as its goal the defining of parameters associated with the development of a CO₂ analyzer which would overcome or mitigate the difficulties mentioned previously.

The following specifications were deemed sufficient for this special purpose analyzer:

- (1) The response time must not exceed 0.1 second.
- (2) The device must be insensitive to other gases which are, or may be, contained in expired air. These gases include N₂, O₂, H₂O, and the popular anesthetic gases such as ether, cyclopropane, nitrous oxide, and chloroform.
- (3) The instrument must have a range of 0 to 7 % CO₂, with accuracy 2 % of the full scale reading.
- (4) The unit must be free of microphonics, leaks, loss of sensitivity with aging, and must have calibration stability.
- (5) The instrument must feature ease of adjustment and readout, so that it may be confidently used by medical technicians not versed in electronic instrumentation.

- (6) The construction must permit packaging for use in combustible atmospheres.

PROPERTIES OF CO₂:

A survey of the literature disclosed several properties of CO₂ which have been utilized, and might be exploited further. Some of the possibilities included the following:

(1) Chemical Methods

Such standard techniques as the Haldane and Orsat analyses provide the ultimate in accuracy, but are slow and consequently do not permit breath by breath analysis.

(2) Sonic Properties

Among the instruments utilizing sonic properties is one described by Stott [1]. This instrument employs a resonant cavity which is maintained in oscillation by an amplifier as the measuring device. A change in frequency results from the introduction of CO₂ into the cavity, and the change in frequency is related linearly to the amount of CO₂ present. The instrument is, however, sensitive to a number of other gases besides CO₂, including many anesthetic gases. The response time is, on the order of 0.5 second for full scale deflection.

(3) Thermal Conductivity

Thermistors have been utilized in gas analyzer construction and one such instrument has been described

by Walker and Westenberg [2]. The tolerances to which sample cell temperature, pressure change, and thermistor current must be held in this instrument are not consistent with the objective of overall system simplicity. The use of thermistors in a CO_2 analyzer for physiological use is questionable since the heat transfer is a function of all gases present. Walker and Westenberg restrict measurements to binary gas mixtures, which is impractical in physiological work. Also, no time constants are mentioned in their paper, but judgement based upon other analyzers employing thermistors would indicate that a period of several seconds is required for equilibrium. Such an instrument could not follow the pulsatile flow encountered in breath by breath monitoring.

(4) Charge to Mass Ratio of Ionized CO_2

The principle of the Mass Spectrometer appears extremely attractive for application to the respiratory gas analysis problem. One such instrument described by Hunter, Stacy, and Hitchcock [3] is based upon the work of Nier, [4] who has described his special purpose mass spectrometer as "portable". This instrument provides for recording continuously the relative amounts of N_2 , O_2 , and CO_2 . High accuracy of analysis has been sacrificed in favor of rapid response, as the instrument was designed for respiratory work. These investigators state, in regard

to this instrument, that, "An instantaneous change in gas composition will appear on the record with a lag of less than 0.2 second, and will require approximately 0.1 second to settle on this new value." The device shows no interactions since the CO₂ beam falls between the N₂ and O₂ beams and it is possible to switch from 100 % N₂ to 100 % O₂ without producing any indication in the CO₂ channel. No mention is made regarding analysis in the presence of anesthetic gases. Trouble would certainly be expected in resolving CO₂ and N₂O.

No specific information regarding the portability of the instrument is provided, although from the construction details of particular parts it is concluded that the size is rather large. This conclusion and others regarding disadvantages of the mass spectrometer are indirectly substantiated by the fact that to date no commercially acceptable medical gas analyzer employing this principle has been produced.

(5) Infrared Absorption by CO₂

An extensive table listing the Infrared and Raman bands of CO₂ is available in reference [6]. On the basis of intensity of absorption, the bands at 667.3, 2349.3, 3609, and 3716 cm⁻¹ are of particular interest. In terms of wavelength the bands are 15, 4.26, 2.77, and

2.69 microns respectively. Good spectral resolution is required to observe the true absorption in the bands, and in general, the absorption is not a continuous function of wavelength. The "bands" may actually exist then, only as a result of insufficient resolution. Nevertheless, it is customary to speak of the absorption "bands," and in the case of CO_2 , those of primary interest are centered at the wavelengths listed above.

It has been determined experimentally that the amount of absorbed monochromatic radiation in a homogeneous medium is linearly related to the quantity of radiation incident upon the surface of the medium and the depth of penetration. The energy absorbed in a thickness dt of the medium can be expressed as

$$dE = -\alpha E(t)dt$$

where α is an absorption constant peculiar to the medium, and is in general a function of the wavelength of the radiation. $E(t)$ is the energy incident upon the element of thickness dt .

For a depth t , the absorbed energy would be

$$\int_0^t dE = \int_0^t -\alpha E(t) dt \quad \text{from which}$$

$$\ln E(t) - \ln E(0) = -\alpha t$$

$$\text{and } E(t) = E_0 e^{-\alpha t}$$

where E_0 is the initial energy incident upon the surface.

This expression for absorption is known variously as Beer's Law, Lambert's Law, and the Beer-Lambert Law.

If the radiation is not monochromatic, but is distributed between wavelengths λ_1 to λ_2 , the above relation holds only if α is constant between λ_1 and λ_2 . Absorption in gases occurs over bands consisting of narrow absorption lines. Therefore, α is highly dependent upon λ . Beer's Law does not hold for gases except at extremely high pressures. In treating gaseous absorption analytically, resort is made to several absorption models which represent the possible ways in which spectral lines may be arranged in a band. Generally at least one of these models will describe the absorption over a portion of the spectrum of a particular gas.

An instrument devised by Stow [5] specifically for CO_2 analysis utilized both the sonic and infrared absorption properties. The underlying principle is based upon the property that if an absorbing gas is irradiated with infrared energy which is interrupted at an audio frequency, an audible sound of the frequency is set up in the gas.

Stow employs two "bottle shaped" chambers filled with CO_2 and resonant at the desired audio frequency. One chamber is in the "standard" infrared beam, and the other is in the "sample" beam.

A current carrying wire is stretched across the opening of each chamber. The wires are cooled by the motion of the gas in the resonant chambers. The greater the absorption, the more pronounced the cooling. As the resistances of the wires depend upon their temperatures, the change in resistance may be translated into a measure of the concentration of absorbing CO₂ in the sample cell.

The instrument described above is non-dispersive. This means simply that the infrared energy is not decomposed into its component frequencies by use of prisms or defraction gratings. A CO₂ analyzer can be built utilizing dispersive devices. This, in effect, amounts to constructing a spectrometer; while such an instrument would be simpler in many details than one with continuous scan and high resolution, the size would still leave much to be desired.

After due consideration of the possible approaches to the problem and in view of the overall requirements of simplicity, small size, and rapid response, the infrared absorption property of CO₂ appeared to offer the most promise.

COMMERCIAL NON-DISPERSIVE INFRARED GAS ANALYZERS

Since CO₂ possesses a particular infrared absorption spectrum, it would appear logical to consider using the gas as its own detector. This property is of course valid for any infrared absorbing gas, and is utilized extensively.

The general basis of operation of several of the more popular commercial CO₂ analyzers can be explained with reference to Figure 1. Energy from the infrared source is reflected by the mirrors so that

DIAPHRAGM TYPE CO₂ ANALYZER

FIG. 1

one beam will pass through gas sample cell A and into chamber C. The other beam passes through standard cell B and into chamber D. Chambers C and D are filled with pure CO₂. C and D are separated by a thin, moveable diaphragm. A small hole is placed in the diaphragm to provide pressure equalization for ambient variations. Chamber B has as its function equalization of the optical paths. It is usually evacuated and sealed or filled with non-absorbing gases similar to those anticipated in the sample. The sample to be analyzed is introduced into cell A. Assuming system symmetry, if A contains no absorbing gases, infrared quanta reaching C and D will be equal and the resulting energy absorption by the CO₂ will produce equal chamber pressures and the diaphragm will not be displaced. If a sample containing CO₂ is introduced into A, absorption will occur in A which will reduce the energy reaching chamber C. The pressure in C will then be less than that in D, resulting in deflection of the diaphragm.

To provide a usable output from this arrangement, it is customary to interrupt the infrared energy with a "chopper." The chamber pressures, and consequently the diaphragm movements, pulsate with the turning on and off of the energy. By placing a fixed plate close to the diaphragm a condenser microphone is formed. The variations in capacitance are measured electrically and interpreted in terms of the energy absorption in sample cell A.

ADVANTAGES AND DISADVANTAGES OF THE DIAPHRAGM UNIT

Instruments employing the basic ideas mentioned above have the advantage that they may be sensitized to detect other absorbing gases

by filling the detecting chambers C and D with a pure quantity of the gas to be measured. Because of overlaps in the absorption spectra of many gases, it is often necessary to employ filter cells in both infrared beams to remove the undesired components. These filter cells contain a quantity of the gas or gases to be suppressed. The result of using filter cells is to remove all the infrared energy at the undesired wavelengths. The detector then responds to the remaining energy. Many ingenious techniques involving detector chamber and filter cell arrangements and mixtures have been devised to separate interfering components.

Another advantage of the diaphragm unit is that it is relatively easy to manufacture. Also, it is capable of detecting 10^{-6} watt of radiation and gives a high signal output for small energy inputs so that a simple low-gain amplifier may be used [7].

Some of the disadvantages as pointed out by manufacturing personnel and operating technicians are as follows:

- (1) The diaphragm unit is microphonic and the smallest vibration produces an unwanted signal.
- (2) The sensitivity is likely to vary over a period of time due to thermal drift.
- (3) The device lacks reliability owing to the small clearance in the diaphragm unit (1.5×10^{-3} inches) and the high insulation resistance needed (at least 10^{14} ohms). Any particle of dust or other foreign matter between the diaphragm plates may well put the

instrument out of commission.

- (4) Leakage of the gas in the detector unit is always a problem, but not particularly serious since a slow leak gives sufficient warning that a replacement unit will be needed.

The result of weighing the advantages and disadvantages of the diaphragm device might best be stated by quoting Martin, Reid, and Smart [7] who are engaged in gas analyzer research and manufacture.

"In spite of these disadvantages, the detecting condenser is widely used and the possibility of breakdown accepted. Replacement is a simple matter and once the instrument has been installed and satisfactorily commissioned, there is every probability that the detector will have a useful life of at least twelve months."

Since the diaphragm detector device has been accorded wide acceptance as the "standard" CO₂ analyzer for physiological investigations, the problem became one of developing a CO₂ transducer having superior characteristics.

PRELIMINARY WORK

Detector:

The use of a photoconductor to replace the comparatively large and delicate diaphragm detector appeared extremely attractive. Commercially available at the time this investigation was begun were cells of PbS, PbSe, and PbTe. Although PbTe has a spectral response beyond 4.5 μ , it was not considered because of the requirement of cooling with liquid N₂. The initial published response curves for room temperature operation of PbSe left some doubt as to whether response would be obtained at the 4.3 μ CO₂ band. Private correspondence with

the British firm manufacturing these cells was reassuring on this point and the decision was made to employ a PbSe cell.

These cells consist of a chemically deposited layer of PbSe on a glass substrate. Active areas of PbSe generally range from 1 mm x 1 mm to 5 mm x 5 mm. Accordingly, the overall size of these cells is small. Utilization of these cells depends upon their property of changing resistance in response to a change in intensity of incident radiant energy. Uncooled PbSe cells have a response time on the order of 10 microseconds.

In operation, the PbSe cell requires a bias current which is modulated by the change in resistance resulting from the changes in incident radiant energy. The voltage thus developed is amplified and can be shown to be a measure of the change in radiant energy.

Response curves published later by the Eastman Kodak Company showing spectral response of their PbS and PbSe cells are reproduced as Figure 2.

INFRARED SOURCE:

As a matter of convenience, an infrared source from one of the commercial analyzers was used. It consisted of a nichrome wire wound in a flat spiral and embedded in a ceramic button. Suitable sources are easily constructed by manipulating nichrome wire into any desired shape. The radiation from such a source is essentially broad-band, but the energy distribution at a given temperature as a function of wavelength is not constant.

SPECTRAL RESPONSE OF
UNCOOLED PbSe AND PbS

FIG. 2

The spectral distribution of blackbody radiation may be calculated from Planck's equation [8].

$$E_{\lambda}(T, \lambda) d\lambda = \frac{2\pi hc^2}{\lambda^5} \frac{d\lambda}{e^{\frac{ch}{\lambda kT}} - 1}.$$

where: h = Planck's constant
 c = Velocity of radiation
 λ = Wavelength
 k = Boltzmann's constant
 T = Absolute Temperature

For bodies not perfectly black, an emissivity factor must be included, and the above expression is written:

$$E_{\lambda} d\lambda = \frac{2\pi hc^2}{\lambda^5} \frac{\epsilon(T, \lambda) d\lambda}{e^{\frac{ch}{\lambda kT}} - 1}$$

The curve described by $E_{\lambda}(T, \lambda) d\lambda$ is shown in Figure 3. As T is increased, the peak increases in amplitude and moves toward the shorter wavelengths. The energy radiated at all wavelengths is increased, and consequently the total area under the curve increases.

Windows for Gas Sample Cell

A survey of materials transparent in the intermediate infrared range indicated the availability of fused quartz, sapphire, various special glasses, KBr, NaCl, and LiF. Several transmission characteristics are shown in Figure 4. A number of substances possessing excellent infrared transparency are not particularly desirable when practical matters such as hygroscopic effects, chemical reaction with

BLACK-BODY RADIATION FLUX
VS
WAVELENGTH
 $T = 300^{\circ}\text{K}$

Curve May be Used For Other Values of
 T by Multiplying Vertical Scale by $\frac{T}{(300)^4}$
and Horizontal Scale by $\frac{300}{T}$.

FIGURE 3

INFRARED TRANSMISSION AT ROOM TEMPERATURE
FOR FOUR COMMON WINDOW MATERIALS

FIGURE 4

sample gases, machining, and mounting are considered. Fortunately, the physical and chemical properties of quartz and sapphire are nearly ideal for this work. A gas sample cell with one inch diameter quartz windows and a gas length of 0.125 inch was available and was used in the initial experiments.

EARLY EXPERIMENTS

Preliminary considerations had indicated the desirability of, if not the necessity for, spectral and electrical filtering. By way of showing that these features were needed, and as a means of becoming familiar with photoconductive cells, a series of four experiments were carried out.

Experiment No. 1:

A PbSe cell was used in the circuit shown in Figure 5. As is evident from the diagram, the approach was to allow the chopped infrared radiation to pass through the gas sample tube and impinge upon the PbSe cell. The cell bias current was modulated by the change in resistance of the PbSe cell which is a function of the impinging radiation. The amount of radiation reaching the cell depends upon the absorption in the gas sample tube.

The voltage induced in the transformer was amplified, rectified and filtered, and the resulting D-C voltage was further amplified by the D-C amplifier. E_o , the output of the amplifier, was set to zero by adjustment of E_b with air in the gas sample tube. CO_2 was then passed through the sample tube and the change in E_o observed.

An output of 100 millivolts was obtained for 100 % CO_2 , but the

system noise and instability were such as to obscure readings for CO₂ concentrations of 10 % or less. While attempting to alleviate some of the difficulties it was discovered that the PbSe cell resistance had changed from its initial value of 237K to approximately 50K and that its sensitivity had fallen to the point of uselessness. No explanation for this deterioration is known as every attempt was made to comply with all published ratings.

Experiment No. 2:

Because some time and expense were involved in obtaining a replacement PbSe cell, work was resumed with PbS cells. The circuit shown in Figure 6 was employed. This circuit is essentially the same as that in Figure 5 except for the system gain. An output voltage of 1 volt was obtained for 100 % CO₂ in the sample cell. This system presented the same noise and zero instability problems of the previous system.

Experiment No. 3:

The system shown in Figure 7 was adjusted for zero output with air in both sample tubes. The output produced by 100 % CO₂ in one sample tube is shown in Figure 9. This output corresponded to a voltage of approximately 3 millivolts at the input of the D-C power amplifier. The noise and zero instability of this system can be observed from the graphic record.

Experiment No. 4:

As a means of observing the behavior of the PbS cells under constant irradiation, the bridge arrangement of Figure 8 was connected. The two active cells were placed in diagonally opposite arms so that the

FIGURE 5

FIGURE 6

FIGURE 7

BRIDGE CIRCUIT

FIGURE 8

RESPONSE OF CIRCUIT SHOWN
IN FIGURE 7

FIGURE 9

resulting effects of unbalance would be additive. The two active cells were irradiated with infrared which had passed through the gas sample tube. The two other cells were irradiated with infrared which has passed through the "standard" sample tube.

The bridge was found to be voltage sensitive in such a manner that the initial balance depended upon the applied voltage. A typical "run" with this bridge produced the following data:

<u>Gas</u>	<u>Decade Resistance (ohms)</u>	<u>ΔR (ohms)</u>
Air	380,700	
100 % CO_2	380,000	700
Air	380,900	900
100 % CO_2	380,300	600

The bridge was not stable. An initial balance could be held for as long as 40 seconds to 1 minute in some cases, but more often, the balance would shift approximately 300 ohms in 15 to 20 seconds. When the balance changed, the effect appeared cumulative in that the system shifted to a new balance point rather rapidly. It was verified that the PbS cells were at fault by replacing them with metallic film resistors similar to those already in the bridge arms. The resulting bridge was very stable.

With the PbSe cell bridge circuit it was possible to produce a change in E_0 from 0.05 to 0.058 volt with 10 % CO_2 in the sample tube. The 0.05 volt output with air in the sample tube represented the best null obtainable using standard shielding techniques. This output corresponds to approximately 25 μv input to the null detector.

More work might have been done to reduce the noise and thus increase the sensitivity, but the problem of resistance instability of the PbS cell appeared formidable.

At the conclusion of this experiment, two new PbSe cells were obtained from the Eastman Kodak Company. When placed in the bridge circuit, the instability was essentially the same as with PbS cells. No new attempts were made to measure CO₂ concentration.

CONCLUSIONS BASED UPON EARLY EXPERIMENTS

The conclusions which might be drawn from these experiments are clouded somewhat by the fact that no precautions were taken to control the effect of water vapor. It was later found that the laboratory air supply did contain varying amounts of water vapor. The observations with PbS cells are particularly inconclusive in this regard as their spectral response range extends only to about 3 μ . Most of the absorption effects observed then included the 2.7 μ CO₂ band which is overlapped by the stronger H₂O band.

In spite of the questionable absorption observations, the experiments justify the following statements.

- (1) It does not appear feasible to use PbSe or PbS cells in a bridge circuit in which two infrared beams are compared because of their resistance instability.
- (2) In view of the random variations in the resistance of the PbSe and PbS cells, a single detector should be used to alternately measure the radiation received through the standard and sample tubes.

- (3) If a broadband infrared source is used with detector cells which also respond over a wide spectral range, some form of spectral filtering is required if undesirable absorption effects are to be eliminated and the desired effects, due to CO_2 alone, discerned.
- (4) In view of the small input signal generated by the photoconductor, a high degree of electrical filtering is required to produce a suitable signal to noise ratio.

Of the requirements outlined above, that of spectral filtering appeared the more difficult to achieve. Accordingly, considerable time was spent investigating possible means of accomplishing this.

THE MONOCHROMATION PROBLEM:

The nichrome infrared source used in this work has effective emission from visible red out to approximately 15μ . The photoconductors used also have rather broad spectral response. The result of attempting to measure the absorption of a specific component in the presence of another absorbing component or components under such conditions has been pointed out. Consideration was given to several possible ways in which a system could be sensitized to CO_2 to the exclusion of other absorbing gases present in the sample. This requires that attention be focused on an absorption band (or bands) of CO_2 which have either no overlap or a minimum of overlap with other gases which may possibly appear in the sample. Several possible approaches to CO_2 sensitization were considered:

- (1) Use of a broadband infrared source, and employing CO₂ as the detector.

This method is widely used in the diaphragm type of analyzer, and in view of the number of manufacturers producing this type, it did not appear likely that any ideas to obviate the difficulties inherent in this instrument would be forthcoming.

- (2) Use of a broadband infrared source, and an optical system employing a prism or diffraction grating.

As mentioned previously, this arrangement involves essentially the construction of a spectrometer. Even though several of the usual spectrometer refinements might be omitted, the system still would be large physically and complex optically.

- (3) Use of an infrared source which emits only at the wavelength(s) of interest.

A quartz discharge tube was constructed with the intention of establishing an arc discharge in CO₂ with the expectation that under such excitation some emission at the absorption wavelengths would result. Because of the fragile nature of the thin tube construction, several successive mishaps occurred in the mounting process, and the tube was damaged before a discharge could be attained.

At this same time, a search of the literature disclosed a paper by Cohen, Lowe, and Hampson reporting their work on this problem. [9]. These investigators employed 10 mega-

cycle power ranging from about 75 to 275 watts which was pulsed up to 30 cps, to excite the CO_2 . Their results indicated that power was emitted at both 2.7 and 4.3μ . The efficiency of conversion of 10 mc power to infrared power at 4.3μ was found to be $(1.39 \pm .20) \%$ at a gas pressure of 2.1 cm H_g and an input power of 140 watts. They also found that several milliseconds were required for the infrared energy to reach a final value upon the excitation of a pulse, and that several milliseconds were required for the energy to decay upon cessation of the pulse. It was observed that the half-life of the infrared energy increased with gas pressure and with input power.

Another important factor which is implied from their investigation is that a significant spectral shift results from the pressure-temperature conditions in the discharge tube. The extent and importance of this spectral shift would require additional study.

Cohen, Lowe, and Hampson conclude that their experiments, "Show strong evidence for the existence of a purely thermal infrared source under the conditions dealt with, and that considerable experimental effort would be necessary to evolve a more efficient infrared source of smaller time constants."

Considerable work has been done by Plass [10] in determining the spectral emissivity of CO_2 as a function of temperature, pressure, and amount of radiating gas. His work shows that a concentration of gas may be found for which the emissivity at the center of the 4.26μ band is nearly unity at low temperatures (300 to 500°K). As the temperature is increased, the emissivity decreases, and the emission shifts toward longer wavelengths.

In addition to the possibility of obtaining a nearly monochromatic infrared source, one of the attractive features of the discharge method has to do with the elimination of the mechanical beam chopper. The fact that several milliseconds are generally required for buildup and decay of the infrared energy would mean that the output signal from a CO_2 analyzer employing such a source would have a frequency less than 100 cps. This imposes no limitation electronically, but better signal to noise ratio is obtained with photoconductive detectors when higher chopping frequencies are used. The main problem appears to be the spectral shift. Also, the conversion efficiency is poor, and heat removal could become a problem.

In view of the above findings it was decided to consider other methods of monochromation.

(4) Use of a broadband infrared source and a spectral bandpass filter.

An investigation of the absorption spectra of gases other than CO_2 which were likely to be encountered, indicated that the 4.3μ CO_2 band was relatively free of overlap. Consideration was then given to the possibility of "bracketing" this absorption band with a band-pass filter. To minimize possible interference and to maximize the effect of CO_2 absorption, it is desirable to fit the filter band-pass characteristic to the absorption band. This requires a filter characteristic with steep sides and a half width of approximately 0.2μ . Such characteristics are best obtained with interference type filters.

An investigation of the properties of interference filters indicated that a multi-layer type would be required to provide band-pass characteristic desired. Several manufacturers were contacted, and each indicated that the construction of a bandpass filter centered at 4.27μ would have to be undertaken on a more or less developmental basis. As a result, it appeared that the cost and final product performance would be somewhat unpredictable. Eventually, one company was located which agreed to provide at reasonable cost, a bandpass filter with the desired characteristics. The resulting filter is a

multi-layer Fabry-Perot type comprised of alternating layers of dielectric having high and low indices of refraction deposited on a semi-conductor substrate which acts as a dielectric at these wavelengths, and which is anti-reflection coated on the obverse side. The spectral response is shown in Figure 10. Compared with other filters investigated it is outstanding in that it is a single unit and provides a moderately narrow pass-band at the desired wavelength. Also, it has no spurious responses within the transmission range of the sapphire optics employed in the gas sample tubes.

This filter has a half-width of approximately 16 % and is classified as a medium bandpass filter. More recently, filters with half-widths of 5 % and 1 % have become available commercially. A 5 % half-width filter centered at 4.3μ would bracket the CO_2 absorption band nicely, and is to be preferred over the 16 % half-width filter.

SECOND EXPERIMENTAL PHASE

Upon receipt of the infrared filter, the system shown in Fig. 11 was assembled. The gas cells were six inches in length and were constructed from 1 inch O.D. brass pipe. The ends were threaded, and a special end fitting with gaskets was made to permit the windows to be removed easily. The nature of this construction can be seen in

FIG. 10

INITIAL FORM OF ANALYZER

FIGURE 11

Figure 12, in which a 2 inch gas sample cell is displayed. Also shown in this photograph are the PbSe photoconductive cell, the infrared filter on its mounting bracket, and two infrared source units.

Two identical chopping wheels were initially employed, one at each end of the gas cells. The choppers were arranged so that they could be rotated on the shaft relative to each other and locked into position. Each chopper wheel consisted of two separate but similar "tooth and notch" plates, one placed on top of the other and held together on the shaft by a common bolt. By loosening the bolt, the plates could be rotated individually for aperture adjustment and then locked into the desired position by tightening the bolt. This arrangement is shown in Figure 13.

The remainder of the system consisted of a single infrared source, energy from which was reflected through the chopper and into the gas cells by the front surfaced flat mirrors. The energy emerging from the gas cells was collected by the spherical mirror and focused upon the PbSe cell through the infrared band-pass filter.

Preliminary observations were made with only the sample gas cell active. The chopping was such that essentially a square wave output was obtained. Samples of $N_2 + CO_2$ then were introduced into the sample cell and the absorption observed in the form of a change in the square wave amplitude. It was found that practically the same amplitude change was obtained for CO_2 concentrations of 1, 5, 10, and 100 %/o. This indicated that with a 6 inch absorption path that 1 %/o CO_2 effectively absorbed all incident infrared energy. A 3 inch cell was then

FIGURE 12

ANALYZER
COMPONENTS

constructed and the following measurements taken:

<u>°/° CO₂</u>	<u>Output Volts</u>
1	1.0
5	1.8
10	2.0

Saturation was still very apparent, but the difference in readings between 1 and 5 °/° CO₂ was encouraging.

As an immediate means of reducing the sample cell length, the quartz sample cell with an absorption path of 0.125 inch which had been used in the early experiments, was mounted over the end of the 3 inch sample cell. The quartz windows in this cell were each 1 inch in diameter and 1 mm thick. The infrared energy reaching the detector was reduced 30 °/° by the addition of the quartz in the optical path. Because of the short absorption path, the signal to noise ratio was low and measurements of infrared absorption by CO₂ were inconclusive.

CHOPPING WHEELS AND OUTPUT WAVEFORM:

The preceding measurements were all made using the gas sample cell only, by noting the change in infrared absorption as CO₂-free air in the sample cell was replaced by the N₂ + CO₂ sample. In a practical instrument it is of course desirable to continuously compare the absorption in the sample cell with that of the standard cell. This involves having the detector "view" alternately one cell and then the other. The resulting outputs must then be compared in some suitable manner.

Considerable attention was given to the question of how to "chop" or switch the beams to obtain the best comparison signal with the least

mechanical and electronic complication. The simple system shown in Figure 13 was finally developed. Theoretically, if the windows are illuminated equally and uniformly, all energy passing through them is collected and focused on the detector. In the absence of absorption in either path, the detector will always receive a constant amount of radiant energy and thus its change in resistance will be zero.

The question might be raised as to the manner in which the radiant energy is commutated. Consider the simplest case in which a cylindrical beam of radiation is interrupted rectilinearly by a flat plate, as shown in Figure 14. The area of the uncovered portion of the window $A(h)$ is given by:

$$A(h) = \pi R^2 - \left[R^2 \cos^{-1} \frac{R-h}{R} - (R-h) \sqrt{2Rh - h^2} \right]$$

where R = Radius of window

h = Distance along vertical axis chopping plate has moved.

Figure 14 shows a plot of $A(h)$ for the case $R = 1$. The opening and closing of the windows is shown by curves C and A respectively. It is obvious from these curves and the simple symmetry of the system that theoretically the detector can be made to see a constant amount of radiant energy when the two optical paths are similar. A plot of $A_b = \frac{\pi}{2}(1 + \cos \theta)$ is also shown to indicate that the function $A(h)$ does not depart greatly from a sinusoid.

Figure 13 shows the chopping wheel as actually constructed with "chopping edges" cut along radii. It is apparent that the energy reaching the detector is not described exactly by $A(h)$ since the line along which h is measured changes direction as the chopping occurs. The

CHOPPER WHEEL

FIG. 13

COMMUTATION OF INFRARED BEAMS

FIG. 14

deviation is reduced as the ratio of the radius of the window to the radius of the chopping wheel is made smaller. This matter is of no particular importance in this instance because the system symmetry is such that the effect of energy passed by opening one window is cancelled at the detector by closing off the same amount of energy from the other window.

It has been found in practice that it is somewhat difficult to commutate the beams so that a constant amount of energy is received by the detector. The actual waveform contains small "pips" or "spikes" at the points of overlap of the two beams. This is not a serious problem however, as the high frequencies involved can be removed by electronic filtering. It is known from observation of the change in "spike" shape and amplitude with adjustment of the system optics, that ideal commutation can be approached by constructing the entire analyzer in accordance with standard instrument machining techniques.

If it is assumed that no absorption occurs in the gas sample cell and that ideal commutation is obtained, the detector receives a constant amount of energy. Under these conditions the detector resistance remains constant, and the output signal is zero. If CO_2 is then introduced into the sample cell, the energy in this beam is reduced and essentially a square wave output is obtained.

There are two principle ways in which the square wave output may be utilized to measure the beam unbalance. First, a synchronous detector may be employed in which case a reference voltage must be provided. Secondly, a frequency selective amplifier may be used. All things con-

sidered, the selective amplifier is perhaps simpler electronically and provides easier adjustment.

FURTHER REFINEMENT OF THE PROTOTYPE:

Experimentation showed that it was possible to eliminate one of the chopper wheels. Accordingly, the wheel closest to the detector was removed. It was also found that two individual infrared sources could be used, thus eliminating the two flat mirrors. This latter modification permitted much easier adjustment of the initial radiation in each optical path, and provided increased optical stability. The system then took the form shown in Figure 15. Details of the transducer section can be seen in Figure 16.

Considerable data were collected with this system, a sample of which is as follows:

Gas Sample Cell Length	2 inches
Infrared Source Current	3 amperes
PbSe Cell Dark Resistance	480K ohms
Fundamental Chopping Frequency	165 C.P.S.
Krohn-Hite Filter Settings	{ 170 CPS (Upper cut-off)
	{ 160 CPS (Lower cut-off)
System Gain at 165 CPS	2.45×10^4
Gas Mixture	$N_2 + CO_2$
PbSe Cell Bias	45 V

MODIFICATION OF ANALYZER

FIGURE 15

FIGURE 16

TRANSDUCER SECTION

<u>o/o CO₂</u>	<u>Output Volts</u> <u>True RMS</u>	<u>E_{in} (microvolts)</u>
0.5	2.7 - 1.25 = 1.45	59
1.05	3.95 - 1.25 = 2.70	110
2.55	5.60 - 1.23 = 4.37	178
3.6	6.10 - 1.20 = 4.90	200
5	7.00 - 1.20 = 5.80	237
7	7.30 - 1.20 = 6.10	249
10	8.1 - 1.20 = 6.90	282

These data are plotted in Figure 17. Note that the output voltage, which is a measure of the infrared absorption, is essentially exponential.

Measurements of the system noise obtained at the time the above data were collected, are as follows:

<u>PbSe</u> <u>Cell Bias</u>	<u>Pre-Amp</u> <u>Input Switch</u>	<u>RMS Volts Noise</u> <u>at Output</u>	<u>Equivalent RMS</u> <u>Volts Noise</u> <u>at Input</u>
(A) OFF	GAL	12×10^{-3}	0.49×10^{-6}
(B) OFF	RECORD	125×10^{-3}	4.9×10^{-6}
(C) 45V	RECORD (Infrared to Detector Blocked)	125×10^{-3}	4.9×10^{-6}

These data can be interpreted by use of the following information in conjunction with Figure 15.

1. The physical arrangement is such that the PbSe cell is located immediately behind the infrared filter, and is connected to a "box" containing the bias batteries and load resistors by a shielded cable approximately 5 inches in length.

FIGURE 17

2. When the PbSe cell bias is OFF, the pre-amplifier input terminals are terminated by the load resistors. When the bias is ON, the load resistors are paralleled by the PbSe cell and battery in series.
3. With the pre-amplifier in CALibrate position, the input grids are shorted together and to ground at the pre-amplifier input terminals.
4. With the pre-amplifier in RECORD position, the pre-amplifier input is connected to the external circuit.

With these facts in mind, condition (A) shows that the noise equivalent input of the amplifier and filter system is 0.49 microvolt. Hence, this represents the minimum detectable signal.

Condition (B) indicates that additional noise is picked up in the cable from the Pre-amplifier to the "bias box" and PbSe cell. This noise equivalent input is 4.9 microvolts which represents the actual minimum detectable signal. This noise can be reduced by constructing the Pre-amplifier and PbSe bias circuitry as an integral unit.

Condition (C) shows that the addition of the PbSe cell and its bias circuit to the system does not change the noise level. The minimum detectable signal remains at 4.9 microvolts.

These noise measurements were made with the chopper motor off and the infrared energy to the detector blocked. With the chopper operating, the RMS voltage output for the best balance of the two infrared beams was 1.2 ± 0.04 volts. The ± 0.04 volt random variation was very slow. This meant that the noise equivalent input at the "zero setting" of the device was 49 ± 1.63 microvolts. This voltage resulted from the rather high 1.3 volt "spikes" in the zero balance waveform, and may be offset on a vacuum tube voltmeter so that the meter will read zero under

the above conditions. The zero stability appears to be governed by the optical adjustments. The laboratory model leaves much to be desired in this regard, as it was constructed so that spatial adjustments could be made easily on all components. Standard instrument machining should eliminate this problem.

Photographs of the signal voltages obtained during a typical test are shown in Figure 18. These photographs were not taken at the time of the above measurements, but represent a typical situation. The sequence of exposures is the same in each picture. The top pair of traces shows the output signal before and after filtering, and represents the "zero setting" for the device. Note that the commutation of the infrared beams is such as to produce "spikes" of approximately 3 to 4 volts peak amplitude. The pair of traces in the center show the result of unbalancing the infrared beams upon introduction of a gas sample. The bottom pair of traces shows the return to zero upon purging the gas sample cell with N_2 .

To obtain miniaturization, and to reduce the sample cell length for a closer approach to linearity in infrared absorption, the model shown in Figure 19 was constructed. The device performed well, but the optical adjustments were extremely critical. This situation was due mainly to the reduction in distance between the collecting mirror and the infrared sources. Because of the optical instability, this particular device was abandoned, but the sample cell section was removed and mounted on the first machine for further observation of absorption in the 7/16 inch gas sample cell.

OSCILLOGRAPHIC RECORD
OF CO₂ ANALYSIS

FIGURE 18

TRANSducer WITH
REDUCED OPTICAL PATH

FIGURE 19

FINAL FORM OF BASIC MODEL:

The final form of the basic model is shown in block diagram in Figure 20. The transducer section is essentially the same as that previously described and shown in Figure 15, except that the spherical mirror was replaced by a parabolic mirror. Electronic modifications included replacement of the Krohn-Hite band-pass filter with a frequency selective amplifier, and elimination of the voltage amplifier preceding the vacuum tube voltmeter.

ELECTRONICS:

The electronic circuitry is governed by two principal requirements. First, since the signal developed by the PbSe detector is in the micro-volt region, high-gain low-noise amplification is required. Secondly, after the signal has been amplified to a suitable level, sharply tuned selective filtering is needed to recover the fundamental frequency component of the output signal.

The first requirement is met with the amplifier circuit shown in Figure 21. The bias current through the PbSe photoconductive cell is modulated by the change in cell resistance which is a function of the quantity of impinging infrared energy. The change in current develops a signal voltage across R_1 and R_2 , which is applied to the grids of a symmetrical difference amplifier. A considerable amount of cathode degeneration is employed to obtain a high degree of common mode rejection and thus to minimize the effect of in-phase noise currents present at the input. The output of the first difference amplifier is amplified by another difference amplifier similar to the first. A zero output adjust

BLOCK DIAGRAM OF FINAL BASIC ANALYZER

PRE-AMPLIFIER AND AMPLIFIER
SCHEMATIC

FIG. 21

control is provided in the cathode of this stage. Additional voltage amplification is obtained with a push-pull amplifier transformer coupled to the unbalanced input of the selective amplifier. The frequency response characteristic of the pre-amplifier is shown in Figure 22. Note that it is essentially flat over the range of 20 to 1000 CPS. The loading of the transformer coupled voltage amplifier following the pre-amplifier is such that a pass-band of 25 to 580 CPS is obtained with peaking in the vicinity of 130 CPS. This provides rather coarse frequency selectivity preceding the selective amplifier.

The characteristics of differential amplifiers have been thoroughly investigated and are adequately reported in the literature. The selective amplifier, on the other hand, is perhaps more novel. The circuit used here is essentially that described by Villard and Weaver, [12] shown in the schematic diagram of Figure 23. Here it is seen that V1 and V2 represent a two-stage constant-output phase shifting amplifier. To see that constant output is obtained, note that the plate voltage E_p is equal to the cathode voltage E_k in amplitude but is opposite in phase, provided that the loading by C_1 and R_1 is negligible. The phasor diagram shows the voltage relations and the manner in which E_g varies in phase as a function of R . It is apparent that the locus of point M describes a circle and that $E_g = E_{po} = E_{ok}$. Theoretically, a single stage could provide 180 degrees of phase shift but this is not achieved in practice, so that much better control of phase shift is obtained when two such stages are cascaded.

There is one frequency at which the phase shifting amplifier will

FIGURE 22

SL70A1771W

$$R_{L1} = R_{K1}$$

$$R_{L2} = R_{K2}$$

FIG. 23
SELECTIVE AMPLIFIER

provide 180 degree phase shift. Hence, if this frequency component is present in E_{in} , it will appear at the grid of V3 shifted 180 degrees from its initial position. This component will also be present at the cathode of V3 with the same phase relation as on the grid. Amplification by V4 produces 180 degree phase shift so that this frequency component arrives back at the input of V1 to provide positive feedback. The amount of feedback is controlled by R which permits the unit to be made highly selective. The pass-band characteristics are shown in Figure 24 for three different settings of the selectivity control R. Experience has shown that the gain and frequency are both very stable.

Figure 25 shows curves of voltage at the selective amplifier input and output terminals vs input voltage to the pre-amplifier. Note that the voltage at the selective amplifier input terminals, which represents the amplitude characteristic of the pre-amplifier and voltage amplifier, is linear over the input voltage range of 10 to 100 microvolts. The output, however, is linear only over an input range of 10 to approximately 30 microvolts. This corresponds to a maximum input voltage to the selectivity amplifier of approximately 600 millivolts RMS. This situation is easily corrected (if necessary) by employing tubes in the selective amplifier having greater signal handling capabilities.

SPECTROPHOTOMETRIC STUDIES:

Before carrying out further CO_2 analyses, a study of infrared absorption by various CO_2 sample mixtures was conducted using a Perkin-Elmer Model 21 Double Beam Infrared Spectrophotometer. Special sample cells were

FREQUENCY RESPONSE OF
SELECTIVE AMPLIFIER
FOR THREE SETTINGS OF
SELECTIVITY CONTROL

FIG. 24

FIGURE 25

constructed to fit the spectrophotometer to replace the rock salt cells normally used since these might have been damaged from the wet gas samples. These special cells were of the same lengths as those used in the basic analyzer, and employed the same sapphire windows.

Figure 26 shows the absorption spectra of two dry $N_2 + CO_2$ mixtures. Note the absorption due to CO_2 at 2.7 and 4.3 microns. The resolution was intentionally reduced by using a rapid rate of scan, as the CO_2 analyzer does not have appreciable resolution. It is seen that the differences in the two traces are due essentially to the difference in CO_2 concentration in the two mixtures. The absorption shown in Trace No. 2 at 4.5μ is probably caused by contamination with N_2O , as stenciling on the cylinder indicates that it was at one time filled with this gas. This absorption appears noticeable in the data collected from the analyzer, in that a slightly higher reading is obtained than that predicted on the basis of analyses of other mixtures. It should be noted from this spectrogram that the change in concentrations of the infrared inert components N_2 and O_2 did not appear to affect the absorption by CO_2 . Observe too, the much stronger absorption at 4.3μ compared with that at 2.7μ .

Figure 27 shows the absorption spectrum of 79.9 % $N_2 + 17.05$ % $O_2 + 3.05$ % CO_2 saturated with H_2O . Note here the increased absorption at 2.7μ due to H_2O . This mixture will be referred to as the "standard breath" as it resembles closely the composition of normal human expiration.

THE EFFECT OF ANESTHETIC GASES:

In the ordinary metabolic study one expects to encounter the standard breath, or slight variations therefrom, by reason of relatively small

FIG. 26

FIG. 27

changes in the concentrations of O_2 and CO_2 . The spectrophotometric data presented thus far shows that the infrared absorption by CO_2 at 4.3μ is not appreciably influenced by changes in concentration of N_2 , O_2 , and H_2O ; therefore, no difficulty was anticipated in obtaining accurate CO_2 absorption measurements when these gases only are present with CO_2 . Because of the importance of monitoring CO_2 levels during surgery, the spectrophotometer was utilized to observe the effects on CO_2 absorption at 4.3μ by mixing the standard breath with several of the popular anesthetic gases.

Chloroform:

Figure 28 shows the absorption from a mixture obtained by bubbling the standard breath through liquid chloroform. The chloroform absorption at 3.5μ is evident, but the CO_2 absorption has been affected only slightly. This spectrum was obtained for a sample saturated with chloroform, so that for the chloroform concentrations normally encountered, no error in CO_2 analysis would be introduced.

Ether:

Figure 29 shows the absorption by the mixture obtained by bubbling the standard breath through liquid ether. Note that the absorption at 3.5μ is beyond the range setting used for this scan. The reduction in depth of the CO_2 absorption at 4.3μ is due to the reduction in CO_2 concentration as a result of the high vapor pressure of ether. The characteristic shape of the CO_2 absorption band appears to be placed upon a constant "ether pedestal." The conclusion reached is that difficulty is to be expected in determining CO_2 is the presence of ether, although

FIG. 28

FIG. 29

negative filtering with ether cells should permit measurement of the CO_2 . The saturation procedure employed here is rather drastic and as such it represents a pessimistic case.

Cyclopropane:

Figure 30 displays the absorption obtained with the standard breath mixed with an equal volume of cyclopropane. Notice here the relative isolation of the 4.3μ CO_2 band from the cyclopropane absorption bands. Again in this case the reduction in depth of the CO_2 absorption is due to the reduction in CO_2 concentration by dilution with cyclopropane. Accordingly, no particular difficulty should be anticipated when cyclopropane is encountered in the usual concentrations.

Nitrous Oxide:

Figure 31 shows the absorption by the dry mixture 80 % N_2O + 16.5 % O_2 + 3.5 % CO_2 . Note the overlap of the N_2O and CO_2 absorption bands. These data point out clearly the difficulty one would encounter in measuring a relatively small CO_2 concentration in the presence of large N_2O concentrations. Negative filtering with N_2O cells and a moderately high degree of detector resolution might be combined to produce a system insensitive to N_2O . Fortunately, N_2O is not extensively used, particularly in cases in which monitoring of expired CO_2 is of importance.

CO_2 ANALYZER MEASUREMENTS:

The following data were collected for various mixtures of N_2 , O_2 , CO_2 , and H_2O under the following conditions.

1. Gas sample cell length = 2 inches.

FIG.30

FIG. 31

2. Infrared source current = 3.2 amperes.
3. PbSe cell bias = 45V.
4. Total RMS output voltage at null adjustment = 7 millivolts (steady).
5. Chopping frequency = 185 CPS.
6. System Gain = 1500.

<u>Mixture</u>	<u>Total RMS output Millivolts</u>	<u>ΔOutput From Null Millivolts</u>	<u>ΔInput From Null Microvolts</u>
99.5°/° N ₂ + 0.5°/° CO ₂	38.5	31.5	21
98.95°/°N ₂ +1.05°/°CO ₂	61	54	36
97.45°/°N ₂ +2.55°/°CO ₂	90	83	56
96.4°/°N ₂ +3.6°/°CO ₂	104	97	63.6
95°/°N ₂ + 5°/°CO ₂	115	108	72
93°/°N ₂ +7°/°CO ₂	124	117	78
89.9°/°N ₂ +10.1°/°CO ₂	137	130	86.7
79.7°N ₂ +19.25°/°O ₂ +1.05°/°CO ₂	60	53	35.3
79.9°/°N ₂ +17.05°/°O ₂ +3.05°/°CO ₂	100	93	62
80.3°/°N ₂ +14.7°/°O ₂ +5°/°CO ₂	115	108	72
79.9°/°N ₂ +13.1°/°O ₂ +7.0°/°CO ₂	124	117	78
79.7°/°N ₂ +19.25°/°O ₂ +1.05°/°CO ₂ +H ₂ O	62	55	36.7
79.9°/°N ₂ +17.05°/°O ₂ +3.05°/°CO ₂ +H ₂ O	100	93	62
80.3°/°N ₂ +14.7°/°O ₂ +5°/°CO ₂ +H ₂ O	115	108	72
79.9°/°N ₂ +13.1°/°O ₂ +7.0°/°CO ₂ +H ₂ O	123	116	77.3

Noise:

	<u>Bias</u>	<u>Pre-amp</u>	<u>Chopper Motor</u>	<u>Output (Millivolts)</u>
(1)	Off	Gal	Off	1.3 to 1.8 say, 1.5
(2)	Off	Gal	On	Same as (1)
(3)	Off	Record	Off	1.6 to 1.8 say 1.7
(4)	Off	Record	On	3.5
(5)	45 V	Record	Off	2.1 to 2.6 say, 2.3
(6)	45 V	Record	On	7 (null output)

The data for the $N_2 + CO_2$ mixtures are plotted in Figure 32. Note that the output voltage, and hence the infrared absorption, is exponentially related to the CO_2 concentration.

Data for the $N_2 + O_2 + CO_2$ and $N_2 + O_2 + CO_2 + H_2O$ mixtures show that variations in the concentrations of the infrared inert components do not influence the CO_2 absorption. In the case of the $79.9^\circ/\circ N_2 + 17.05^\circ/\circ O_2 + 3.05^\circ/\circ CO_2$ mixture, an output voltage of 90.5 m.v. is obtained from the curve in Figure 32, while a value of 93 m.v. was measured. This higher value may well be due to the slight N_2O impurity found in the spectrophotometric analysis.

ANALYZER MEASUREMENTS WITH ANESTHETIC GASES

Chloroform:

To observe the effect produced by chloroform in the CO_2 analyzer, the arrangement shown in Figure 33A was assembled. A quantity of chloroform sufficient to cover the bottom of flask No. 2 was introduced and N_2 was brought in at point (a). The resulting mixture increased the voltage output reading from a null value of 7 m.v. to 8 m.v. which indicated that chloroform would not influence a CO_2 measurement. Introduction of $79.9^\circ/\circ N_2 + 17.05^\circ/\circ O_2 + 3.05^\circ/\circ CO_2$ at point (A) produced the same output reading as $79.9^\circ/\circ N_2 + 17.05^\circ/\circ O_2 + 3.05^\circ/\circ CO_2$ alone.

Ether:

When the arrangement shown in Figure 33A was used with ether in the bottom of flask No. 2 and N_2 introduced at point (A), the output remained rather constant at 47 m.v. Upon replacing the N_2 with $79.9^\circ/\circ N_2 + 17.05^\circ/\circ O_2 + 3.05^\circ/\circ CO_2$, the output jumped to approximately 140 m.v. and dropped

FIGURE 33a

FIGURE 33b

GAS MIXING ARRANGEMENTS

rather slowly after the $N_2 + O_2 + CO_2$ was cut off, eventually returning to 47 m.v. The initially high value is approximately what one would expect if the absorption of the $N_2 + O_2 + CO_2$ sample were added to the "steady state" ether absorption. The decay apparently is produced by the high vapor pressure of ether causing dilution of the $N_2 + O_2 + CO_2$ sample.

It appears likely that negative filtering with ether cells or use of an infrared filter with a narrower pass band would result in a CO_2 analyzer suitable for use in the presence of ether. During this experimental work the vapor pressure of ether was vividly demonstrated by closing off the line to the analyzer and observing that the ether vapor pressure forced the water out of flask No. 1 when line A was open.

Cyclopropane:

An output of 58 m.v. was obtained when 100° cyclopropane saturated with H_2O was introduced into the CO_2 analyzer. This output is practically the same as that obtained with 79.7° N_2 + 19.25° O_2 + 1.05° CO_2 alone. The arrangement shown in Figure 33B was used to mix indeterminate amounts of cyclopropane with 79.9° N_2 + 17.05° O_2 + 3.05° CO_2 . Cyclopropane concentrations, up to an estimated 25° of the final mixture, did not noticeably affect the CO_2 measurement.

Nitrous Oxide:

In view of the spectrophotometric analysis it was considered pointless to observe the effect of 80° N_2O + 16.5° O_2 + 3.5° CO_2 in the CO_2 analyzer. Additional investigation would be necessary to devise an analyzer sensitive to small changes in CO_2 concentration in the presence of large N_2O concentrations.

CO₂ MEASUREMENTS WITH A 7/16 INCH SAMPLE CELL

As a matter of convenience, the foregoing measurements with the anesthetic gases were made using the 2 inch gas sample cells. To more nearly approach a linear relation between infrared absorption and CO₂ concentration, and to reduce the sample cell volume for rapid filling, a gas sample cell with an absorption length of 7/16 inch was tested.

Measurements with this cell are as follows:

Frequency (chopping) = 170 CPS

System Gain = 2800

Null adjustment output voltage = $5.2 \pm .25$ m.v.

Null adjustment equivalent input voltage = $1.86 \pm .0893 \mu v$

<u>MIXTURE</u>	<u>TOTAL RMS OUTPUT (Millivolts)</u>	<u>ΔOUTPUT FROM NULL (Millivolts)</u>	<u>Δ E_{in} (Microvolts)</u>
99.5°/°N ₂ + 0.5°/°CO ₂	17	11.8	4.21
98.95°/°N ₂ + 1.05°/°CO ₂	34	28.8	10.3
97.45°/°N ₂ + 2.55°/°CO ₂	62	56.8	20.3
96.4°/°N ₂ + 3.6°/°CO ₂	74	68.8	24.6
95°/°N ₂ + 5°/°CO ₂	89	83.8	29.9
93°/°N ₂ + 7°/°CO ₂	105	99.8	35.6
89.9°/°N ₂ + 10.1°/°CO ₂	125	119.8	42.8

These data are plotted in Figure 34.

Figure 35 shows photographs taken with the 7/16 inch gas sample cell in operation. The selectivity control can be advanced still further to obtain greater voltage output before the selective amplifier begins to oscillate.

The sequence of traces in each photograph is the same and is as follows:

- (A) The topmost pair of traces shows the selective amplifier

FIGURE 34

79.7% N_2 + 19.25% O_2 + 1.05% CO_2

79.9% N_2 + 17.05% O_2 + 3.05% CO_2

80.3% N_2 + 14.7% O_2 + 5% CO_2

79.9% N_2 + 13.1% O_2 + 7% CO_2

output and input for the null adjustment.

- (B) The center pair of traces shows the selective amplifier output and input when a gas sample is introduced into the gas sample cell.
- (C) The bottom pair of traces shows the return to null upon purging the gas sample cell with N_2 .

CONCLUSIONS:

As a result of the work done in the development of this analyzer the following conclusions appear to be valid.

1. The instrument is free of microphonics other than those inherent in the vacuum tubes of the pre-amplifier. This is not a serious problem and could be eliminated entirely by employing low-noise transistors which would also contribute to miniaturization.
2. The response time is very rapid, so that readout is limited by the response of the meters or pen recorders used.
3. The analyzer responds only to the infrared energy within the pass-band of the interference filter. Filters are available commercially which will provide higher spectral resolution for the detection of CO_2 than is provided by the CO_2 itself as employed in the diaphragm detector.
4. The device is electronically stable and dependable and requires very few controls for normal adjustments.
5. The zero stability depends upon the optical stability, which in turn depends upon the mechanical rigidity of the optics. Standard

instrument machining should be adequate.

6. By using other narrow-band infrared filters, the analyzer may be sensitized for other gases having useful absorption spectra with wavelengths as long as 5μ . By employing other detectors and window materials, the range could be extended much farther into the infrared.
7. The sensitivity of the system may be increased greatly, permitting the determination of very small concentrations of CO_2 , by employing longer gas sample cells, or by increasing the pressure within shorter cells.
8. By modifying the optical system, the size of the transducer section (including the pre-amplifier) can be made relatively small. It is anticipated that a model occupying 125 cubic inches can be attained without complex machining.
9. No "all electronic" approach to chopping appears simple enough to justify its replacing the extremely simple and reliable motor driven wheel.

FUTURE WORK:

Having defined the basic system parameters in the foregoing work, immediate future plans call for construction of two prototypes containing the size reducing modifications previously mentioned. One of these units will be used in the Biophysics Laboratory at Baylor University College of Medicine, and the other will be employed in the Vital Studies Laboratory at the Institute for Rehabilitation and Research.

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(used PbSe photocell to detect 4.3μ band and prism to get band)

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