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A Method for Binary Gas Analysis Utilizing Ultrasonic Velocity Detection

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▶ A method for binary gas mixture analysis based upon a positive displacement gas mixing pump with ultrasonic velocity detection is described. The method is capable of achieving a precision of 0.05%. The accuracy is dependent upon the proper design of the mixing pump to ensure operation of the device in the linear response region of the ultrasonic detection system. Accuracies to four significant figures are attainable with most binary mixtures for the concentration range from 1 to 50%.

GASES of known composition are used extensively in the calibration of a variety of gas analysis instruments, particularly instruments which are used for continuous monitoring and are specific for a single gas such as oxygen or carbon dioxide. The usual approach for calibration is to purchase certified or analyzed gas mixtures from suppliers and utilize the data supplied by the manufacturer for calibration. The gas manufacturers commonly use standard analytical equipment equivalent to that utilized by the purchaser. This means the manufacturer in turn must have standards for calibrating his own instruments. Normally the manufacturer prepares his own standard using techniques similar to those employed in preparing the high pressure mixtures, but at lower pressures where mixing effects and deviations from perfect gas law behavior are less pronounced. (At least one gas producer, Precision Gas Products, Westfield, N. J., utilizes gravimetric techniques to eliminate these problems and reports accuracies to 4 and 5 significant figures.)

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Our own experience has shown that each specific analytical instrument or technique employed for analysis can provide reasonably precise results. When compared against a different approach, however, agreement may be to as few as one or two significant figures. We have attempted to circumvent the influence of operator competence through the development of a technique requiring little or no operator skill or experience and with only pure gases needed for single point calibration. The method as developed to this point utilizes the high precision inherent in the phase multiplier system of ultrasonic detection (1) with the simplicity of positive mechanical displacement and mixing of two gases. Although not required by this technique, the high reproducibility of the ultrasonic detection principle simplifies repetitive analyses performed over long time intervals.

EXPERIMENTAL

Basic Concept. With a detection system which provides perfect linearity of response over the range of 0 to 100% for binary gas mixtures, calibration could consist of simply replacing the pure major component with the pure minor component, thereby determining the absolute difference in response. If the minor component were present at a concentration of precisely 10%, then the response difference between the pure major component and the mixture would be precisely 0.1 the calibration value.

Although the change in ultrasonic velocity with concentration is not linear over the entire 0 to 100% range, a system has been investigated which reproducibly dilutes binary mixtures with the major component. In this way the detector can be operated in its linear range regardless of sample concentration, thereby providing linear calibration.

Figure 1 shows a schematic flow diagram of the system. Although shown schematically as two separate syringes, the mixing pump consists of a concentric, flow-through syringe, both chambers of which are fully isolated to prevent cross-leakage. The input to each chamber is controlled by independent directional-flow valves. When actuated, these valves shut off the gas flow to each chamber. Simultaneously, a drive motor is actuated, continuously displacing the contents of the larger chamber through the detector (which is on the output of the mixer) to provide a baseline value. After a predetermined time interval to insure stabilization of the baseline, a mixing valve is actuated, thereby directing the flow of gas from the smaller chamber into the mixer. This results in a step change in response, the height of which is dependent upon the composition of gas in each chamber. The actual operating sequence, referred to Figure 1, is as follows:

Pistons in full out position, all power off, valves *A* and *B* open to piston, valve *C* open to vent. Reference gas flows through chamber *L* to detector cell, sample gas flows through chamber *S* and vents.

Motor drive and valves *A* and *B* actuated simultaneously. Both sample and reference gases vented. Pistons displace gases from chambers *S* and *L*. Gas from chamber *L* establishes baseline value while gas from chamber *S* vents.

Valve *C* actuated. Gas from chamber *S* is directed to mixing chamber. Mixed gas passes to detection cell and results in a step change in response.

Valve *C* shut off. Sample gas vents, baseline returns to previous value.

Limit switch 2 shuts off drive motor and valves *A* and *B*.

Drive motor reversed until stopped by limit switch 1. The unit is now ready for the next analysis.
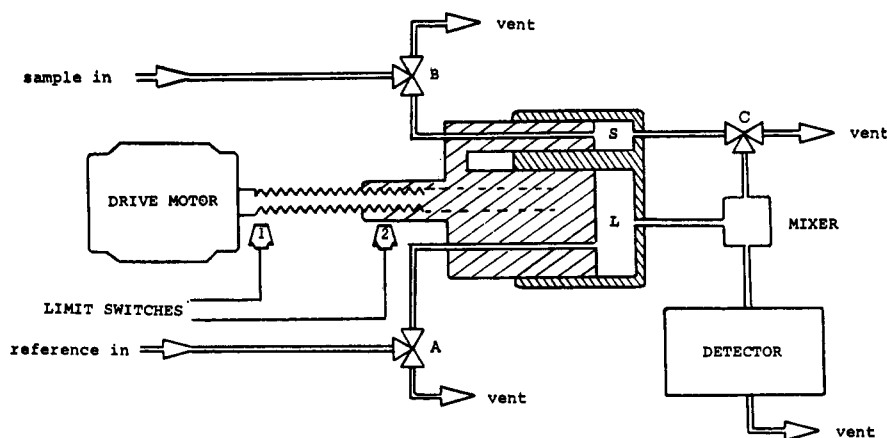
Although we exclusively used an

Figure 1. Schematic flow system for binary analysis

analog readout and manually measured the height of the step change in response, a digital readout is also possible.

As an example of operation, if the large piston chamber contains air and the small piston chamber contains carbon dioxide, mixing of their contents will calibrate the system for the analysis of carbon dioxide in air provided the total mixture is within the linear response region of the detector. If the gas whose composition is precisely 10% CO_2 in air is used in the small piston chamber and air of equal purity to that used in preparing the mixture is used in the large piston chamber, then mixing of their contents will produce a step change precisely 0.1 as large. Because it is essential that the detector

operate in a linear response region, the response vs. concentration must be known. Figure 2 illustrates the response-concentration curve for carbon dioxide in air with the phase-measuring ultrasonic detector operating at 6 Mc. From these data, it was determined that the response is linear (to 1%) up to 7% carbon dioxide in air. The ratio

of chamber volumes in the concentric syringe was designed to be 100:5, thereby ensuring operation in the linear region. Results of tests on the system using carbon dioxide–air mixtures analyzed by the National Bureau of Standards are shown in Table 1.

Response vs. Binary Concentration. As emphasized above, successful application of this technique requires that the linear response range for any binary mixture of interest be known. The data of Figure 2 were obtained using a flow system consisting of the components shown in the block diagram of Figure 3. In this system the flow rate of gas A was measured and kept constant at about 50 ml./minute. A manual three-way valve allowed the mixing of gas B at selected flow rates with gas A. The ultrasonic cell configuration provided for gas flow perpendicular to the sound transmission path, thereby eliminating sensitivity to the resulting flow rate changes through the cell. The two gases were then exchanged to provide complete coverage of the concentration range from 0 to 100%. Thirty-five additional binary combinations of common fixed gases were examined for re-

Table I. Analysis of CO_2 in Air Using Concentric Syringe Pump

	CO_2 in air, %		
Concentric syringe	20.19 ± 0.08	10.45 ± 0.03	6.41 ± 0.01
NBS analysis[a]	20.1 ± 0.1	10.6 ± 0.1	6.4 ± 0.1

[a] Values obtained by mass spectrometry for Wade Marshall, Laboratory of Neurophysiology, National Institute of Mental Health, NIH, Bethesda, Md.
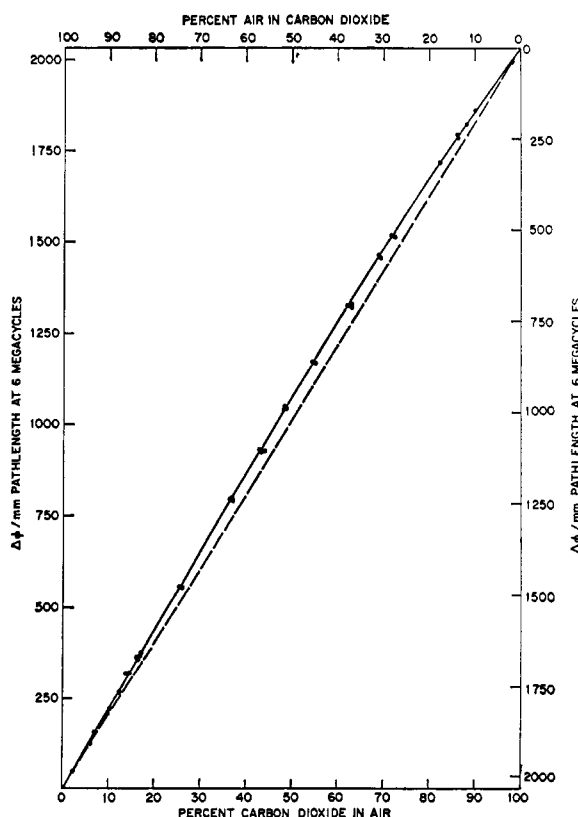

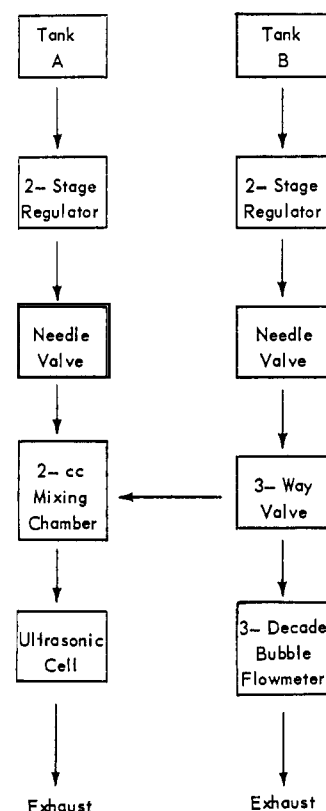Figure 2. Response for carbon dioxide–air system at 25° C.

Figure 3. Block diagram of binary flow mixing system

Table II. Maximum Linear Range for Per Cent Sample in Carrier

	Reference								
	H₂	He	CH₄	N₂	CO	O₂	A	CO₂	N₂O
H₂	..	6	16	11	11	10	15	6	5
He	11	..	10	9	8	12	13	26	6
CH₄	11	22	..	11	22	6	6	16	20
N₂	6	12	17	..	3	23	4	26	21
CO	10	16	5	9	..	10	3	21	5
O₂	11	25	20	24	26	..	3	19	17
A	6	12	7	12	16	10	..	22	24
CO₂	5	6	6	7	25	27	21	..	..
N₂O	6	10	4	14	13	6	13	..	..

sponse linearity by this technique. The gases used were hydrogen, oxygen, nitrogen, carbon dioxide, carbon monoxide, helium, argon, methane, and nitrous oxide. The maximum linear response range (to 1%) for each combination is shown in Table II. For example, the maximum linear range for hydrogen using helium as a reference is 0 to 6% while the maximum linear range for helium using hydrogen as a reference is 0 to 11%.

Sound frequency of 6 Mc. was used for all gas mixtures except those containing nitrous oxide or hydrogen. The high attenuation of sound in many gases limits their use to ultrasonic systems of lower frequency, particularly if the gas is a mixture of two or more components. Hydrogen can, for example, be used at 6 Mc. provided the concentration of mixing gas is less than 20% or greater than 80%. Nitrous oxide can be used at 6 Mc. only if its concentration in a gas of lower sound attenuating characteristics is less than about 5%. Accordingly, data points for these gases were obtained using a 2 Mc. ultrasonic system. (All 36 response vs. concentration curves may be obtained by writing the author.)

Precision of Measurement. We have mentioned in a previous publication (1) the inherent precision of a

phase multiplier ultrasonic system. For this gas analysis technique specifically, the phase multiplier attachment is of significant interest. (An ultrasonic detection system is commercially available from Micro-Tek Instruments, Inc., Baton Rouge, La. The phase multiplier attachment, however, is not available commercially.) The basic phase measuring ultrasonic system has excellent precision for phase changes greater than 180° because of its inherent feature of folding over at each 180° interval. That is, with a recorder capable of 0.25% precision, a phase change of 180° can be read to a maximum precision of 0.25%, regardless of the higher precision capabilities of the system. However, for a phase change of 1800° (which represents 10 full-scale deflections of the recorder and phase meter), the precision can be 0.025%. Phase multiplication can be accomplished only by precise integers. Hence, multiplication of a 180° phase change by 10 or an 18° phase change by 100 allows a precision of 0.025% to be obtained using a standard 0.25% recorder. This is the approach we have used: the step response of the system actually consisting of up to 15 full-scale recorder deflections. The precision obtained in calibrating the carbon dioxide–air system was 0.05% and decreased directly

with sample concentration in the mixture due to fewer deflections, even with phase multiplication.

The time required for recording an analysis was 1.5 minutes, consequently a recorder of moderately high response speed (0.5 second full-scale) was required to follow the fold-over response.

DISCUSSION

The binary gas analysis approach described above offers a high degree of operational simplicity, reliability, and precision. It does not, however, make full use of the precision and reproducibility of the ultrasonic system. The phase measuring ultrasonic system is a primary, rather than secondary, measuring device. The only instrumental variables which influence its response are sound path length and sound frequency, both of which are interdependent and both of which can be controlled and held constant to better than five significant figures. Therefore, calibration data of the type plotted in Figure 2, but of higher accuracy, could be used directly for binary gas analysis without the necessity for utilizing additional devices such as the gas mixing pump described above. With an accurate knowledge of sound pathlength (which can be measured) and gas temperature (which can be precisely controlled), such data obtained in one laboratory can be utilized by all other laboratories similarly equipped with the same frequency detection system.

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Primary Standards for Trace Gas Analysis

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▶ The permeation rates of gases enclosed in sections of plastic tubing permit the dispensing of nanogram quantities at will. Following an initiation period of a few hours to several weeks, permeation proceeds at a highly constant rate until the enclosed gas is nearly exhausted. The rate of permeation is highly temperature-dependent, but is independent of normal changes in pressure and composition of the atmosphere. Methods for the fabrication, calibration, and use of permeation tubes are described. Data are presented to illustrate the precision of these methods.

THE development of sensitive ionization detectors, such as those now used in gas chromatography and other instrumental methods of analysis, has run far ahead of the ability to prepare accurate low concentrations of gases and vapors. While the analyst finds it relatively easy to detect a volatile compound present in nanogram or even picogram quantity, he is often frustrated in trying to establish primary standards against which to compare the exact quantity present in an unknown sample. This is particularly true in air pollution research, where the analyst often wishes to establish the quantitative

relationships of a dozen or more members of a complex mixture, no one member being present to a greater extent than a fraction of a part per million.

Previously reported methods of producing low (p.p.m.) concentrations of gases vary from direct volumetric or gravimetric (4, 5, 6) dilution, through diffusion in tortuous channels (7), to linear steady-state diffusion (1) in tubes of precisely known dimensions. The method presented here is simpler than its predecessors in both equipment and application. Requiring no cumbersome or delicate equipment other than