Measurement of Concentration Fluctuations with an Electrical Conductivity Probe

D. E. LAMB, F. S. MANNING, and R. H. WILHELM
Princeton University, Princeton, New Jersey

An electrical conductivity probe capable of measuring liquid phase concentration fluctuations occurring at frequencies up to 8 kc. is described. The design permits concentration measurements in volume elements of the order of 3 x 10^{-5} cc. The probe was applied successfully to the measurement of turbulent concentration fluctuations.

The ability to measure local spatial and temporal variations in fluid composition is of research interest in relation to many industrial processes that rely on turbulence to bring about the diffusive transport of matter and the mixing and reaction of components. Usually such variations are distributed randomly about mean values and require reduction of results to statistical expression. There is need in the growing fields of process analysis, control, and optimization for a variety of capabilities in the measurement of both regular and random variations of point compositions. The present paper is concerned with the design and characteristics of a concentration probe for measuring such local concentration variations by means of the corresponding instantaneous changes of electrical conductivity of a tracer substance (sodium-chloride solution) as it mingles with a flowing stream of water. A previous probe design by Prausnitz and Wilhelm (*4*) consisted of two electrodes of equal size and encompassed a much larger volume element than the present device which utilizes an electrode pair of greatly disparate size. Concentration variations in liquids also have been measured by means of conductivity cells by Kramers, Baars, and Kroll (*1*).

The electrical conductivity probe here described is capable of measuring liquid-phase concentration fluctuations of frequencies up to 8 kc. Concentration variations in volume elements of the order of 3 x 10^{-5} cc. may be detected over a concentration range of six orders of magnitude. The probe has been applied successfully to the measurement of turbulent concentration fluctuations (*2*).

PROBE

The flow of alternating current through electrolytes follows Ohm's law:

$$I = E/Z_T \qquad (1)$$

The total probe impedance depends primarily on the specific conductivity of the electrolyte and the size and geometry of the electrodes. Consideration of the potential fields existing between the electrodes is essential in determining the probe geometry best suited for measuring the concentration of a small volume element. These potential fields extend to infinity, and hence the total flow of current between the electrodes is related to the conductance of all the fluid volume elements present. Specifically the importance of any given volume element in determining the total current flow is proportional to the current density in that element. Hence a probe design capable of measuring the concentration of a small volume element must produce a relatively high current density in that element. Such a design is obtained when one electrode approaches a point in size, the unattainable case of an infinite current density and resistance being the limit. A practical compromise is an electrode of very small but finite size such that the current density in the immediate vicinity of the electrode is high relative to that at all other points in the fluid. By decreasing the size of one electrode the cell becomes sensitive to progressively smaller volume elements.

For inhomogeneous fluids in which specific conductance varies spatially, modification of the potential fields occurs. Calculation of the potential field for arbitrary spatial variations in specific conductivity is difficult. Fortunately the current density near the small electrode is so high relative to that in all other regions that even large variations in specific conductance in far distant regions have negligible effect on the total impedance. Variations in specific conductance in the vicinity of the small electrode where the current density is high have correspondingly large effects on the total impedance.

In the present large-and-small electrode pair the current flow is dependent on the dimensions of the small electrode and independent of the size and shape of the second electrode and the distance of separation, provided that both size and distance dimensions are large relative to those of the smaller electrode. Since the equipotential surfaces near the small electrode are nearly spherical with the electrode as their center, the directional orientation of the large electrode relative to the small electrode also is unimportant. The optimum cell design consists of one electrode of small dimensions with a second relatively large electrode located anywhere in the fluid except near the small electrode. The effect of relative sizes and distances are most easily determined by a three-dimensional model conductivity experiment, discussed later.

CONSTRUCTION

The conductivity probe is shown in Figure 1A. The small electrode comprises the probe tip and consists of an exposed circular cross-sectional end of platinum wire, 0.003 in. in diameter, the lateral surfaces of which are insulated. A stainless steel tube, 0.13 in. O.D., serves as both the large surface electrode and the containing sheath for the probe assembly. The assembly, approximately 2.5 ft. long, is arranged with a wire contacting the small electrode which is placed axially within the metal tube and insulated from it by a glass

---

D. E. Lamb is at the University of Delaware, Newark, Delaware; F. S. Manning is at Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

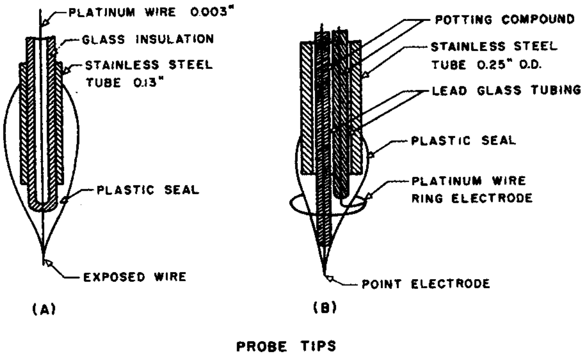


Fig. 1. Alternate versions of conductivity probe-tip construction.

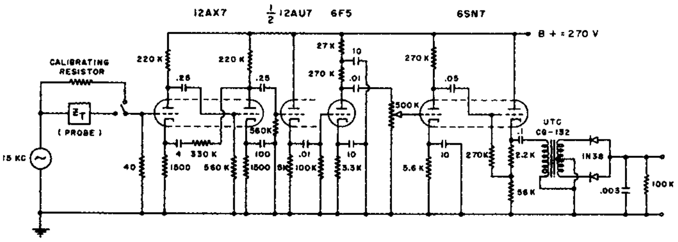


Fig. 3. Circuit for electrical conductivity probe.

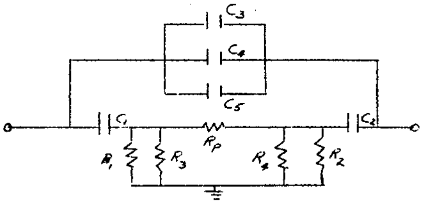
tube. The lower end of the assembly is sealed with an epoxy thermosetting resin. The resin is tapered from the metal tube to the probe wire and also forms a continuous insulation on the lateral surface of the wire up to the exposed end. A tight seal is obtained by curing the resin for 1 hr. at 180°C. The other end of the assembly terminates in a plastic block that serves to receive wires connected to the two electrodes through binding posts and also to attach the probe firmly to a mechanical positioning device.

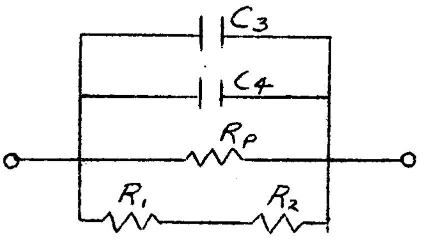
A second probe was constructed, Figure 1B, which was designed to be used in the vicinity of grounded metallic conductors. In this case the small electrode consisted of the cross-sectional area of a 26 guage platinum wire, while the second electrode was in the form of a wire ring having an exposed area of 0.04 sq. in. The most important modification was the grounding of the stainless steel sheath which minimized the effect of the exterior grounds by associating with the probe assembly a substantially constant and preferential path to ground. To minimize the effects of mechanical vibration the interior of the probe assembly was potted with methyl methacrylate resin.

It was shown (2) through the construction and use of tips of substantially different lengths and shapes that probe geometry did not noticeably affect concentration fluctuation measure. It was concluded that within the twofold range of dimension variation (2) the flow streams about the probe tips were not altered sufficiently to cause changes in the concentration fluctuation measure in the immediate vicinity of the tip.

ELECTRICAL CHARACTERISTICS

The equivalent circuit is shown below.





An order of magnitude analysis produces considerable simplification. Unless one electrode is within a few millimeters of a grounded metallic conductor, $R_1 << R_3$, and $R_2 << R_4$. The capacitances C_1 and C_2 are so large that even at low frequencies the capacitive reactances X_{C1} and X_{C2} are negligible compared with the resistive components of the circuit. Also the interelectrode capacitance C_5 is much smaller than C_3 or C_4. The equivalent circuit now becomes

The total impedance is

$$Z_T \cong \left(\frac{1}{R} + \frac{1}{X_C}\right)^{-1} \qquad (2)$$

where

$$R = \left(\frac{1}{R_P} + \frac{1}{R_1 + R_2}\right)^{-1} \qquad (3)$$

R is the quantity the probe is designed to measure. The quantity X_C is the capacitive reactance due to C_3 and C_4:

$$X_C = \frac{1}{j\,\omega(C_3 + C_4)} \qquad (4)$$

The capacitive reactance of the probe can be obtained by making $R \to \infty$; then $Z_T = X_C$. This limit may be achieved by measurement of total probe impedance when the electrolyte between the electrodes is replaced by dry air. The order of magnitude of X_C was found to be 250,000 ohms at a frequency of 15 kc. This corresponds to $(C_3 + C_4) = 100\ \mu\mu$f. Knowing X_C one can solve Equation (2) for R:

$$R \cong \frac{Z_T X_C}{X_C - Z_T} \qquad (5)$$

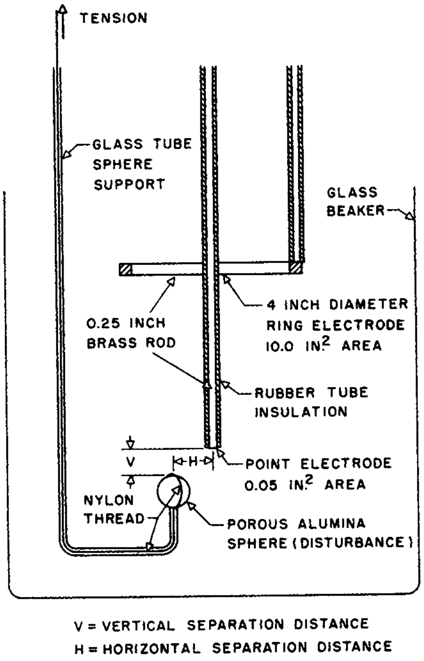


Fig. 4. Arrangement for three-dimensional conductivity probe experiment.

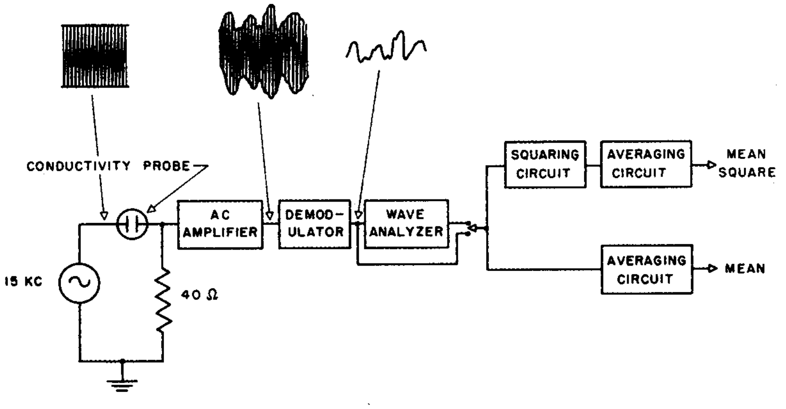


Fig. 2. Block diagram of components for reduction of electrical signal resulting from concentration fluctuations.

A probe constant analogous to cell constants of conductometric analysis is determined experimentally by the use of Equation (6):

$$k = \frac{K}{R} \qquad (6)$$

The resistive component of the total impedance is obtained when the probe tip is immersed in a solution of known specific conductance at constant temperature. Probe constants were of the order of 20 cm.$^{-1}$. Specific conductance of unknown solutions can now be identified through measurement of R and use of Equation (6).

MEASURING EQUIPMENT AND DATA PROCESSING

The circuit diagram is shown in Figure 2. Variations in probe impedance resulting from concentration changes near the small electrode are transformed into a voltage signal by using the probe impedance variations to amplitude modulate a 15-kc. carrier. The resulting signal is amplified, rectified, and filtered to yield an output voltage inversely proportional to the probe impedance. In the present application the probe impedance varied in a random manner. The block diagram shows conventional equipment used in the statistical analysis of random signals. Squaring and averaging circuits are used to obtain mean-square and time-average values of the voltage signal. These circuits are also shown combined with a wave analyzer to obtain the power spectrum of the random signal.

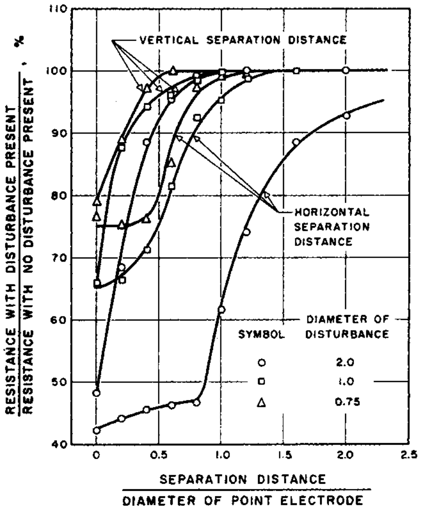


Fig. 5. Location of conductive spheres of different sizes (relative to probe-tip size) to achieve a threshold signal.

A detailed diagram is shown in Figure 3. Of particular importance is the input circuit including the carrier oscillator, the probe, and the 40 ohm load resistor on the grid of the first amplifier. To insure linear modulation it is necessary that both the output impedance of the oscillator and the value of the load resistor be low relative to the probe impedance. It is also necessary that the capacitive reactance of the probe at the carrier frequency be an order of magnitude greater than the resistive part of the probe impedance.

Mathematical analysis of the relationship between the resistive part of the probe impedance and the voltage appearing at the grid is generally greatly complicated by the presence of the probe capacitance since a set of nonlinear equations results. An experimental approach was adopted in the circuit design such that linear performance was closely approached. Satisfactory operation was secured with an oscillator output impedance of less than 100 ohms and a load resistor of 40 ohms with a probe resistance of 30,000 to 150,000 ohms, probe capacitance less than 100 $\mu\mu$f. and carrier frequency of 15 kc. The load resistor is sufficiently small to insure modulation linearity and at the same time large enough to prevent prohibitive attenuation.

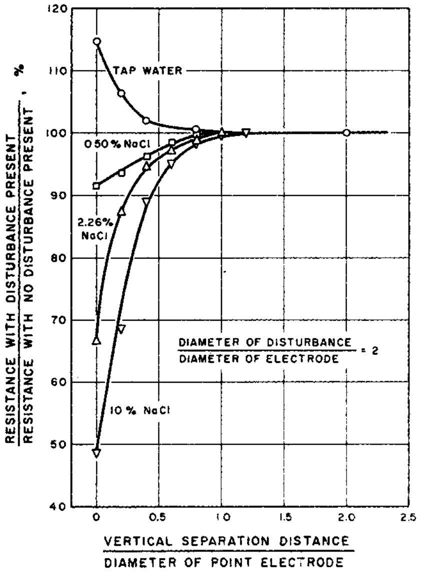


Fig. 6. Effect of conductivity and location of a turbulent eddy analogue (porous sphere filled with sodium chloride solutions of different concentration) on the electrode system resistance. Traverse is at a constant horizontal separation distance of 0.00.

To calibrate the electrical system a precision resistor was substituted for the probe. Since the relation between demodulator output voltage and probe impedance is linear, it is necessary only to establish the proportionality constant by this procedure.

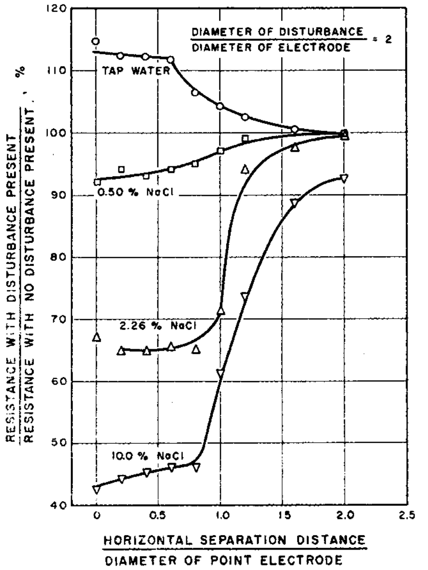


Fig. 7. Effect of conductivity and location of a turbulent eddy analogue (porous sphere filled with sodium chloride solutions of different concentration) on the electrode system resistance. Traverse is at a constant vertical separation distance of 0.00.

PERFORMANCE

An important conductivity probe characteristic is the surrounding volume within which a concentration nonuniformity will become evident as a measurable signal variation. The size of this volume was determined experimentally on a probe model (Figure 4) which for convenience of manipulation was scaled up by a linear factor of 16, retaining the electrode area ratio of 200:1 as in the prototype (2).

The net effect of a conductivity nonuniformity at various positions in the electrical field was determined by an impedance measurement between the electrodes, referred to the impedance when the disturbance was removed completely from the system. The effects of disturbance size, conductivity, and position were investigated and are presented in Figures 5, 6, and 7. The electrode assembly, Figure 4, consisted of the model placed in a large glass beaker of water together with a simulated concentration nonuniformity which could be located at defined geometric positions in relation to the small electrode. The simulated nonuniformities (representative of concentration fluctuations in a dynamic system) comprised porous ceramic spherical pellets which were filled with conductive solutions of sodium chloride. The conductive spheres in various sizes were held firmly to the end of a glass tube by means of a monofilament nylon thread. The glass tube in turn was attached to a compound vise positioner. As shown in Figure 5 and 6 the volume size to which the probe is sensitive is nearly independent of the disturbance conductivity. Within the range of disturbance diameters, 0.75 to 2.0 small electrode diameters, the region of sensitivity is approximately five disturbance volumes.

Sensitivity of the system to changes in concentration in the vicinity of the probe tip was such that concentration variations of the order of one part in 10^6 could be accurately measured. These fluctuations contained measurable frequency components over the range of 0 to 8,000 c/sec. In the absence of mechanical vibration of the probe the signal to noise ratio of the entire system decreased from a value of 20:1 at 20 c/sec. to a value of 3:1 at 8,000 c/sec.

ACKNOWLEDGMENT

The authors acknowledge the financial assistance in the form of fellowships and research assistantships given by Celanese Corporation of America, Consolidation Coal Company, and Shell Development Company. The gift of electronic equipment by Electronic Associates, Incorporated, also is appreciated.

NOTATION

C = capacitance, farads
$C_{1,2}$ = large values of capacitance resulting from orientation of ions and polar molecules in the fluid at electrode surfaces
C_3 = capacitance existing between wires connecting probe to electronic equipment
C_4 = capacitance resulting from presence of dielectric between probe wires
C_5 = capacitance between two exposed electrodes
E = potential, v.
I = current, amp.
j = $(-1)^{1/2}$
K = probe constant, cm.^{-1}
k = specific conductance, $(\text{ohms})^{-1}(\text{cm.})^{-1}$
R = resistance, ohms
R_P = total resistance of conducting fluid
$R_{1,2}$ = resistances from each electrode to grounded probe sheet; infinite if grounded probe sheet is not used
$R_{3,4}$ = resistances from each electrode to ground via conducting fluid
X_C = capacitive reactance, ohms
Z_T = probe impedance, ohms
ω = angular frequency, radians $(\text{sec.})^{-1}$

LITERATURE CITED

1. Kramers, H., G. M. Baars, and W. H. Knoll, *Chem. Eng. Sci.*, **2**, 35 (1953).
2. Manning, F. S., Ph.D. dissertation, Princeton Univ., Princeton, New Jersey (1959).
3. Prausnitz, J. M., and R. H. Wilhelm, *Rev. Sci. Instr.*, **27**, 941 (1956).

Manuscript received June 26, 1959; revision received February 1, 1960; paper accepted February 1, 1960. Paper presented at A.I.Ch.E. San Francisco meeting.

Mixing in a Jet-Stirred Reactor

WILLIAM BARTOK, CARL E. HEATH, and MALCOLM A. WEISS

Esso Research and Engineering Company, Linden, New Jersey

Measurements were made of the over-all mixing in a gas phase flow reactor stirred by the entering feed jets. The mixing was studied by following the decrease in exit concentration after sharp cutoff of a radioactive tracer gas krypton —85. The data showed that over the entire range of average residence times investigated, about 0.4 to 16 sec., the reactor behaved as though 85% of its volume was perfectly stirred and the remaining 15% was in piston flow in series with the stirred region. Relocation of the feed jets would probably increase the fraction of volume that is effectively perfectly stirred to about 95%.

A study was made of the over-all quality of mixing in a gas phase flow reactor stirred by the incoming feed jets. The reactor was designed to be completely stirred, that is completely uniform in composition, and the intent of this study was to determine how closely the design objective had been realized. The mixing study was essentially a study of the distribution of residence times of gases flowing through the reactor. Because the ideal completely stirred reactor represents one extreme of distribution of residence times varying exponentially from 0 to ∞, its theory has been analyzed extensively by a number of workers, for example (*1 through 5*). At the other extreme is the ideal piston flow reactor in which all material has the same residence time. Despite the theory no gas-phase reactor has been shown to be perfectly stirred in practice, although Longwell and Weiss (*6, 7*) found it useful to assume perfect stirring for their spherical combustion reactors.

EXPERIMENTAL PROCEDURE

The jet-stirred reactor used in this study was a squat cylindrical vessel with an inside diameter of 3.5 in. and an inner length of 1.125 in. Its net reaction volume, between inlet and outlet holes, was 161 cc. The photograph in Figure 1 presents an exploded view of the reactor. The flow through the reactor is shown schematically in Figure 2.

The gas feed, entering at the left, jets into the reactor tangentially through holes in the sixteen feed quills. Each quill has eight 0.0135-in. holes spaced 0.125 in. apart. The jets cause the reactor contents to swirl around the axis, and the gases finally leave the reactor through sixty holes, 0.0595-in. diameter, in the cylindrical surface on the reactor axis.

The mixing was studied by means of a tracer-decay technique developed in this laboratory (*8*) with krypton-85 gas which