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CONF-830622--7

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WITH HIGH-SPATIAL-RESOLUTION FOR USE IN VERY-SALINE SOLUTIONS

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SUBMITTED TO The ASES Annual Meeting in Minneapolis, Minnesota,
on June 1-3, 1983.

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DEVELOPMENT OF A POINT-ELECTRODE CONDUCTIVITY SALINOMETER WITH HIGH
SPATIAL RESOLUTION FOR USE IN VERY SALINE SOLUTIONS*

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ABSTRACT

A conductivity probe and circuit were developed to measure salinities in sodium chloride salt-gradient solar ponds. A point-electrode salinometer design was chosen to give a spatial resolution of approximately 1 mm (0.039 in.). Such high spatial resolution was necessary to study the behavior of thermohaline columns in the vicinity of convective/conductive zone boundaries. The point-electrode conductivity instrument was designed for use in up to 25 wt % salinities with immersion times of about 0.1 year or longer. Drift in the instrument, however, caused principally by changes in the surface condition of the platinum probe tip and reflected by changes in the probe cell constant, required periodic *in situ* calibration against the measured specific gravity of withdrawn fluid samples.

1. INTRODUCTION

In the course of an investigation into the hydrodynamics of sodium chloride salt-gradient solar ponds,^{1,2} specifically the behavior of thermohaline columns in the vicinity of convective/conductive zone boundaries, we found it necessary to develop a salinometer capable of spatial resolution of approximately 1 mm (0.039 in.), to operate in salinities up to 25 wt %.

Because saline solutions are electrolytic, it is possible to measure salinity (percentage by weight of salt in solution) as a function of specific conductivity and temperature.³ Measurements are done with devices called conductivity cells (usually dual electrode) that measure ac conductivity** in the kilohertz region and use a bridge for signal detection. Electrodeless (induction) conductivity cells are also available⁴ and can show superior long term stability because they do not have electrodes that deteriorate.

Commercial conductivity probes generally have spatial resolution of several centimeters and are usually intended to measure salinities < 3%. A survey of the literature revealed the development of point-electrode conductivity probes to achieve high spatial resolution.⁴⁻¹² These point-electrode probes are a variation of the dual-electrode conductivity cells, but with the second electrode having several hundred times the surface area of the first (rather than being of equal area as in the usual conductivity cells). Because the surface area of the point electrode is so much smaller than the secondary electrode and the same total current flows between each electrode, the volumetric current density is much higher at the point electrode than at the secondary electrode. Hence, the conductivity of the solution in the vicinity of the point electrode is weighted much more heavily than the conductivity of the solution in the vicinity of the secondary electrode by approximately the ratio of the secondary-electrode area to the point-electrode area. For an area ratio of several hundred, the effect of the solution conductivity in the vicinity of the secondary electrode is negligible.

2. SALINOMETER CIRCUIT THEORY AND DESIGN

The work of Broughton,¹⁰ Lambert et al.,⁷ and Khang and Fitzgerald¹¹ forms the

*This work performed under the auspices of the US Department of Energy, Office of Solar Heat Technologies.

**Set of conductivity curves for sodium chloride solutions compiled by Beckman Instruments, 89 Commerce Rd., Cedar Grove, NJ 07009.

⁴Beckman Instruments, 89 Commerce Rd., Cedar Grove, NJ 07009, manufactures both electrode and electrodeless conductivity instruments.

basis of the salinometer circuit and probe design reported here. T. J. Fitzgerald had developed a breadboard circuit of an improved design that had been used at Oregon State University to measure species concentration. This circuit, adapted for use in very saline solutions, comprises an oscillator, a multiplier, and a quad operational amplifier,* and uses a dual-electrode point probe to measure the conductivity of an electrolyte. A schematic of the circuit is shown in Fig. 1. The principle of operation is described in Grimmer et al.¹³

Figure 2 shows a block diagram of the wiring between the IC packages that were used to construct the schematic circuit shown in Fig. 1. Table I lists the components for the circuit. Figure 3 shows the linearity of the probe circuit. A decade resistor box was used to provide R_p values.

Several versions of this salinometer circuit were built and tested. The circuit was found to be extremely stable, particularly when insulated from rapid temperature changes.** In normal operation in very saline solutions, the solution conductivity was brought into the linear range of the circuit (< 12-Vdc output) by putting a 625 Ω , 0.1% precision resistor in series with R_p . The alternative is to vary the gain of the circuit.

In the course of other work¹³ to develop a point tetraprobe (four-electrode electrical conductivity probe), we learned that Pt electrodes degrade in chloride solutions without capacitive blocking of dc current⁺ or when the peak-to-peak voltage (at the electrodes) exceeds 0.6 V. To eliminate this problem, we decreased the output of the oscillator with a voltage divider before inputting the signal to the first op-amp at pin 5 of the LM349 (see Fig. 2) to lower the voltage at the electrodes. This should not turn off the oscillator and will effectively reduce circuit gain and voltage across R_p .

*Literature on the quad operational amplifier LM 348 is available from National Semiconductor Corp., 2900 Semiconductor Dr., Santa Clara, CA 95051

**To avoid periodically rezeroing the salinometer circuit voltage for infinite resistance (zero conductivity), a switch may be used in series with the probe and two voltages read with the switch closed and open. The true solution voltage is found by subtracting the open-circuit voltage from the closed-circuit voltage.

⁺This information provided by M. J. Head, Head Designs, Encinitas, CA 92024, 1982.

Fig. 1. Schematic for salinometer circuit.

Fig. 2. Block layout of the wiring between the IC packages to construct the schematic circuit shown in Fig. 1.

Fig. 3. Plot of circuit output voltage (in volts) vs probe conductivity (in mho's).

TABLE I
SCHEMATIC AND LAYOUT COMPONENTS LIST

R_1	= 100 000 Ω
R_2	= 24 000 Ω
R_3	= 18 000 Ω
R_4	= 1 200 Ω
R_5	= 5 100 Ω
R_6	= 8 200 Ω
R_7	= 1 800 Ω
R_8	= 8 200 Ω
R_9	= 300 000 Ω
R_{10}	= 300 000 Ω
R_{11}	= 81 000 Ω
R_{13}	= 6.8 k Ω
R_{14}	= 100 k Ω slide-wire pot
C_1	= 0.01 μ F
C_2	= 1.0 μ F
C_3	= 1.0 μ F
C_4	= 0.001 μ F (polystyrene)

3. POINT-CONDUCTIVITY-PROBE DESIGN AND CONSTRUCTION

After several design variations, the probe shown in Fig. 4 was chosen as a standard. The probe has a point electrode and a secondary electrode coiled around the probe tip to shield the point electrode against dc bias in electrolyte conductivity measurements.¹¹ Both electrodes are made from 0.51-mm (0.020-in.) -diam platinum (Pt) wire.

The probe is constructed in the following manner: A 5- to 7-cm (2- to 3-in.) length of Pt wire is cut for the point electrode. A 2.5-cm (1-in.) length of 2-mm standard Pyrex glass tubing is broken to slide over the point-electrode wire as an insulator. The glass tube is sealed to the Pt wire in the following fashion: The Pt wire is heated red-hot with a torch to drive off absorbed gases in the metal. After the wire is allowed to cool, the glass tube is slid over the wire to act as an insulating shroud. The wire/glass assembly is then heated to red-hot, at which point the glass begins to soften and seals to the Pt. Starting the sealing process with the torch at the probe tip and working along the glass shroud away from the tip, one can see the glass wet to the Pt wire as the torch is worked along the length of the wire/glass assembly. Describing the Pt wire initially and sealing the glass to the Pt wire as described above will avoid the formation

Fig. 4. Schematic of dual-electrode conductivity probe design.

of gas bubbles trapped in the glass. The Pt wire protruding from the glass is trimmed flush on the conductivity tip end and left approximately 8 mm (5/16 in.) long on the opposite end. The conductivity tip is filed smooth and then polished with crocus cloth before platinizing.

Further construction details are found in Grimmer et al.¹³ We should note, however, a critical step in the construction process is to apply generous amounts of Dow Corning DC 730 RTV fluorosilicone to all areas that are to be covered with shrink-tubing before the tubing is applied. The fluorosilicone acts as an insulator to prevent salt water from contacting the coaxial and platinum wire inside the probe. In addition, to eliminate the possible formation of air bubbles underneath the shrink-tubing, heat shrinking should be done from the middle of the tube length working outward to both ends.

In the early stages of our work, no glass shroud was used and the conductivity-point Pt wire was encapsulated with epoxy only. These epoxy-shrouded tips all deteriorated over time when immersed in the very saline solutions. Cracks appeared in the epoxy near the Pt tip, presumably caused by expansion and contraction mismatch between the metal and the epoxy. Degradation was much faster in epoxy resins with fillers (usually Al_2O_3 microspheres). The epoxy became chalky as the saline solution attacked the epoxy resin around and between the Al_2O_3 microspheres, which provide the solution a much larger resin surface area for attack than would a pure resin surface.

Before use, the point conductivity probe electrodes are platinized with black platinum in an electroplating process, using a Beckman Model PK 1A Platinizing Kit. The black platinum plating on the platinum probe

tip prevents salt water from attacking the surface of the platinum metal and thus minimizes the drift in probe calibration. The approximate schedule suggested by Beckman for cleaning Pt conductivity cells was followed: 100 mA for 6 min with 60-s reverse polarity.* However, the schedule for platinizing could not be followed because the point-probe electrodes have a much smaller surface than the electrode area of a standard Beckman conductivity cell. The tip became crusted over with black platinum powder. The tip should be only lightly platinized; excess platinum black will eventually dislodge and result in an irreversible change in the probe calibration. A platinizing time of 60 s at full current (~100 mA) reverse polarity and 30-s normal polarity was generally sufficient; however, a trial-and-error method with each probe was necessary. Cell constants (in cm^{-1}), which are defined as the measured resistance (in ohms) of a solution of known salinity times the known specific conductivity (in $\Omega^{-1} \text{cm}^{-1}$) of the solution, have generally been in the range from 5 to 15 cm^{-1} . As deterioration of the platinized tip progresses, the cell constant increases because of an increase in probe-tip surface-contact impedance.

After platinizing, the probe was calibrated in situ against samples extracted from the salt water in which it was immersed. Details of this procedure, along with specific conductivity vs salinity and temperature data may be found in Grimmer et al.¹³

4. SALINOMETER TEST RESULTS

Stability of the salinometer was examined first by immersing the probe in a solution of constant salinity for several weeks and establishing long-term drift. The probe was not removed from solution during this time. Results of this type of stability measurement are shown in Fig. 5. Over a 32-day period, the measured cell constant drifted up to 14.2% from the original value. The general increase in cell constant indicates an increase in point-electrode surface impedance.

A second stability analysis involved measuring the conductivity of a number of samples with different salinities and then monitoring changes in those cell constants. The probe was moved from one solution to another for measurement and, when not in use, it was immersed in fresh water. Results of this kind of measurement indicate changes of up to 6.5% in the cell constants from one day to the next. The

*Reverse polarity implies (+) terminal to center electrode and (-) to secondary-electrode coil.

Fig. 5. Salinometer measurement using probe immersed in a solution of constant salinity (nominally 5%) for several weeks to establish long-term drift. Over a 32-day period, the measured cell constant drifted up to 14.2% from the original value. Dashed lines indicate some data not plotted.

behavior agrees reasonably with that shown in Fig. 5 for day-to-day fluctuations in the cell constant.

The observed drift of cell constant indicated that in situ calibration of the point probe would be necessary for precise and reliable measurements of salinity in thermohaline columns. This procedure is discussed in the next section.

5. POINT-SALINOMETER APPLICATION: SALINITY AND TEMPERATURE TRAVERSES IN A THERMOHALINE COLUMN

Salinity and temperature traverses were performed in a thermohaline column set up in the laboratory to study the hydrodynamics of salt-gradient solar ponds. Salinity was measured with the point-electrode salinometer described above. A Type T thermocouple was used to measure temperatures in the column in this instance. The probe was calibrated by independently measuring the salinity in both the well-mixed lower convective zone (LCZ), where the salinity is about 15-20‰ and in the well-mixed upper convective zone (UCZ), where the salinity is about 1-2‰. This independent salinity measurement is done by sample fluid extraction and specific gravity determination. Additional calibration points taken from the nonconvecting zone (NCZ) between the LCZ and UCZ are obtained by the sample fluid-extraction method. Stainless steel hypodermic-tubing taps at the precise level of the point probe are used to extract fluid for correlation with the output voltage of the point probe. A cathetometer establishes the exact height

of the probe tip and tubing centerline positions.

The results of the overall salinity and temperature traverses are shown in Fig. 6 (a) and (b), respectively. Note that the NCZ/LCZ boundary as measured by the temperature profile extends about 1.25 cm (0.5 in.) below the boundary as measured by the salinity profile. This effect is presumably caused by the greater relative diffusivity of heat than that of salt in

Fig. 6 (a). Results of a salinity measurement traverse in a thermohaline column.

Fig. 6 (b). Results of a temperature measurement traverse in a thermohaline column.

Fig. 7 (a). Profile of the boundary between the NCZ and LCZ for a salinity measurement in a thermohaline column.

Fig. 7 (b). Profile of the boundary between the NCZ and LCZ for a temperature measurement traverse in a thermohaline column.

the thermohaline column.¹⁴ Figures 7 (a) and 7 (b) show this boundary between the NCZ and LCZ in greater detail. Fluctuations in the salinity profile at the NCZ/LCZ boundary are noted in Fig. 7 (a). This behavior is not detected in the comparable temperature profile at the NCZ/LCZ boundary shown in Fig. 7 (b) nor in either the salinity or temperature profiles of the NCZ/UCZ boundary. From inspection of Fig. 7 (a), we see the region of fluctuation in the salinity profile of the NCZ/LCZ boundary to be approximately 1 cm (0.39 in.) thick and is caused, we theorize, by plumes of relatively cool fluid entering the LCZ from the boundary. Clearly, the point-electrode salinity probe can resolve spatial separations of about 1 mm or better.

6. CONCLUSIONS AND RECOMMENDATIONS

A point-conductivity instrument has been described for use in high-salinity solutions, with spatial resolution on the order of 1 mm (0.039 in.). Problems with long-term drift are present, but in situ calibration of the salinometer output voltage against the specific gravity and conductivity of withdrawn solution samples makes the instrument usable over the period of a traverse (3 h). Recommendations for future development of salinometers with 1-mm (0.039-in.) spatial resolution for use in high-salinity solutions include research on a miniaturized, electrodeless (induction) conductivity-type probe and on an ultrasonic density-type instrument.¹³

7. ACKNOWLEDGMENTS

The authors wish to thank the following individuals: D. Nepper for enlightening

discussions of thermohaline column behavior; L. Dalton and J. Hauser for excellent technical support, and J. Dreicer, K. Hedstrom, and C. Bates for assistance in data gathering.

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