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AEC RESEARCH AND DEVELOPMENT REPORT

ACID CONCENTRATION MONITOR

H. R. TILLEY, SR.

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Instruments
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ACID CONCENTRATION MONITOR

by

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ABSTRACT

An instrument for automatically measuring nitric acid concentrations over the range 0.1 to 2.75 normal is described. Acid concentration is determined by measuring conductivity with an electrodeless conductivity cell. The instrument is reliable, capable of continuous remote operation, and accurate within $\pm 5\%$ of reading above 0.5 normal. Temperature compensation is accomplished electronically with a thermistor.

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INTRODUCTION

Essentially continuous monitoring of the nitric acid concentration of plant process streams is a necessary part of an automatic sample analysis system under development. To meet the requirements for safe process operation, the monitor must be reliable, capable of remote operation, and accurate within $\pm 5\%$ of reading for acid concentrations between 0.5 and 2.75 normal.

Since solution conductivity varies with acid concentration, conductivity measurements can be used to indicate acid concentrations if certain precautions are taken. One requirement is to eliminate or compensate for anything other than acid concentration that will affect solution conductivity, such as temperature changes and other solution constituents. Most conductivity cells used in the past have had electrodes immersed in the solution. These cells have been unsatisfactory for remote, unattended operation over long periods of time due to electrode effects such as metal plateout, surface poisoning, and capacitance variations. An electrodeless conductivity cell does not have these limitations.

DISCUSSION

An acid concentration monitor is to be included in an automatic sample analysis system under development for one stage in the fuel reprocessing plants at the Savannah River Plant. A separate sampling system will provide process stream samples intermittently to the monitor, at a frequency many times greater than that needed for process control. Initial installation will be on a nitric acid stream that is controlled to about 4 normal. For process control, measurements must be made over a range of 3 to 5N with $\pm 10\%$ accuracy. Since the curve of nitric acid conductivity versus concentration (Figure 1) peaks at about 5N, the sample will be diluted with water (1 to 1 ratio) before measurement to ensure against signal reversal at higher concentrations. The instrument range of 0.1 to 2.75N was chosen to monitor the diluted solutions, where conductivity is the most linear function of acid concentration. The dilution ratio will be held constant and will be used as a multiplier to determine the actual acid concentration from the instrument readings. Known nitric acid solutions will be used periodically for checking the instrument

calibration. The calibrating solutions will also be fed through the diluter to check the dilution ratio.

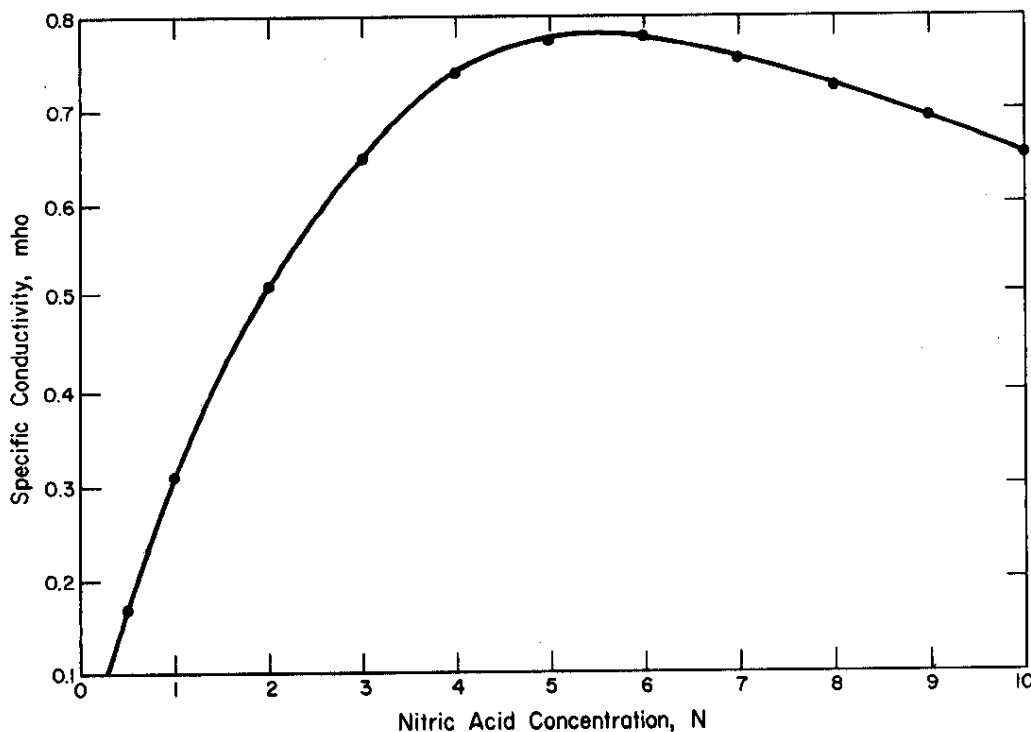


FIG. 1 CONDUCTIVITY VS CONCENTRATION OF NITRIC ACID (BECKMAN CURVE)

THEORY

The electrical conductivity of ionic solutions is dependent on the number and mobility of the individual current carriers or ions. Because the mobility of the hydronium ion (H_3O^+) present in nitric acid solutions is five to ten times that of other ions,¹ it is usually the controlling factor. If conductivity is to be used as an indication of acid concentration,² it must be known in advance that other sample constituents will not add appreciably to the sample conductivity. Ionic mobility is also a function of temperature (Figure 2); therefore conductivity measurements must be made under controlled temperature conditions or compensation must be applied to the measurements. Compensation may be accomplished electrically by using a thermistor in the sample line adjacent to the cell.

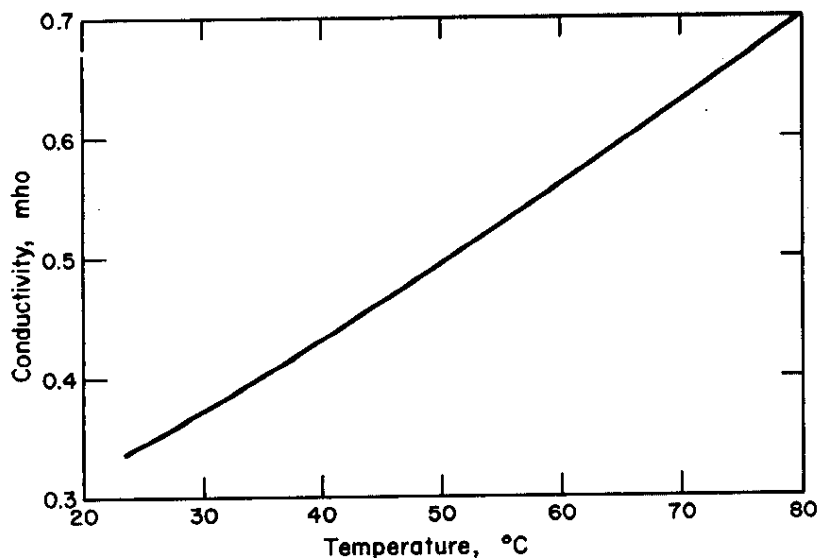


FIG. 2 CONDUCTIVITY OF NITRIC ACID VS TEMPERATURE
(1 NORMAL NITRIC ACID)

GENERAL DESCRIPTION

An electrodeless conductivity cell (Figure 3) manufactured by the Industrial Instruments Division of Beckman Instruments, Inc., was selected because it is simple and reliable.³ Its main advantage is that it does not depend on electrodes immersed in the sample, thereby eliminating many of the problems associated with cells using electrodes. In the electrodeless cell, two toroid coils are coupled electrically by a single turn loop, part of which is the liquid-filled sample line and the remainder a stainless steel bar. The coefficient of coupling between the toroids varies with the conductivity of the liquid loop. The coupling coefficient is measured by exciting one toroid with an 18-kHz signal and detecting the voltage induced in the second toroid. The cell, which is 15 cm long and 0.42 cm in diameter, has a "Teflon"* liner.

A disadvantage of the electrodeless conductivity cell is that it requires more complex electronic circuits for its operation than an electrode type cell. However, the electronic system developed uses all solid-state components which have had no

* Du Pont's trademark for its fluorocarbon plastic.

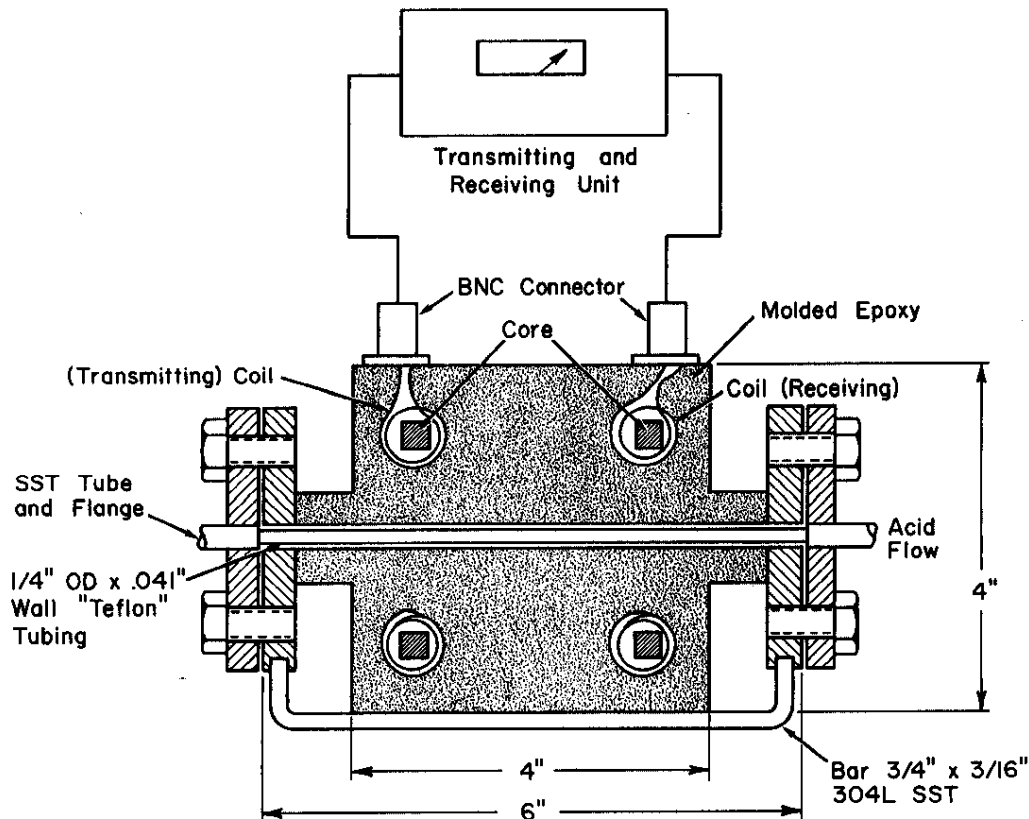


FIG. 3 ELECTRODELESS CONDUCTIVITY MEASURING SYSTEM

failures during several months of testing. The acid concentration is read from a meter calibrated from 0.1 to 2.75 normal. Measurements made by the instrument were compared with titration analyses made on the same samples (Table I). Agreement was within 2% at a controlled temperature of $25 \pm 1^\circ\text{C}$. Other tests were made over a temperature range of 25 to 50°C with various acid concentrations to check the accuracy of the temperature compensation circuit. Compensation error varied with concentration from ± 1.2 to $\pm 3\%$ (Table II).

Stability of reading is good although there is some drift during the first hour, until the oscillator comes to operating temperature. Once the oscillator output stabilizes, noise and drift are too low to be seen on the meter. If the sample has bubbles, they will break the conducting path in the probe and the meter will indicate zero.

TABLE I

Various Nitric Acid Concentrations
at Constant Temperature (25°C)

Sample No.	Instrument Reading (normality)	Laboratory Analysis (normality)
101	2.53	2.52
102	2.29	2.27
103	2.04	2.00
104	1.70	1.68
105	1.33	1.33
106	0.98	0.987
107	0.755	0.755
108	0.595	0.587
109	0.445	0.437
1	2.74	2.77
2	2.46	2.47
3	2.15	2.16
4	1.98	1.96
5	1.51	1.52
6	1.01	1.02
7	0.76	0.778

TABLE II

Temperature Compensation Error at Different
Concentrations of Nitric Acid

Normality	Compensation Error, % (25-50%)
1/8	±2
1/4	±3
1/2	±1.5
3/4	±2
1	±1.2
1-1/3	±2.5
1-2/3	±2.5
2	±2
2-1/3	±3
2-1/2	±3

CIRCUIT DESCRIPTION

In addition to the conductivity cell, the instrument consists of a transmitter, a receiver, power supplies, and a self-test circuit (Figure 4). The transmitter is a crystal controlled oscillator model S200CR made by Connor-Winfield Corporation. The oscillator has an output of 18 kHz at a nominal 5-volt rms. The frequency stability is $\pm 0.02\%$, and the amplitude stability is $\pm 0.1\%$ after warmup.

The receiver contains three Burr-Brown Type 1510 operational amplifiers. Two of the amplifiers are used as low-gain, high-stability amplifiers, and the third is used as a precision half-wave rectifier with some gain. Each amplifier has a closed loop gain of 13 and the rectifier stage a closed loop gain of 5. These

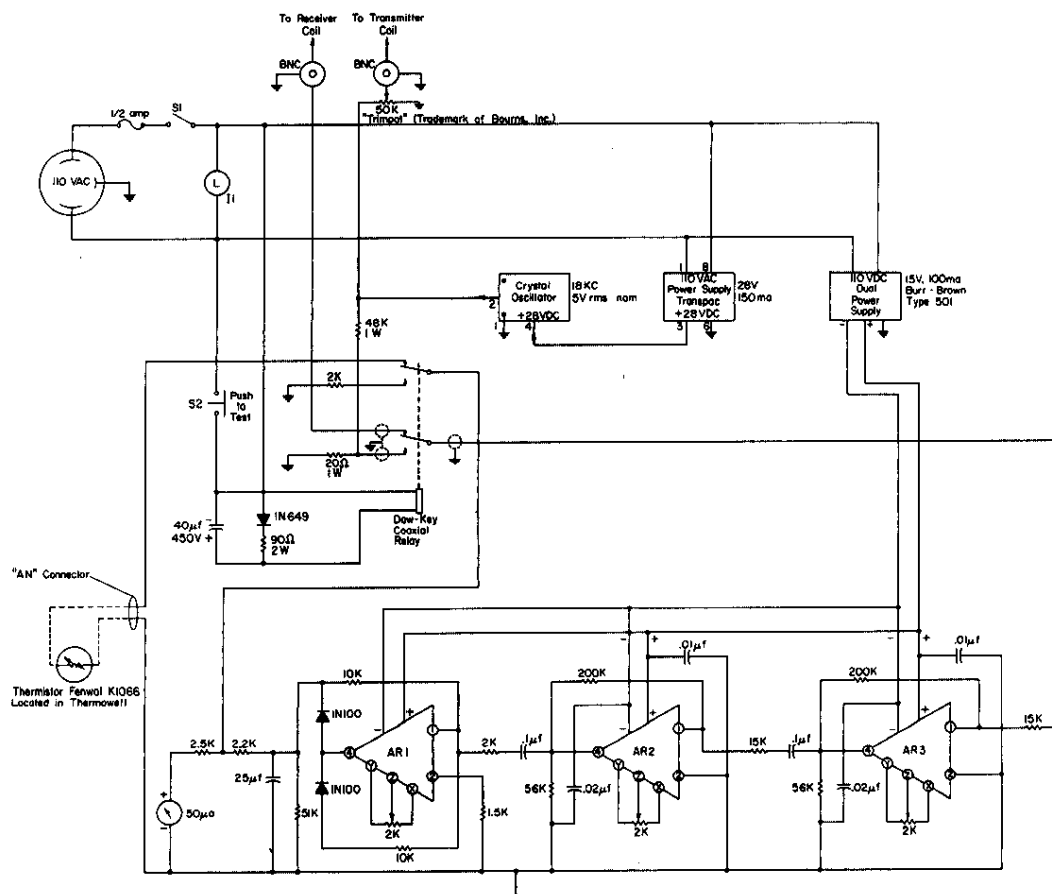


FIG. 4 ACID CONCENTRATION MONITOR ELECTRONICS

amplifiers have an open loop voltage gain of 3×10^4 ; because most of this gain is reduced by negative feedback, the stages are very stable and have negligible thermal drift.

STANDARDIZATION

The output of the transmitter oscillator is fed to a potentiometer whose value can be adjusted in the field to compensate for the shunting effect of cable capacitance. This system was calibrated in the laboratory with an output signal level that would exist if 100 feet of RG58/U cable were used to connect the instrument to the cell. The output of the oscillator is also connected to a voltage divider network from which a small percent of the signal is supplied to a coaxial relay. The relay, in its de-energized position, connects the signal from the receiver coil in the cell to the receiver input. In the energized position, the attenuated oscillator output is supplied to the receiver input giving a standard deflection on the meter for test purposes. The thermistor in the temperature compensating circuit is also switched out by an auxiliary set of relay contacts and a 2000-ohm resistor is switched in so that the test point will be unchanged regardless of sample temperature. Thus, the oscillator and receiver are tested simultaneously.

The power supply for the amplifiers is a Burr-Brown Type 501 dual supply with ± 15 -volt dc outputs. The receiver draws 6.5 milliamperes from the $+15$ -volt dc supply and 6.2 milliamperes from the -15 -volt dc supply when the coupling loop resistance is 110 ohms. The power supply for the oscillator is a Transpac Model No. TR30LQ, with the voltage adjusted to 28-volt dc.

The temperature compensation circuit uses a specially calibrated and housed thermistor, made by Fenwal Electronics, Inc., Type ISO-CURVE No. K1066-4K. It is mounted in a stainless steel holder, Fenwal Type H/33 modified to have a 0.036-inch-diameter hypodermic needle to house the thermistor itself. The housing gives a fast response to temperature changes: 6 seconds in still water (Fenwal data). This type of thermistor is made to match a standard calibration curve to $\pm 1/4\%$ between 25 and 50°C so that replacement units can be used without recalibration.

CELL CALIBRATION

An independent calibration test was made of the electrodeless cell using a decade resistance box connected in a series with a one-turn wire loop going through the cell. This test simulated acid solutions of various conductivities. Figure 5 shows the relationship of loop resistance to meter reading. At this time, the meter had not been calibrated in normality, so readings are recorded in arbitrary meter units from 1 to 100.

The cell was then filled with an acid solution of known concentration. The meter reading obtained with the acid solution was converted to an equivalent resistance using the curve in Figure 5. The specific conductivity was then calculated from the resistance and the cell dimensions. The value of conductivity thus obtained was compared to published data of conductivity versus concentration. Several values measured in this manner are plotted on the published curve in Figure 6.

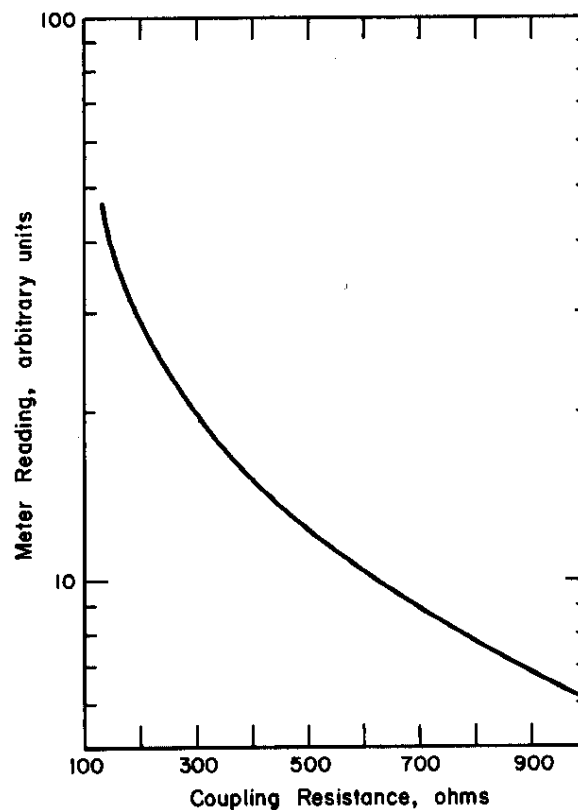


FIG. 5 COUPLING RESISTANCE VS METER READING

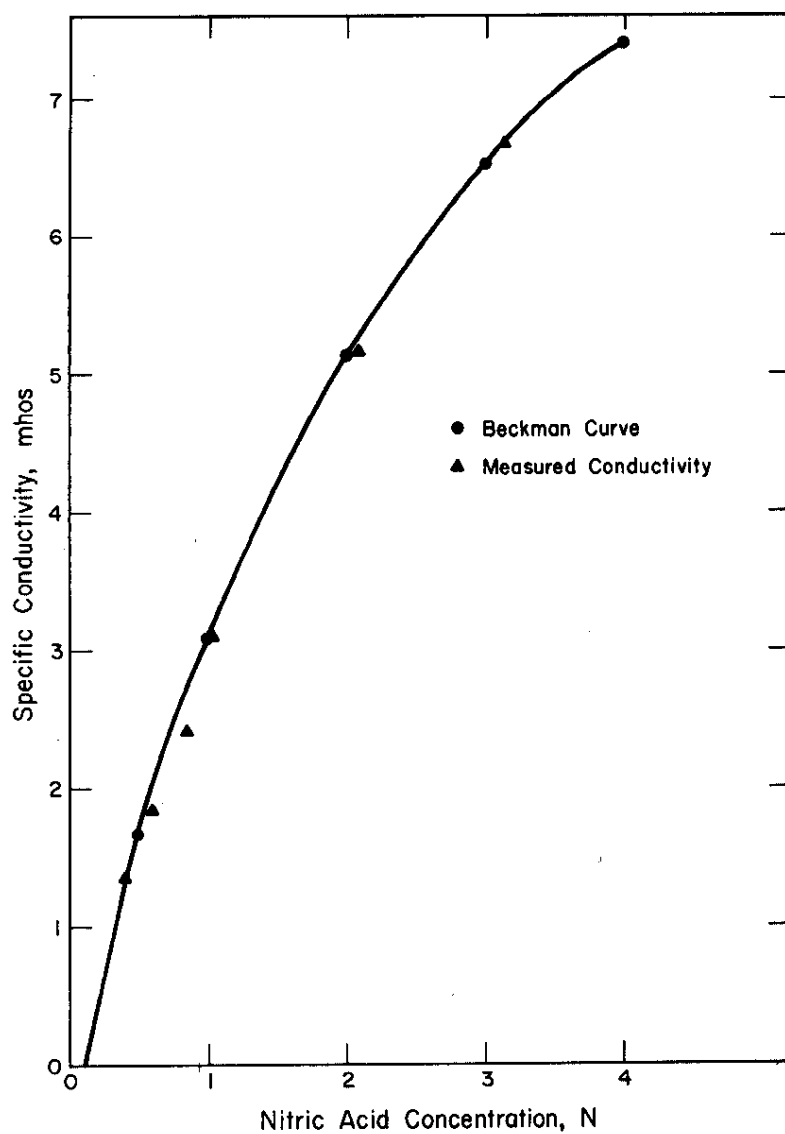


FIG. 6 COMPARISON OF MEASURED CONDUCTIVITY
AND PUBLISHED (BECKMAN) CURVE

REFERENCES

1. S. Glasstone. An Introduction to Electrochemistry. D. Van Nostrand Co., Inc., New York (1942).
2. R. C. Propst. Conductometric Acidimetry in the Presence of Hydrolyzable Ions. USAEC Report DP-76, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1955).
3. E. A. Sperry, III. "Conductivity Measurements with Electrodes," presented April 21, 1966, ISA Twelfth Annual Southeastern Conference, Augusta, Georgia (CONF-660408).