HEDL-SA-1894-FP

CONF-800401--15

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DEVELOPMENT OF A MODIFIED DIFFUSION TYPE CARBON ACTIVITY METER FOR LIQUID SODIUM

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January, 1980

Second International Conference on Liquid Metal Technology in Energy Production

April 20-24, 1980

Richland, WA

HANFORD ENGINEERING DEVELOPMENT LABORATORY
Operated by Westinghouse Hanford Company, a subsidiary of Westinghouse Electric Corporation, under the Department of Energy Contract No. DE-AC14-76FF02170

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DEVELOPMENT OF A MODIFIED DIFFUSION TYPE CARBON ACTIVITY METER FOR LIQUID SODIUM

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ABSTRACT

A high sensitivity automated carbon activity meter has been developed by combining elements of technology used in other instruments. The basic principle is the diffusion of carbon through an iron membrane driven by the concentration gradient between the sodium being measured and the sweep gas. The membrane used is similar to that used by Harwell workers, i.e., a coil of small diameter iron tubing with an oxide coating on the inner surface. A sweep gas of helium is used to pick up the carbon oxides generated by the reaction of carbon and iron oxide. The carbon oxides are converted to carbon dioxide in a copper oxide bed and measured with a gas chromatograph employing a helium ionization detector. This measuring system has an excellent signal-to-noise ratio and requires fewer gases than the flame ionization detector usually employed. The concentration of CO_2 in the sweep gas was in the range of 0.2 to 2 ppm when measuring carbon activity in a stainless steel system.

INTRODUCTION

Early work on measuring the concentration of carbon in sodium by both combustion analysis for total carbon and by the carburization of various materials for active carbon showed an excess of inert carbon. The property of primary concern in an operating sodium system is carbon activity. This has been measured by various methods. The currently accepted "standard" method involves equilibration of foils of Fe-12% Mn in sodium at 750°C followed by combustion analysis of the metal for its carbon content. A number of instrumental methods of measuring carbon activity have also been developed. They all rely on the transport of carbon through an iron membrane with evaluation of the carbon transported by various methods. Four of these can be described as equilibrium methods and two as dynamic. The equilibrium methods include the electrochemical cell of Salzano, et al of BNL,[1] the British electrochemical cell,[2] the indirect electrochemical cell of ANL[3] (designated COCOO), and the equilibrium gas pressure cell of ANL.[4] The dynamic methods are those developed by workers at UNC[5] and Harwell.[6]

The dynamic methods that have been developed depend on the transport of carbon through an iron membrane. In the UNC meter, a sweep gas of moist argon and hydrogen is used to convert the carbon to carbon monoxide, which is then converted to methane in a catalyst and measured by a flame ionization detector. The Harwell meter employs an iron membrane with an oxide layer on the gas side, where the diffusing carbon is converted to carbon monoxide and carbon dioxide. An argon sweep gas picks up the carbon oxides, after which hydrogen is added to the gas stream to convert the carbon oxides to methane for measurement as in the UNC meter. Different membrane geometries are employed. The UNC meter uses a cylindrical piece ∿1/2 inch dia x 4 inches long and a 0.010 inch wall thickness. The Harwell meter uses a thin walled tube of 3 mm dia. The UNC meter has the disadvantage of introducing hydrogen into sodium. This is particularly undesirable on small systems.

The present system uses a similar membrane to the Harwell system. But it converts the carbon monoxide to carbon dioxide on copper oxide, and it also employs a gas chromatograph to isolate the carbon dioxide from other gaseous species and a helium ionization detector to measure the concentration. The system offers the following potential advantages: (a) isolation of the desired chemical species (CO_2) from impurities reduces background interferences, (b) the helium ionization detector gives a high signal to noise ratio permitting measurement at low concentration levels, and (c) use of helium ionization detector eliminates the need for hydrogen and air to feed the flame ionization detector.

DESCRIPTION OF METER

Membrane Assembly

To fit in the carbon meter module of the Prototype Applications Loop (PAL) where the meter was to be tested, the membrane coil had to pass through a Marman Conoseal fitting with an internal diameter of 1.59 cm (0.625 in.). The membrane coil was wound from an 87 cm (34 in.) length of ingot iron tubing (3.18 mm (0.125 in.) OD with 0.43 mm (0.017 in.) wall thickness. Extensions of 304 SS tubing were welded to the ingot iron tubing to reduce or eliminate atmospheric corrosion. Other coil configurations will be used as needed to match the ports on other systems to be tested. Figure 1 is a diagram of the test membrane.

DIFFUSION CARBON METER PROBE

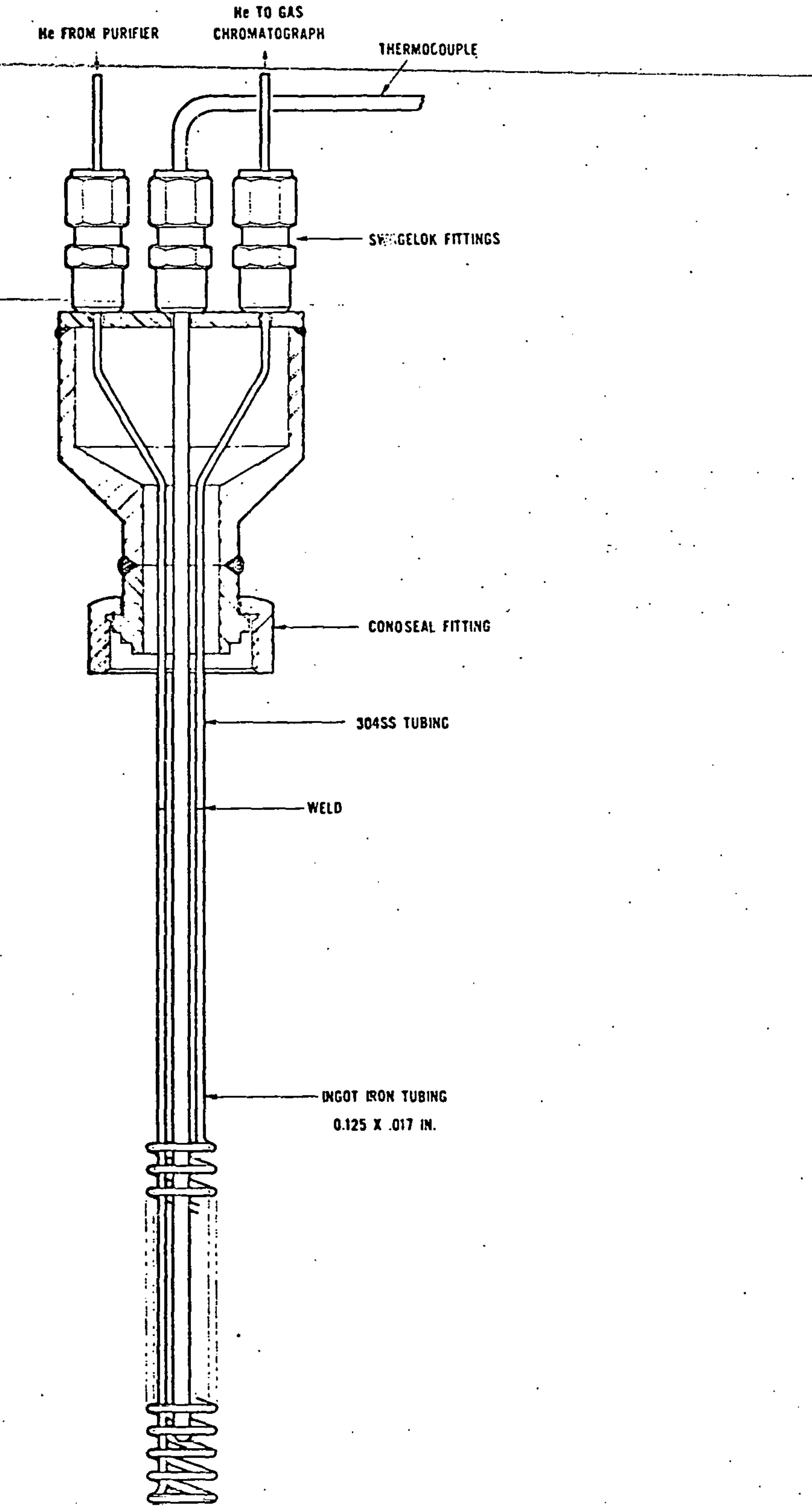

FIGURE 1. Diffusion Carbon Meter Probe

Gas Chromatograph - Manual Sampling

A helium ionization detector with its supporting power supply and electrometer was procured from Varian Instruments Company and assembled locally into a chromatograph. Sampling of the sweep gas was performed with a rotary plug gas sampling valve. The chromatographic column was 3.18 mm (1/8 inch) x 92 cm (3 ft) stainless steel tubing packed with 80-100 mesh Poropak Q. The column and detector were included in a common oven operating at 338°K (65°C). A catalyst bed of wire form CuO was contained in a stainless steel tube heated to 573°K (300°C). The sweep gas flows through the carbon meter membrane, the catalyst bed and the sample valve, then a flowmeter and control valve so the flow can be adjusted to the desired rate.

Gas Chromatograph - Automated Sampling

When it was established that the gas chromatograph system would satisfactorily measure the carbon dioxide concentrations found in the sweep gas, the chromatograph was automated by addition of an electronic integrator to measure the peak, a sample valve actuator, and a timer.

TEST RESULTS

High Carbon Activity Levels

A preliminary test of the membrane was performed with the membrane immersed in sodium contained in a nickel pot heated to 1023°K (750°C). A laboratory gas chromatograph employing thermal conductivity for measuring the carbon dioxide concentration was used. The results of a run to follow the removal of carbon from sodium by titanium are shown on Figure 2.

Low Carbon Activity

The Prototype Applications Loop (PAL) is a pumped loop of approximately 0.378 m^3 (100 gal) sodium capacity. It is constructed of 304 stainless steel and operated at sodium temperatures of 539-927°K (600-1200°F). The membrane was installed in the carbon meter module of this loop and the sweep gas was directed through the manual sampling gas chromatograph using the helium ionization detector. The carbon meter module is independently heated so the membrane could be operated at a temperature different from the main pool.

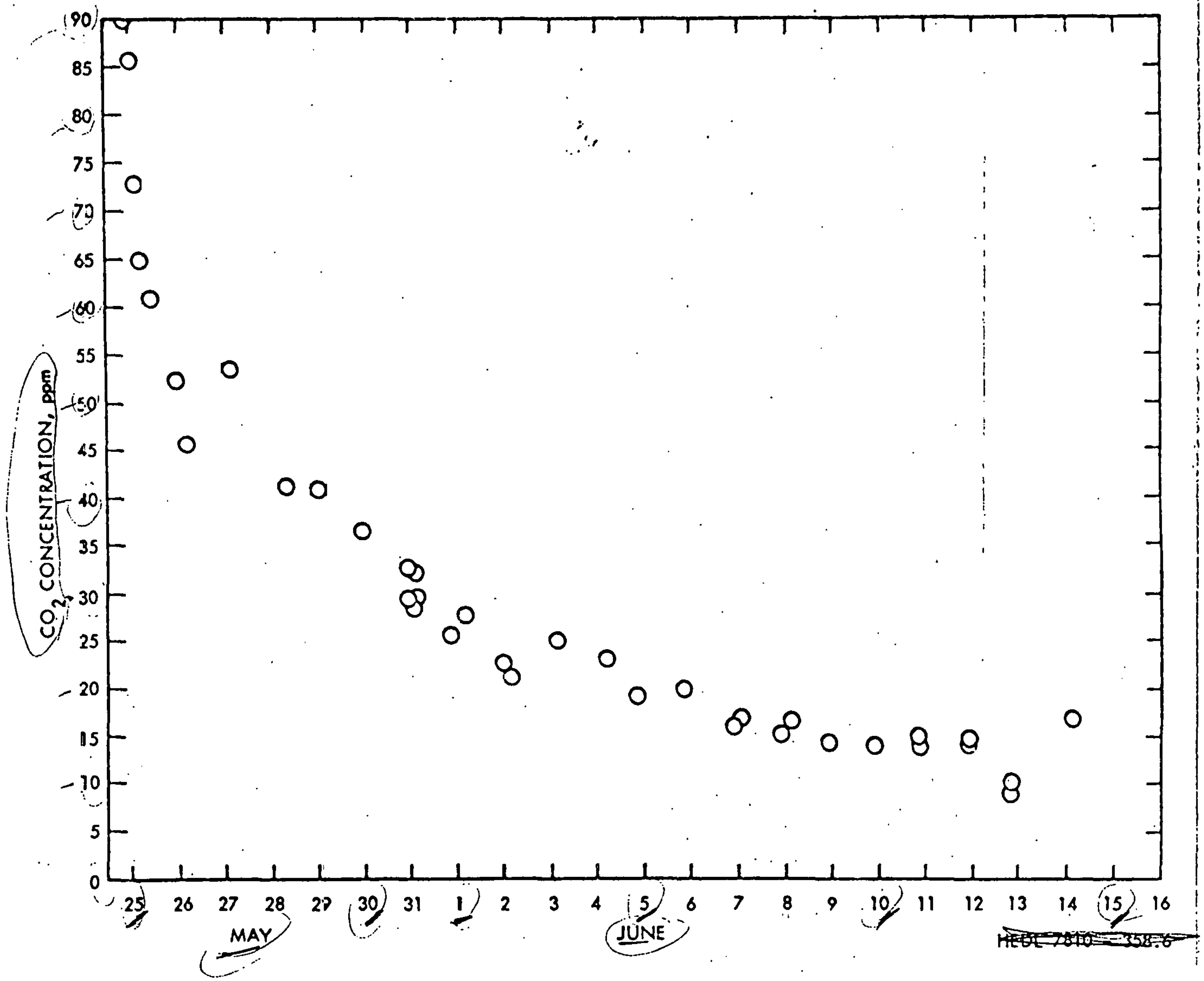

FIGURE 2. Carbon Dioxide Concentration in Sweep Gas - Titanium Sponge Gettering of the Carbon in the Sodium

Most measurements were made at 1023°K (750°C). One series of measurements at different temperatures was performed to determine the temperature response. These results are shown in Figure 3.

Short-term changes in carbon concentration were seen when the sodium in contact with a new piece of steel was heated from 700-811°K (800 to 1000°F) See Figure 4.

Two Fe-Mn foils were run in the PAL multipurpose sampler at different times to measure the carbon activity, and the carbon meter reading during or following this time was compared. The first foil analyzed 0.16 ± .06 ppm C in Na, and the meter reading following it was 0.64 ± .07 ppm CO_2 in the sweep gas. The second foil measure 0.08 ± .06 ppm C in the Na, and the meter reading was 0.24 ± .06 ppm CO_2 in the sweep gas.

The average level of CO_2 in the sweep gas seemed to decrease with use. The data are insufficient to determine whether this represents changing response of the meter or changing carbon level in the sodium of the system.

Automated Sampling Chromatograph

The chromatograms from the PAL system measurements exhibited a slow eluting peak that was identified as due to water. Thus, it appears the iron membrane passes both carbon and hydrogen. The elution time for the carbon dioxide peak is about 45 sec and for the water peak about 10 minutes. By modifying the flow pattern so the water was removed by backflushing, the analysis could be completed in less than four minutes. Automation of the sampling was combined with backflushing of the column.

The first valves used for this automated system were of the Teflon diaphragm type. They did not perform satisfactorily as the CO_2 peak was lost. It is theorized that it diffused through the thin diaphragm.

Replacement of the diaphragm valves with a rotary plug valve cured the loss of CO_2. Before the calibration of the water peak as a measure of H_2 in the sodium was established, the PAL system was shut down.

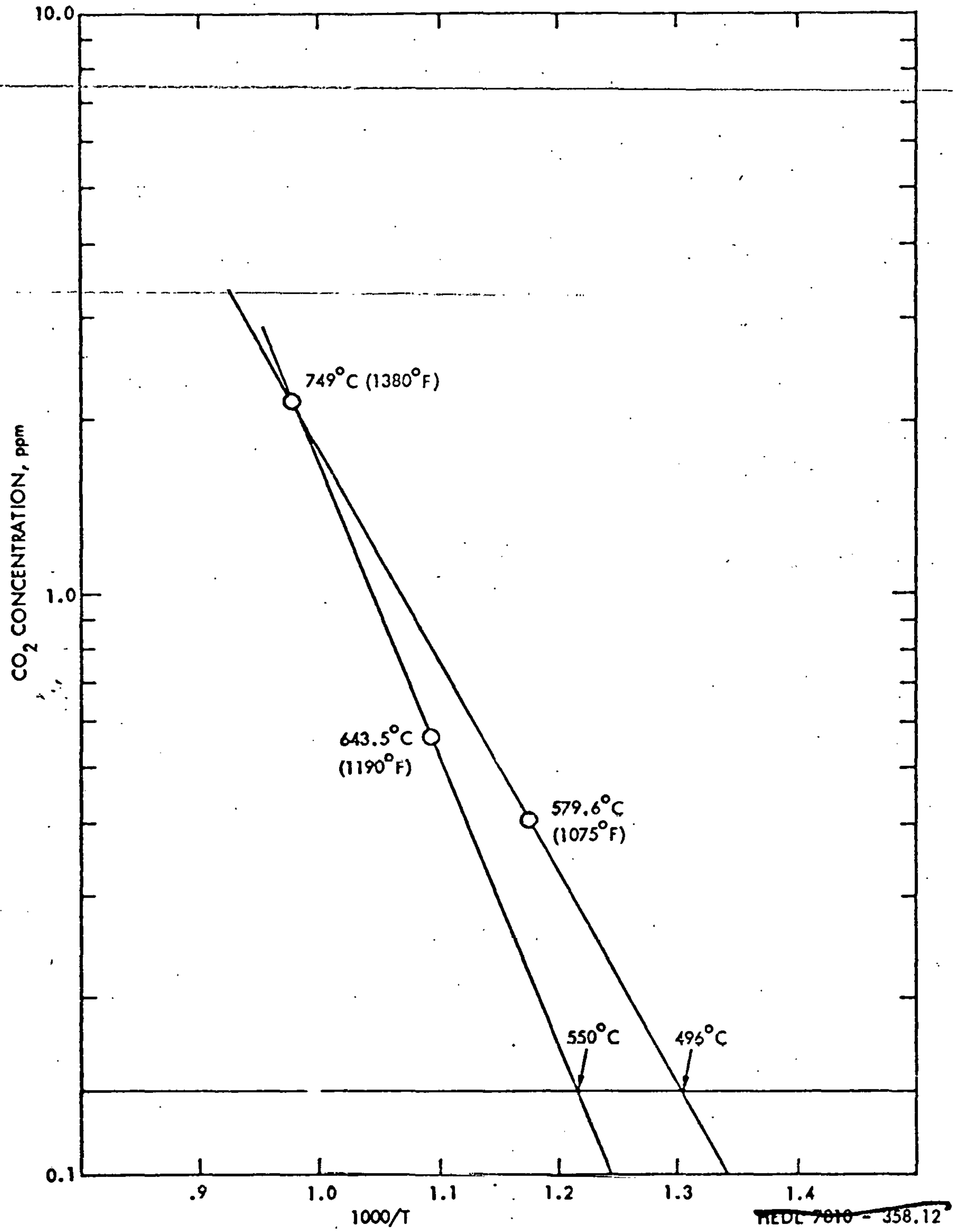

FIGURE 3. Carbon Dioxide Concentration in Sweep Gas vs Sodium Temperature at Membrane Coil.

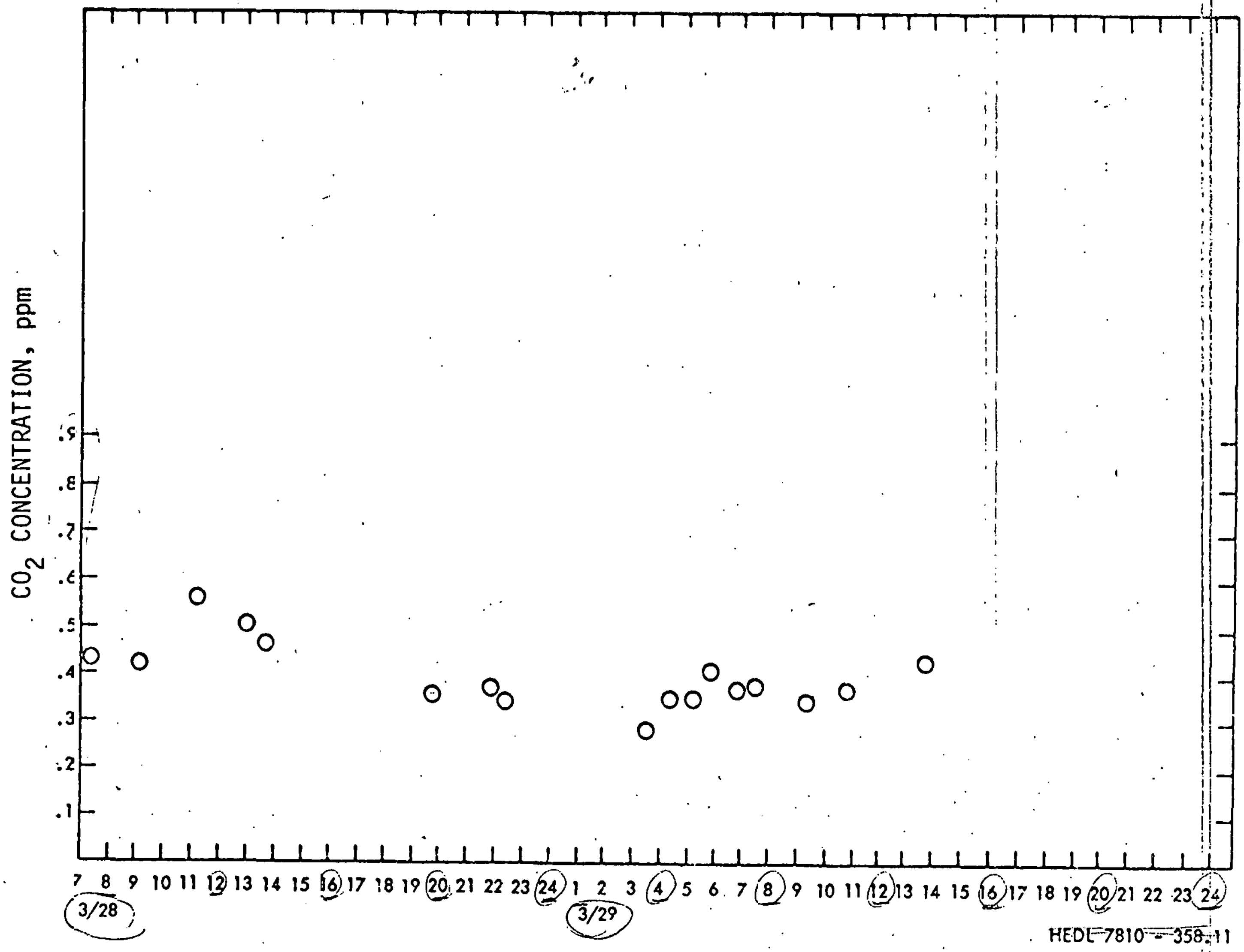

FIGURE 4. Carbon Meter Response to Heating Relatively New Steel in FIP Loop Attached to PAL. (Steel in System 1000 hrs at 1000°F. Temperature increased from 700°K to 811°K (800°F to 1000°F) over period from 9 to 10:30.)

FUTURE WORK

It is planned to transfer the system to another small pumped loop where the proportion of the water peak to the hydrogen content of the sodium can be verified. If this is satisfactorily established, a modified system incorporating an oxygen meter of the type used in the oxygen-hydrogen meter assembly will be tested to determine the practicality of combining carbon, hydrogen and oxygen sensors in a single assembly.

CONCLUSIONS

A diffusion type carbon meter has been assembled using a gas chromatograph to isolate the carbon dioxide and a helium ionization detector to measure the concentration.

It has been demonstrated that the carbon dioxide concentration changes as the carbon activity in sodium changes over a range from that produced by mild steel to that in equilibrium with a stainless steel system. (Activity range $\sim$0.75 to 10^{-3}).

This modified meter also offers the prospect of measuring hydrogen without further modification.

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