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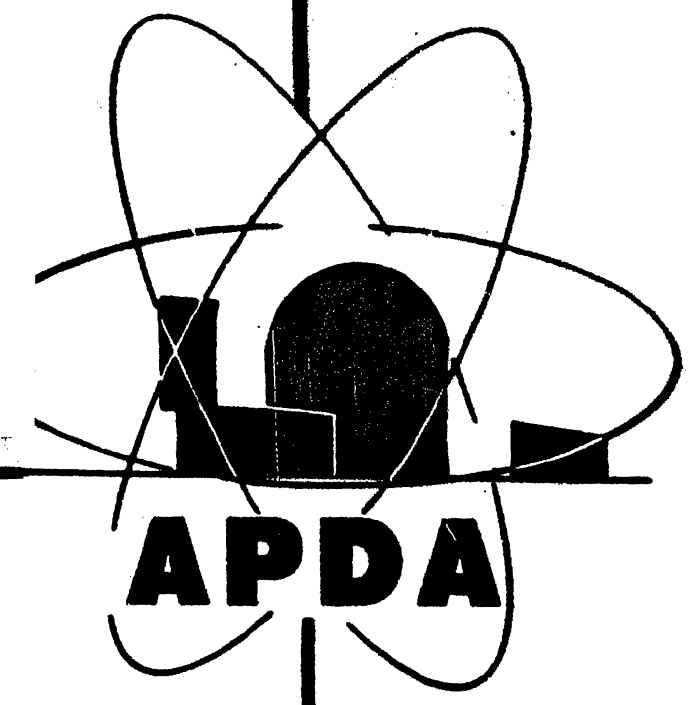

OPERATION OF THE SODIUM TECHNOLOGY LOOP FOR CONTAMINATION METER EVALUATIONS

AEC Contract AT (11-1)-865, Project 3

March 25, 1964

ATOMIC POWER
DEVELOPMENT ASSOCIATES, INC.

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ABSTRACT

The Blake Rhometer operating range was extended from 600 F to 1000 F and a variable-orifice plugging meter was developed. Both instruments were evaluated in the Atomic Power Development Associates Sodium Technology Loop against weighed or metered contaminants. The loop injection series included: water, hydrogen, carbon monoxide, carbon dioxide and methane gases; and tea bag injections of sodium carbonate, sodium hydride, sodium hydroxide and sodium monoxide. Cover gas was monitored and temperature varied during and after each injection run, and the test loop cleaned by cold trapping after each run. A Continuous Hydrogen Monitor attached to the loop cover gas system, and a Nickel Diffusion-Tube Hydrogen Monitor connected to the loop proper were evaluated for sensitivity and response.

INTRODUCTION

Operation of the APDA Sodium Technology Loop in 1963 was an extension of the original series of experiments conducted in these facilities in 1962 under the same auspices (Reference 2). The need to improve the Blake Rhometer and thereby extend the range of studies was made apparent in the earlier work, and critical lines of investigation were indicated. The new and improved contamination meters developed in this program, and the meter evaluation tests conducted with various impurities over a wide range of temperatures have increased the understanding of the physical and chemical behavior of contaminants found in sodium systems. It is believed that the meters, the loop hardware, and loop operating techniques described in this report will find ready commercial application. The procedures developed in this program will be useful in the study of other liquid-metal systems. Perhaps more important, the indicated patterns of chemical and physical behavior of sodium impurities will point the way toward improved methods of cleaning sodium systems, better laboratory techniques for the determination of sodium impurities, and a fuller understanding of the effects of these impurities on loop and reactor hardware.

SUMMARY OF RESULTS AND CONCLUSIONS

Adjustable circuits were added to the original temperature compensator circuit and signal summation circuit of the Rhometer. This extended the operating range from 600 F to 1000 F. These new circuits are manually adjusted at 10 F intervals in accordance with a series of calibrated zero set-points which have been put in chart form.

A hydrogen monitor, based on the comparative thermal conductivities of clean and dirty gas streams, was operated in the argon cover gas system of the test loop. A sensitivity of 50-ppm hydrogen was achieved and the meter performed satisfactorily in the 100-to 2000-ppm hydrogen range with a 25 second response to the system.

A nickel diffusion-tube hydrogen monitor was connected to the test loop to produce a continuous signal. The hydrogen evolution rate was very low, even at high contamination levels. The meter failed to respond to massive water injections and thermal ramps in the sodium system under surveillance. It was possible to generate an acceptable signal by sealing off the vacuum pump and reading the rate of rise in pressure. This varied significantly with the sodium contamination level.

A variable-orifice plugging meter was installed in the test loop. The meter consisted of a single pass counter-current air-cooled exchanger and a special valve which had precise clearance settings across the seat. This meter produced plugs from 213 F to 670 F under test, with reproducibility to $\pm$ 5 F, and furnished consistent values for sodium hydride contamination which were not attainable with the previous meter. Plugging temperatures obtained under sodium monoxide contamination agreed well with accepted solubility data. Under sodium hydride contamination the plugging temperatures were lower than anticipated values. Sodium hydroxide contamination plugging temperatures were higher than anticipated, and approximated the solubility curves for the decomposition products. This shift from expected solubility values may have been caused by partial decomposition of the sodium hydroxide. The meter showed a very high sensitivity to sodium-water reaction products, down to 13 ppm water.

Values obtained in the water injection run could not be related to a summation effect for the mixed contaminants present. These plugging temperatures approximated the predicted values for sodium monoxide alone, and it was thought that the meter was somewhat selective in this environment. Plugging temperatures for carbonate corresponded very closely to solubility values but were difficult to identify in most experimental runs. The variable orifice clearance was optimum at 7.5 mils for low contamination levels, producing 0.25-gpm flow. The optimum flow at high contamination levels was 1.5 gpm.

The Rhometer performance was satisfactory for all contaminants except sodium carbonate, which produced a weak erratic signal at temperatures below 900 F. The increased signal strength above 900 F may be an effect of carbon solution. Threshold sensitivity to water contamination was 26 ppm water. The Rhometer signal gain during the water injection run approximated a summation of response values obtained for the several sodium-water reaction products. The data are shown in Table I.

The theoretical signal-gain index for the "first order" sodium-water reaction* is 0.556 %r 100 ppm water. For the "second order" sodium-water reaction** the theoretical index is 0.53 %r per 100 ppm water, based on values in Table I. Experimental values were 0.63 %r and 0.43 %r respectively.

To explain the "non-ideal" behavior of the Rhometer signal in this mixed contaminant environment, it is observed that sodium hydroxide produces the greatest signal gain. This gain may actually be greater than the reported signal indicated in the sodium hydroxide tea bag injection experiment, because of unavoidable partial decomposition in the loop during this test. During the water injection series, sodium hydroxide was also decomposed and it is suggested that at 570 F decomposition was inhibited by the high level of sodium hydride in solution, which resulted in a stronger Rhometer signal. At 770 F, the increased thermal effect on the decomposition of sodium hydroxide overshadowed this inhibiting action, and the Rhometer responded to the drop in hydroxide level by again producing a lower signal.

When the Rhometer was operated in conjunction with the plugging meter, a definitive pattern emerged which could be interpreted to designate contaminants, particularly where impurities with low Rhometer signal gain indexes produced high plugging temperatures, and vice versa.

Response to sodium monoxide contamination, as reported in Table I, was approximately 10 percent of the signal value reported in Reference 2. An explanation of this apparent degradation in signal strength was thought to be a bias in the earlier run. The 0.25 %r signal gain index per 100 ppm sodium monoxide indicated in Reference 2 may have been generated by other contaminants introduced in the process of unloading a cold trap to produce oxide contamination. This error was further compounded by the reported practice of using a plugging temperature or cold trap equilibrium temperature to determine the sodium monoxide level in the loop.

* $H_2O + 2\,Na \longrightarrow NaOH + NaH$ at 570 F and below

** $H_2O + 4\,Na \longrightarrow Na_2O + 2NaH$ at 770 F and above

TABLE I

RHOMETER RESPONSE TO CONTAMINANTS

Impurity	Impurity Range, ppm	Loop Conditions	Rhometer Signal Gain Index, % r per 100 ppm
H_2O	0 - 60	470 F	0.430
	60 - 160	570 F	0.630
	160 - 320	770 F	0.430
	0 - 320	Overall	0.570
Na_2O	0 - 300	770 F	0.020
	0 - 500	770 F	0.021
	500 - 1000	770 F	0.022
NaOH	0 - 100	470 F	0.180
	100 - 300	570 F	0.120
	0 - 300	Overall	0.146
NaH	0 - 250	570 F (Original run)	0.166
	0 - 250	570 F (Rerun)	0.170
Na_2CO_3	0 - 250	450 F - 720 F (CO_2 Gas)	0.020
	0 - 400	770 F (Teabag Injection)	0.020

Experiment also showed that within the limits of loop operation the sodium hydroxide could be decomposed, and that the sodium hydride could not. Sodium hydride resisted dissociation for 8 days at nearly 1000 F, and sodium hydroxide appeared to decompose at 770 F in 48 hours.

Evolution of hydrogen gas from the water contaminated loop into the cover gas system was observed during water injection, and also during thermal ramps in this same injection procedure. It was reasoned from this behavior that a hydrogen monitor would not provide a conclusive signal of water leakage unless a significant difference in signal response could be established between maximum temperature ramp effects and minimum leak rate effects.

The apparent degradation of Rhometer sensitivity suggested by the earlier sodium monoxide run is most probably a reflection of more accurate metering technique as argued in the foregoing discussion, and was not caused by actual impairment of the signal gain resulting from modifications to the meter circuits, or from fouling of the circuit switches as reported after loop test operations were concluded.

Both carbon monoxide and methane failed to react in the test loop. Carbon dioxide gas injections reacted readily, and hydrogen gas injections to a limited degree. The meters did not indicate hydrogen reaction beyond the limit of sodium hydride solubility in the loop. Because of this temperature dependant behavior and observations in the literature (Reference 6) to the effect that hydrogen reaction was influenced by the level of sodium monoxide contamination present,it was concluded that hydrogen gas injections should not be used to simulate water leaks for the purpose of checking out the continuous hydrogen monitor or other water leak detectors in commercial loops.

RECOMMENDATIONS FOR FURTHER INVESTIGATIONS

It would be desirable to obtain confirming data on meter calibrations by conducting reruns. These operations are of particular interest in view of the conflicting data presented for oxygen contamination, and the apparent degradation of meter response to sodium monoxide. Development of laboratory techniques to confirm weighed or metered contamination levels will be of major interest in any rerun series. Reruns may be performed in two phases (1) repeating the injection series as described in this report, and (2) collecting parallel data during loop cleanup.*

In conjunction with these reruns, the partial data presented in this report on thermal stability of contaminants should be expanded in a series of high temperature experiments to establish the rate of decomposition of the various impurities as a function of temperature.

The effect of carbon contamination was not demonstrated successfully by earlier runs[2] because of the former temperature limitations of the Rhometer. In the carbonate experiment outlined in this report, the Rhometer again failed to respond below 900 F. A complete series of experiments with carbon and carbonate at temperatures above 900 F would now be in order, as laboratory back-up becomes available for confirmation of metered loop contamination levels.

Cover gas contamination from outgasing graphite presents a complex in reactor operations which varies with the graphite and with the thermal cycle to which the graphite is exposed. Rather than synthesize this effect it would be worth while to perform a single experiment with a typical graphite specimen, observing the response of in-line meters to this environment in a series of thermal cycles.

* Note: Cold trap equilibrium values employed in Reference 2 would not be applicable in the proposed series of reruns because of mixed contaminant release from the cold trap each time it is reopened to establish flow.

TEST HARDWARE

The APDA Sodium Technology Loop is constructed of a 4-inch, type 304 stainless steel tubing. All joints are welded. The major components include a 200-gallon dump and storage tank, a 200-to 300-gpm sodium pump, a 45-gallon surge tank, a zirconium hot trap and a cold trap with economizers, and appropriate vent and drain service lines. Figures 1 and 2 are a photograph and schematic drawing of the loop. The active loop inventory is 790 pounds of sodium and 7 cubic feet of argon cover gas. Before October 1963, a 30-gallon retention tank was also attached to the loop. With the retention tank in the loop, the sodium inventory was 1000 pounds and the cover gas system was 8 cubic feet. The Rhometer (Figure 2) is described in Reference 2. The plugging meter shown in Figures 2, 3, and 4 is described in this section.

The loop cold trap is air cooled and consists of a 30-gallon verticle tank with a 4-inch downcomer inlet. There is York-mesh packing in the tank, and a 5-micron filter frit on the discharge. The cold trap was designed to trap approximately 70 pounds of solids[7]; however, it was necessary to replace the unit after an estimated 7 pounds of solids had been trapped. As the trap approached saturation it became more difficult to maintain flow. After one freeze-up the unit was isolated, heated to 1000 F, and dumped. The resulting improvement in performance was short lived. The saturated trap was finally drained and sealed for future examination.

The variable-orifice plugging meter was developed and installed after considerable operating difficulty with the original orifice and cooler components. Principal among these difficulties was the failure to meter sodium hydride contamination and inadequate cooling capacity. The replacement cooler shown in Figure 3 is a single-tube, counter-current air-blown exchanger with axial cooling veins. The cooler is designed to produce a constant temperature drop in the sodium stream, and to plug from a 1000 F loop at 3-gpm flow through the meter. The original plugging orifice consisted of a 1-inch packed angle valve with a serrated disk. This unit was replaced by the special 1/2-inch bellows seal globe valve shown in Figure 4. The conical seat on this valve is ground to a 15-degree angle for close control of clearance. A special, fine thread on the stem and a position indicator permits clearance settings to a tolerance of one mil in a 0-to 50-mil range. Experiment has shown that reproducibility of plugging temperatures in the order of $\pm$ 5 F can be achieved by setting the orifice to a 0.25-gpm flow (or approximately 7.5-mil clearance) at low contamination, and a 1.5-gpm flow at high contamination. For reasons which are not thoroughly understood, the geometry of this variable orifice and cooler produces more sharply defined end points than the original plugging device.

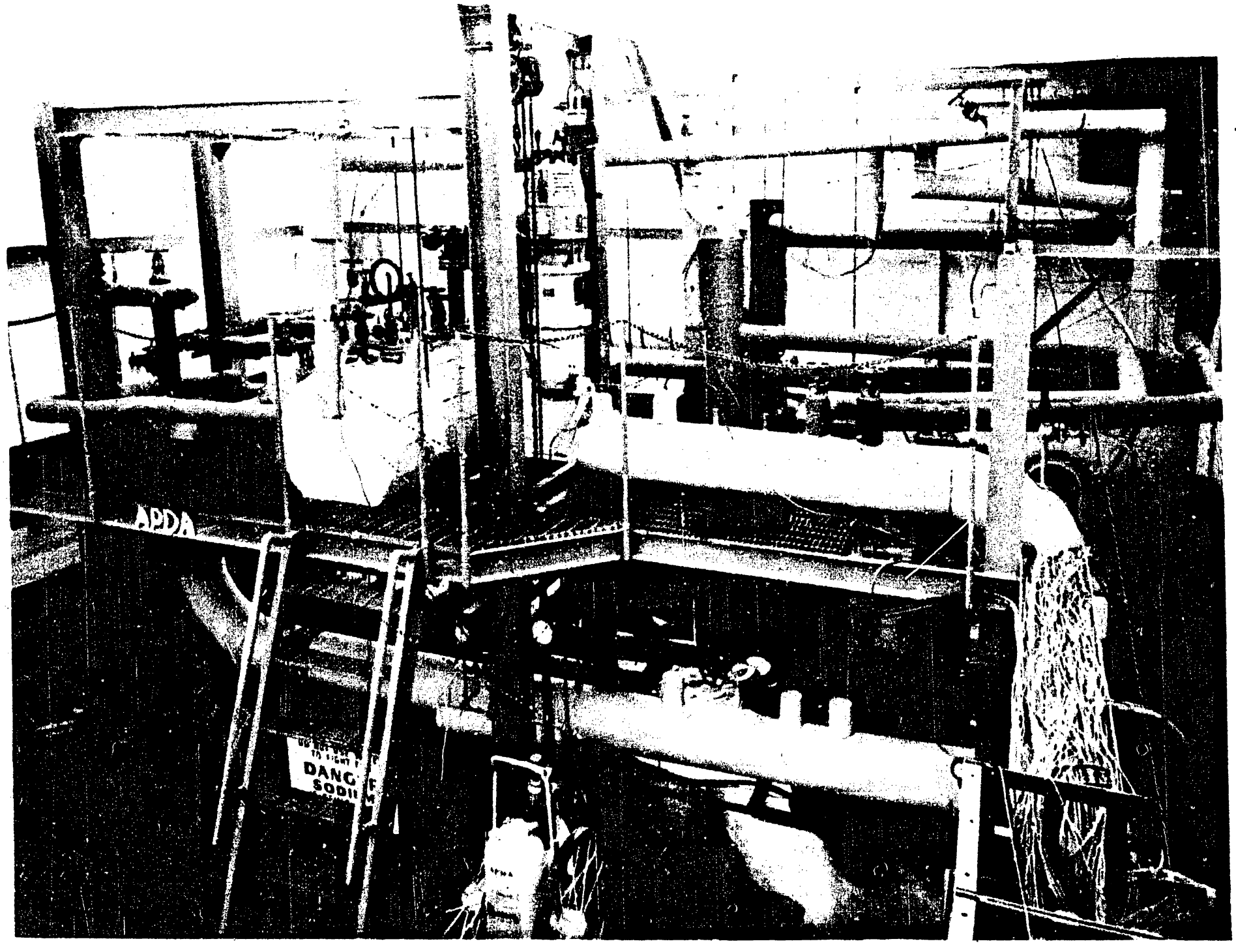


FIG. 1 SODIUM TECHNOLOGY TEST LOOP

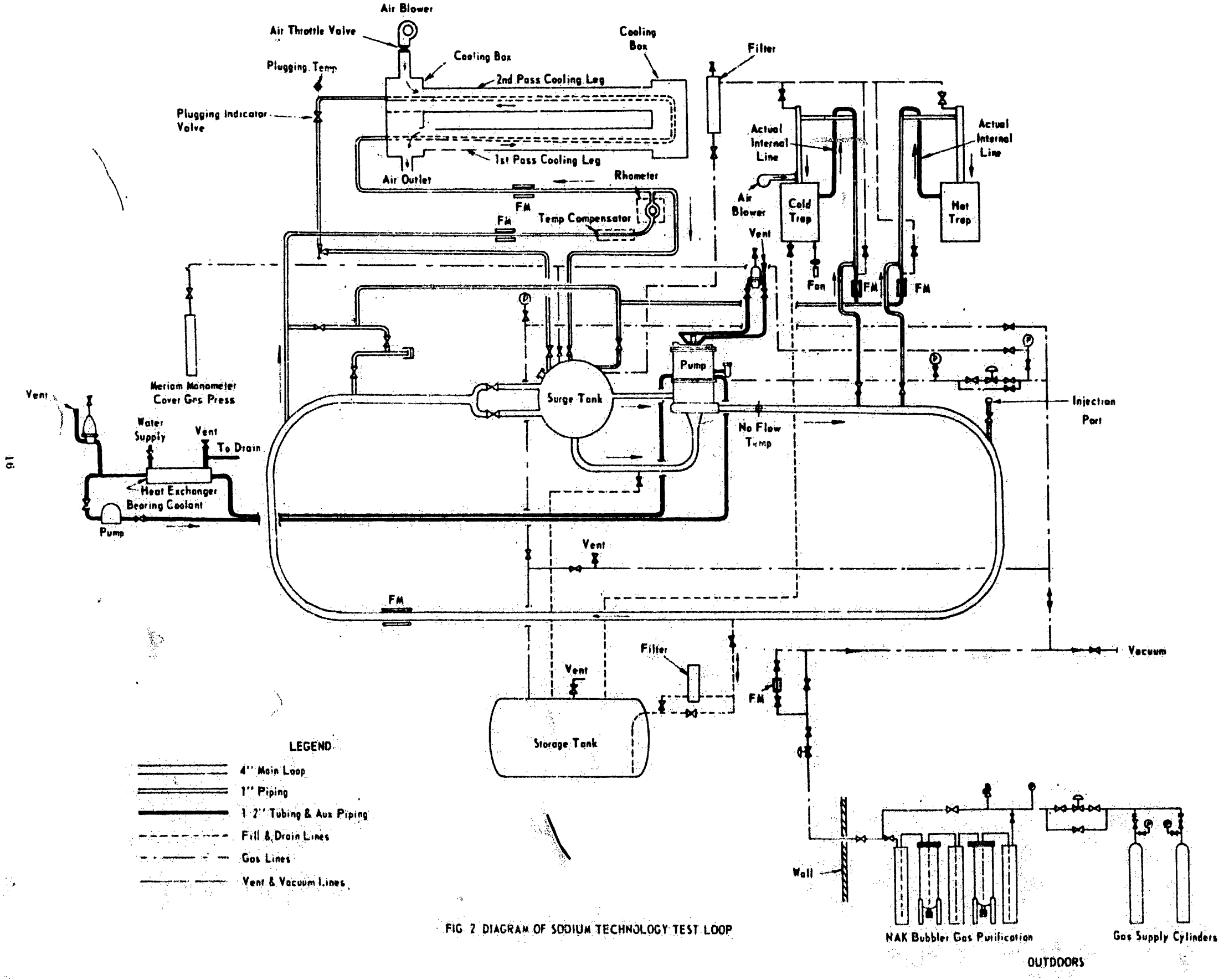


FIG. 2 DIAGRAM OF SODIUM TECHNOLOGY TEST LOOP

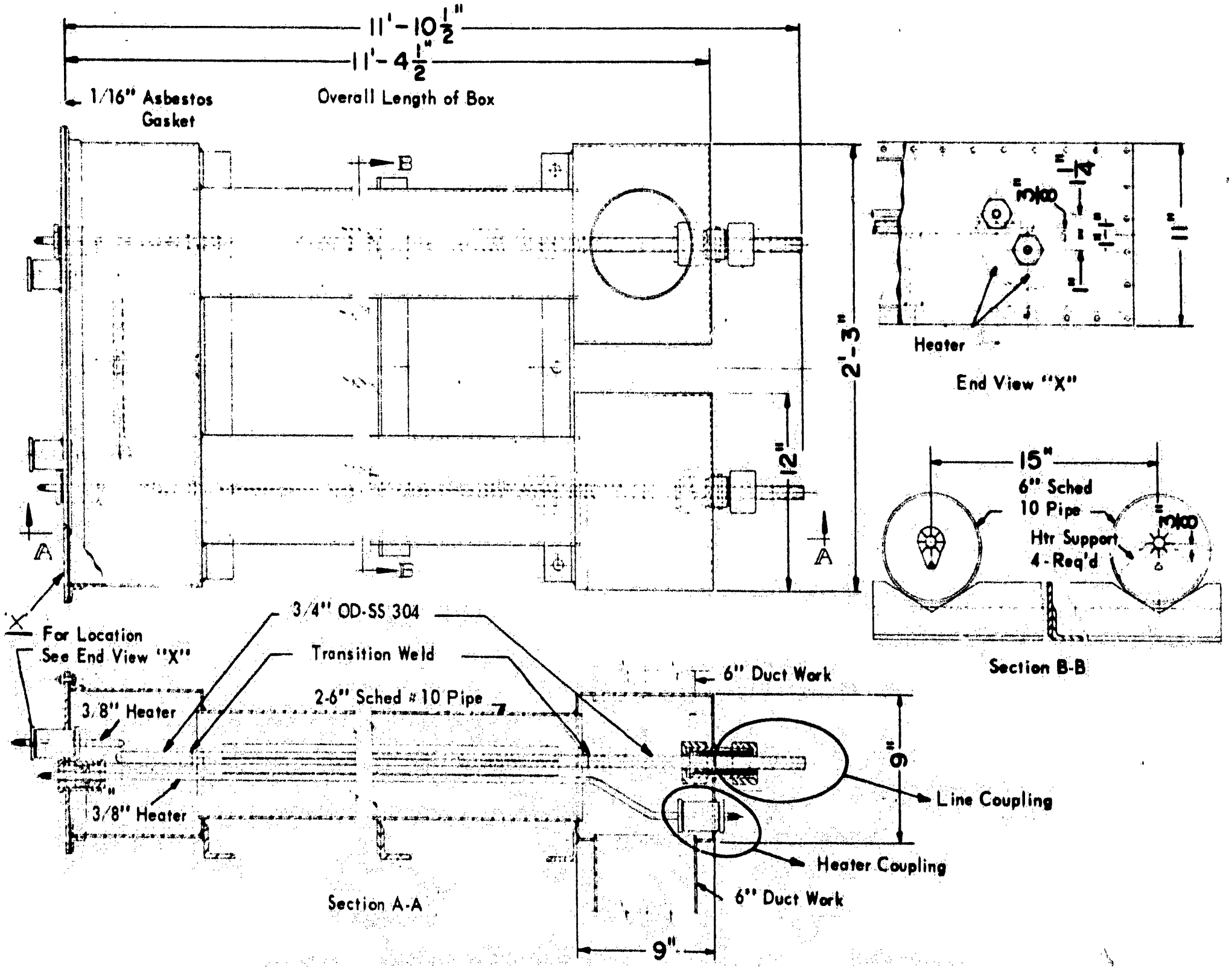


FIG. 3A DRAWING OF VARIABLE-ORIFICE PLUGGING METER COOLER

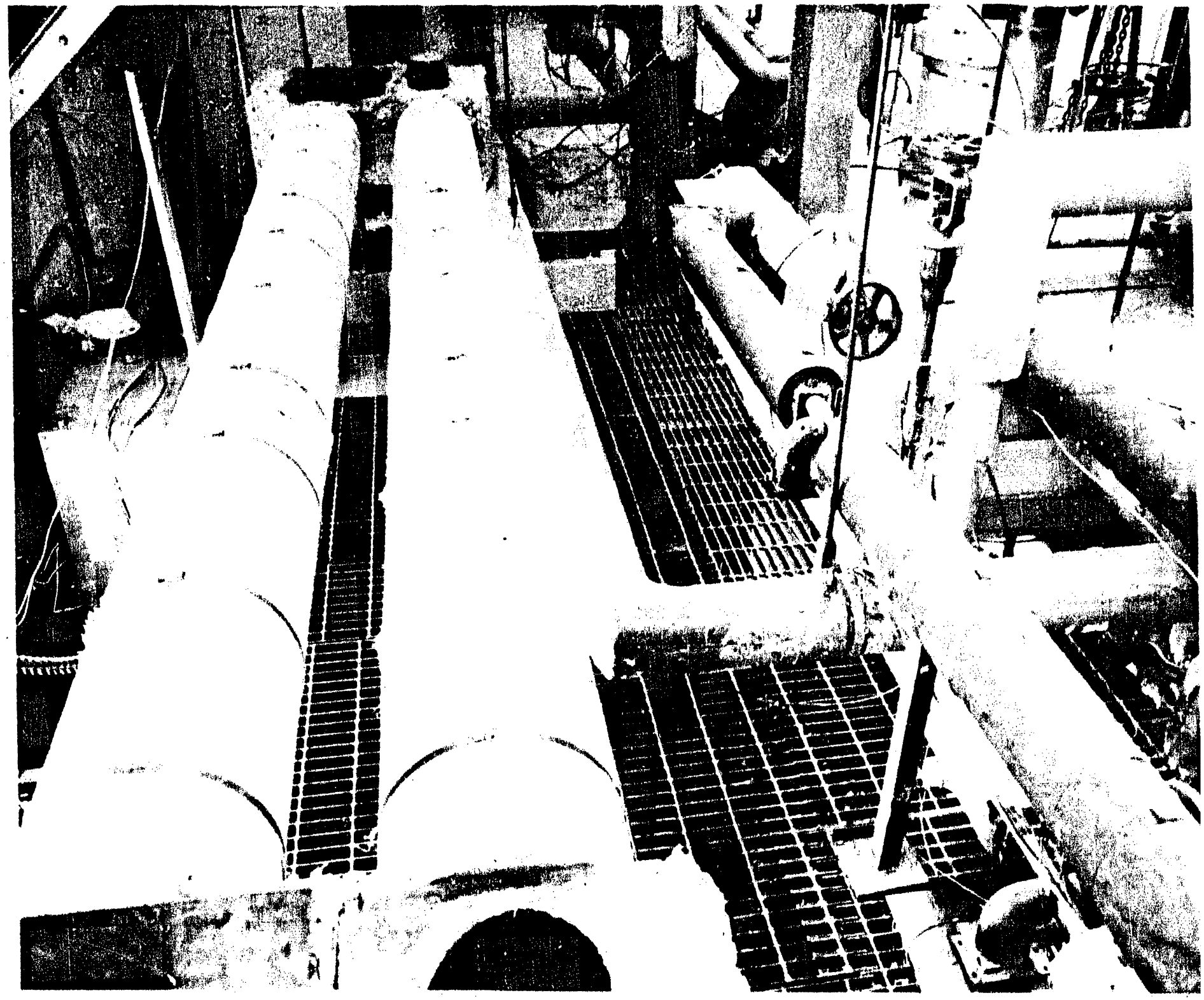


FIG. 3B VARIABLE-ORIFICE PLUGGING METER COOLER

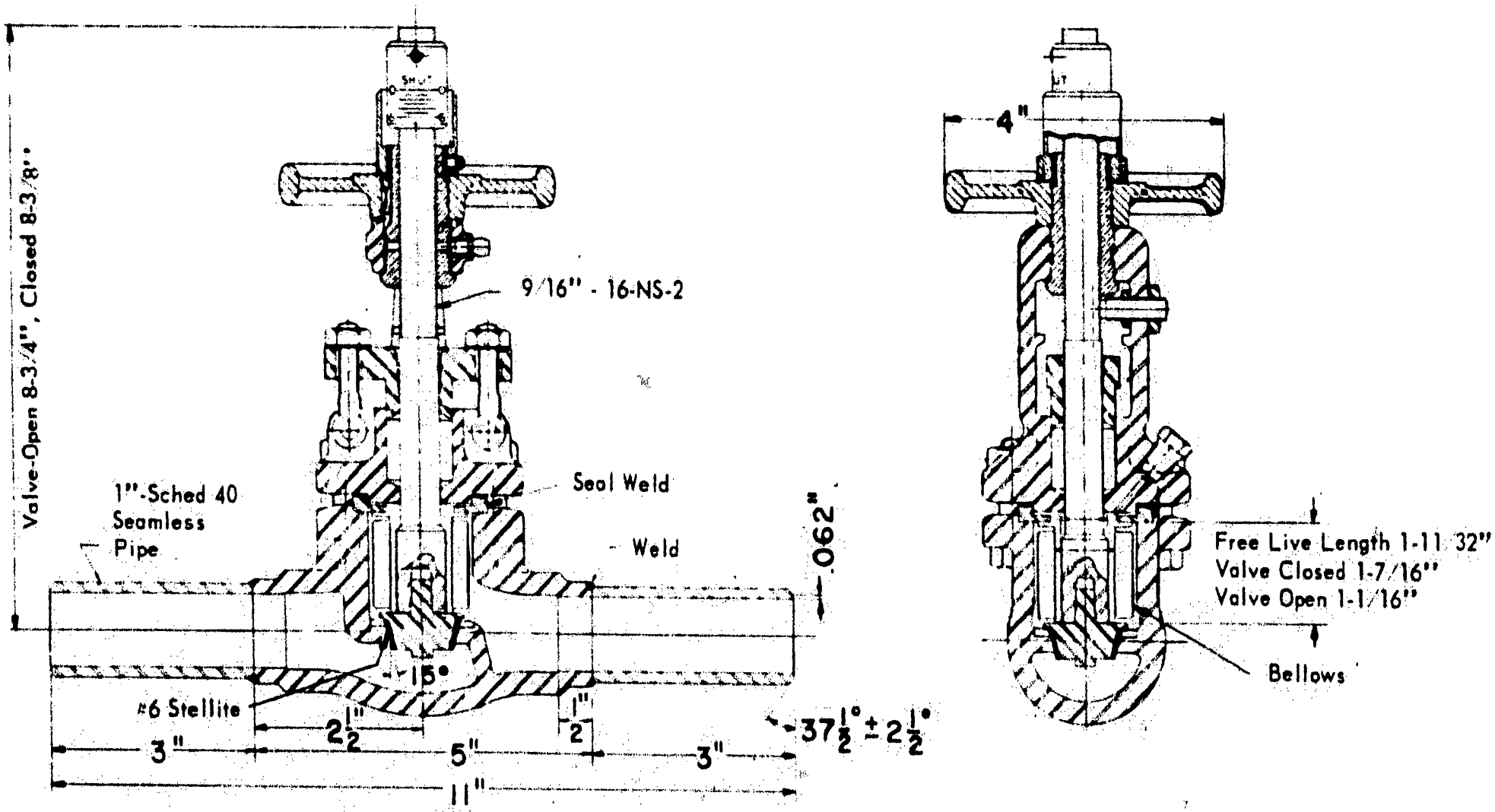


FIG. 4A DRAWING OF VARIABLE-ORIFICE PLUGGING METER VALVE

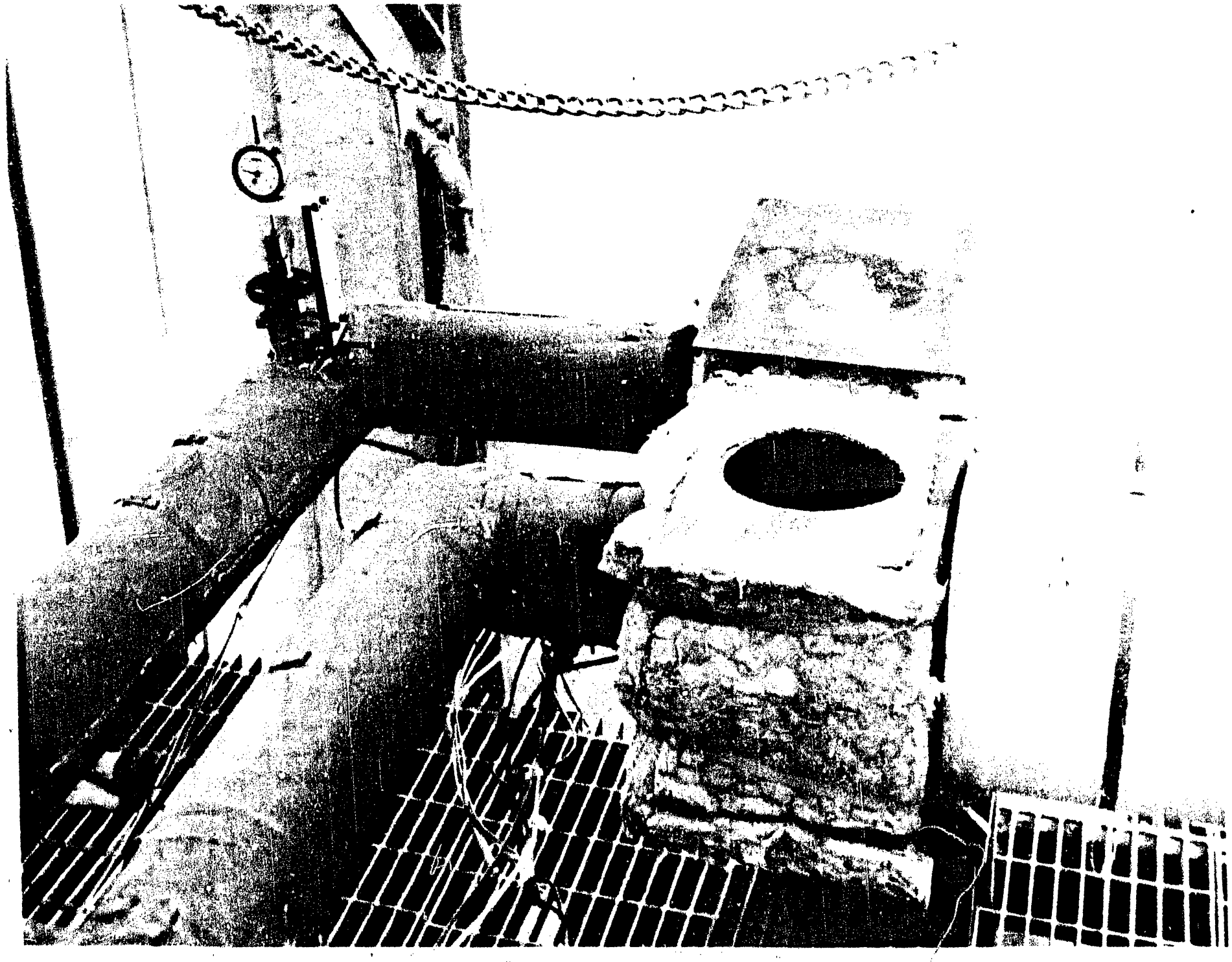


FIG. 4B VARIABLE-ORIFICE PLUGGING METER VALVE

The sodium pump is of the vertical, single-stage centrifugal type rated for 100 feet at 100 gpm, and is equipped with a variable-speed d-c drive. A gravity-fed, water-cooled oil shaft seal system is attached to the pump tank packing gland.

After 15 months of loop operation, two line sections were removed for metallurgical inspection. Photomicrographs of these specimens are shown in Figures 5 and 6 and their position in the loop is shown in Figure 2. The Rhometer discharge line shows no deterioration. The cold trap line which had been torched to 1500 F on several occasions shows carburization to a depth of 1 mil, but no intergranular corrosion.

In a general loop overhaul, the packed OS&Y drain valves which had not been operated for over a year were frozen shut, and were opened with great difficulty after repeated torching. Distortion of the valve stem and permanent damage to the valve resulted.

The F & M 500 gas chromatograph which monitored the argon cover gas had the threshold sensitivities for gas impurities shown in Table II. The cycle time varies from 5 to 15 minutes, depending on the display required.

TABLE II
GAS SENSITIVITY OF F & M 500 CHROMATOGRAPH

Gas Impurity	Threshold Sensitivity, ppm
H_2	2
O_2	50
N_2	50
CO	400
CO_2	150
CH_4	100

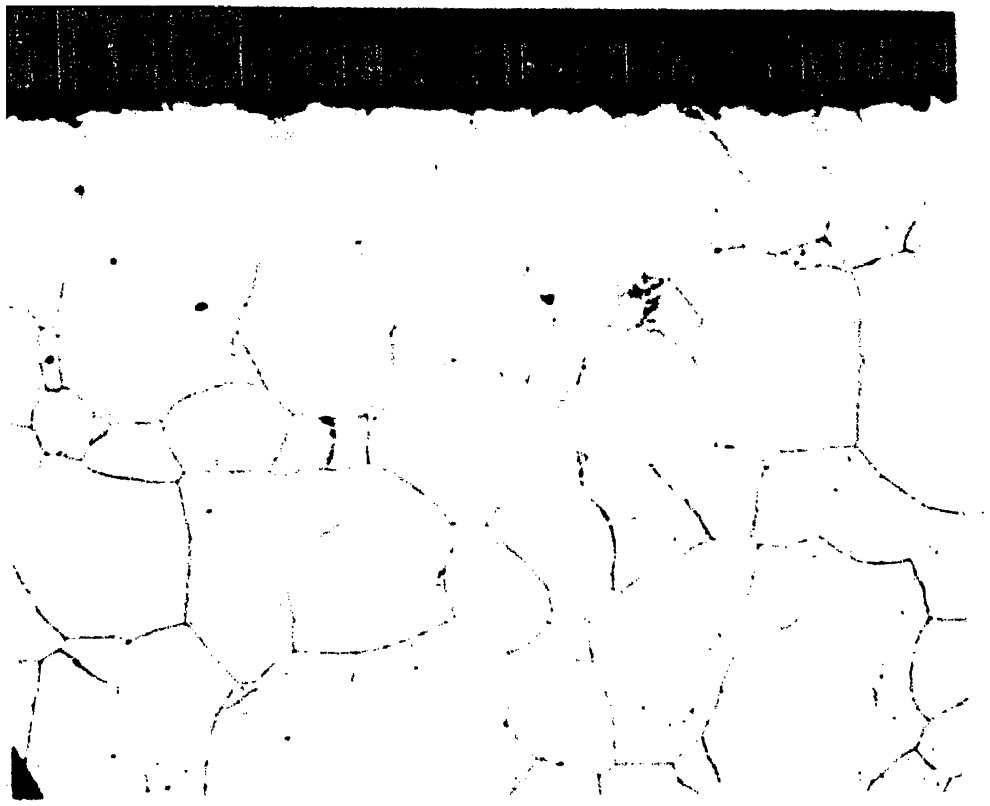


FIG. 5A TOP OF THE DISCHARGE LINE

FIG. 5B BOTTOM OF THE DISCHARGE LINE

FIG. 5 PHOTOMICROGRAPH OF THE COLD TRAP DISCHARGE LINE

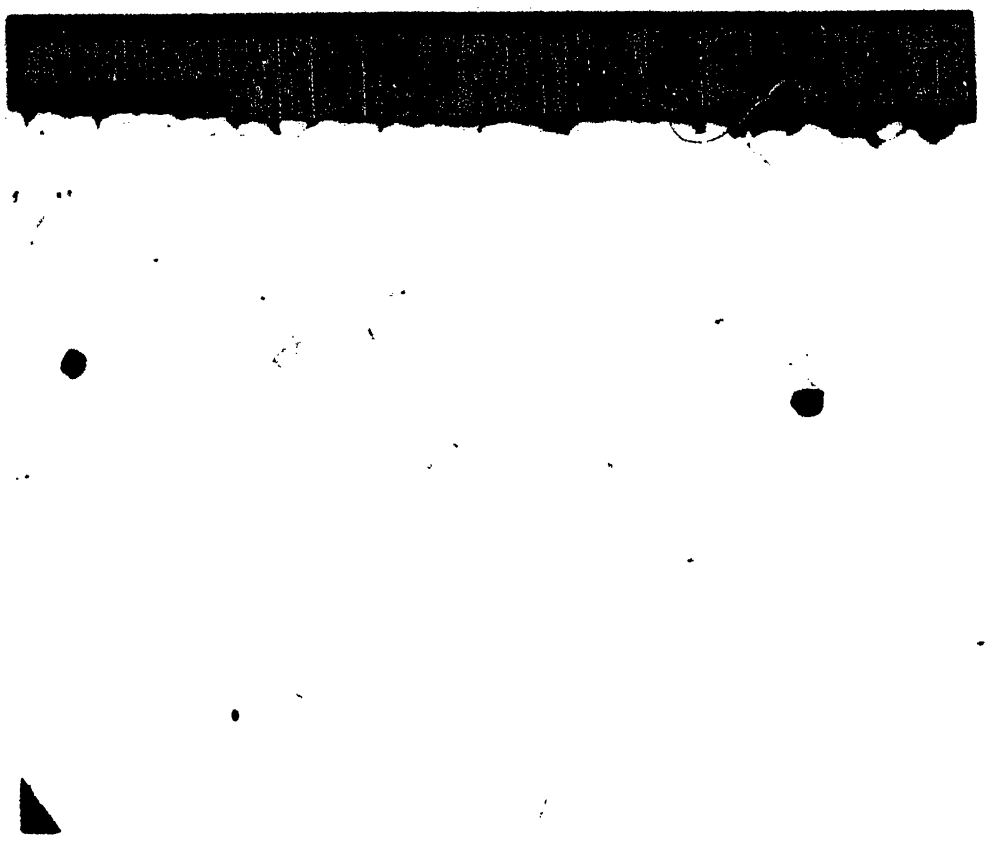


FIG. 6A TOP OF THE INLET LINE

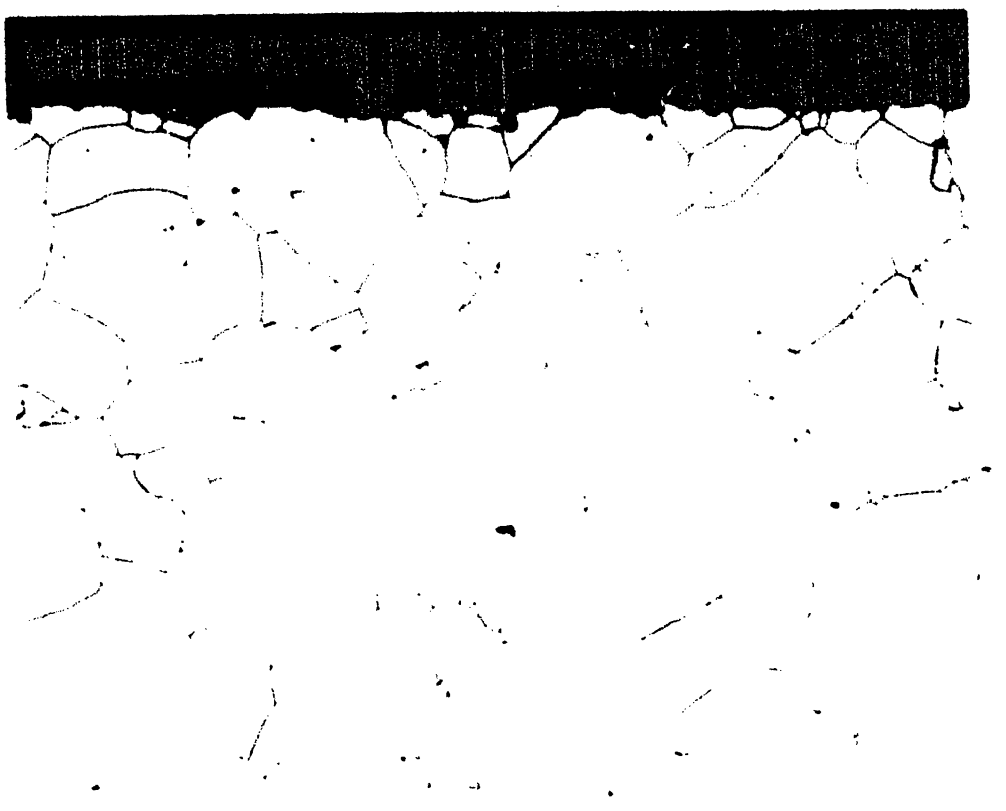


FIG. 6B BOTTOM OF THE INLET LINE

FIG. 6 PHOTOMICROGRAPH OF THE RHOMETER INLET LINE

RHOMETER MODIFICATIONS

GENERAL DISCUSSION, RHOMETER THEORY

The basic components of the Blake Rhometer are illustrated in Figure 7. The sensor element of this mete- is the electrical transformer, shown as a two-window core of Super-Mur..etal with primary excitation winding (N) designed to produce a constant flux under conditions of constant line voltage and constant core temperature. The probe coil (n) and the toroid pipe are secondary windings. Liquid metal flows through the toroid pipe, and the current generated with in the toroid constitutes the transformer load. For all practical purposes, since the energy required to magnetize the core is negligible, the current in the primary winding is determined exclusively by this toroid loading current. It can be postulated that voltage drop across any element of the primary circuit is a direct reflection of the loading current in the toroid circuit and of the ratio of primary to secondary turns which is constant. Toroid current is a function of induced voltage in the single-turn winding and the electrical resistance found in the toroid circuit.

Neglecting the minor effect of the stainless steel pipe wall for the moment, it would appear that voltage drop across R_2 in the primary circuit would be an indication of the resistance of the liquid metal flowing through the toroid. The primary current is very small, and the suggested mechanism does not generate an adequate signal. For this reason a probe coil is provided to pick up the effective voltage generated in the toroid. The probe coil voltage multiplies the effective voltage by n turns to intensify the signal.

The probe coil voltage, and the voltage drop across the primary circuit resistors are all scaled by multiple tap transformers T_1, T_2, and T_3. The relative ratios of these transformers are adjustable by switching arranged according to per cent relative resistivity of the liquid metal. The outputs of these transformers are series summed with appropriate phasing relative to each other to obtain a voltage balance or null when the switches are set to existing resistivity and temperature conditions. A change of resistivity from the set value upsets the balance and produces an error voltage, θ. The error voltage has an in-phase or out-of-phase polarity that is relative to the phase-sensitive-detector reference voltage appearing across R_3. The output of the phase detector is a d-c voltage whose amplitude and polarity are dependent upon the amplitude and phase of the a-c error voltage.

A small-amplitude adjustable a-c voltage (with quadrature phase relationship to the error signal) is summed with the probe winding output to cancel the signal quadrature component, whose presence would degrade the signal null.

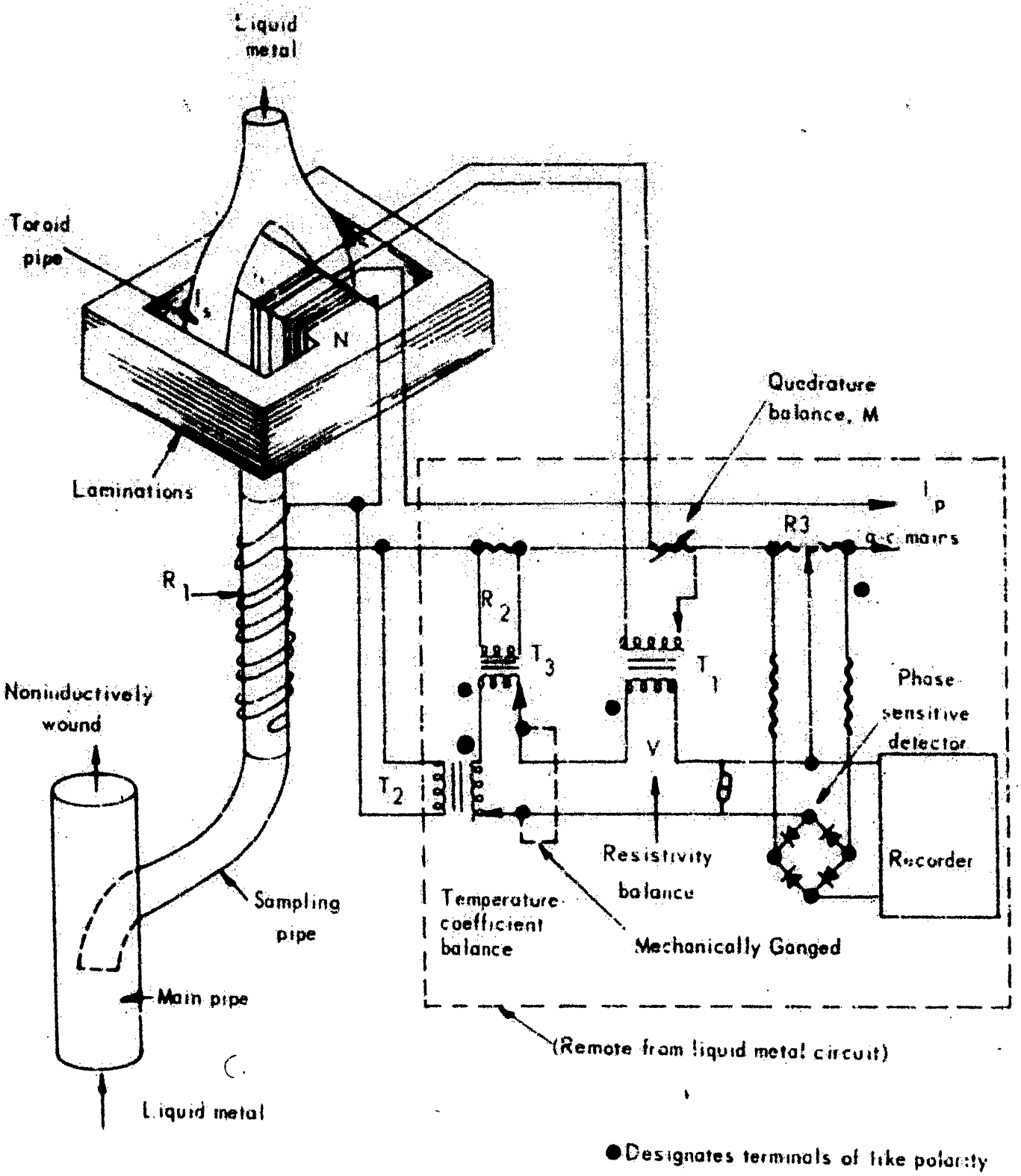


FIG. 7 RHOMETER

Liquid sodium has both a large and linear temperature coefficient of resistivity. A 0.07 F temperature change results in a resistivity change of one part in 10^4, corresponding to a significant quantity of impurities. Accordingly, the thermal compensation provision forms a critical part of the Rhometer circuit. A noninductively wound temperature sensitive resistance, R1, in close thermal contact with the toroid inlet pipe serves to provide the required variation (proportional to temperature) of the primary circuit series resistance, across which the current measurement voltage is obtained. Resistance R2 is temperature stable. By a suitable turns-ratio combination and summation of phase-opposing voltages from T2 and T3, a close match of compensator coefficient to the thermal coefficient of resistivity of the toroid circuit is obtained for a limited temperature range. Range limitation is imposed by differences in the second and higher order terms in the R1 and the toroid thermal coefficients. A more detailed description of the Rhometer operating principles is presented in Appendix I.

Signal response to various impurities is shown on Figure 8. It was theorized that some relation could be traced between Rhometer signals measured as absolute resistivity and molar concentrations of impurities. This does not appear to be the case as seen in Figure 9.

RHOMETER CIRCUIT MODIFICATIONS

The Rhometer employed with the APDA sodium loop is a Mark I unit designed for operation with a platinum temperature compensator. Compensation within an error of 0.355 per cent equivalent resistivity was obtained over a temperature band of ± 10 F about a mean temperature selected by switches. The highest temperature that could be selected was about 600 F.

Figure 10 shows a typical plot of the compensator error characteristic. The curve shown is for an arbitrarily selected null median temperature of 122 F. To obtain this curve the Rhometer compensator dials were set in accordance with known calibration data. The decade dials, or resistivity balance controls, were arbitrarily set at 103.07, which placed the null or zero slope point at the -0.055 per cent reading. Ideally, the compensator would hold the recorder at the - 0.055 per cent reading over the entire temperature range of interest.

APDA's sodium contamination studies required operation to 1000 F. A brief study of the feasibility and problems associated with modification of the Rhometer to extend operation to the desired maximum temperature disclosed several possibilities, these being:

1. Extension of the original voltage ratios of transformers T2 and T3, with limited continuous range, and adjustable to 1000 F as shown in Figure 7.

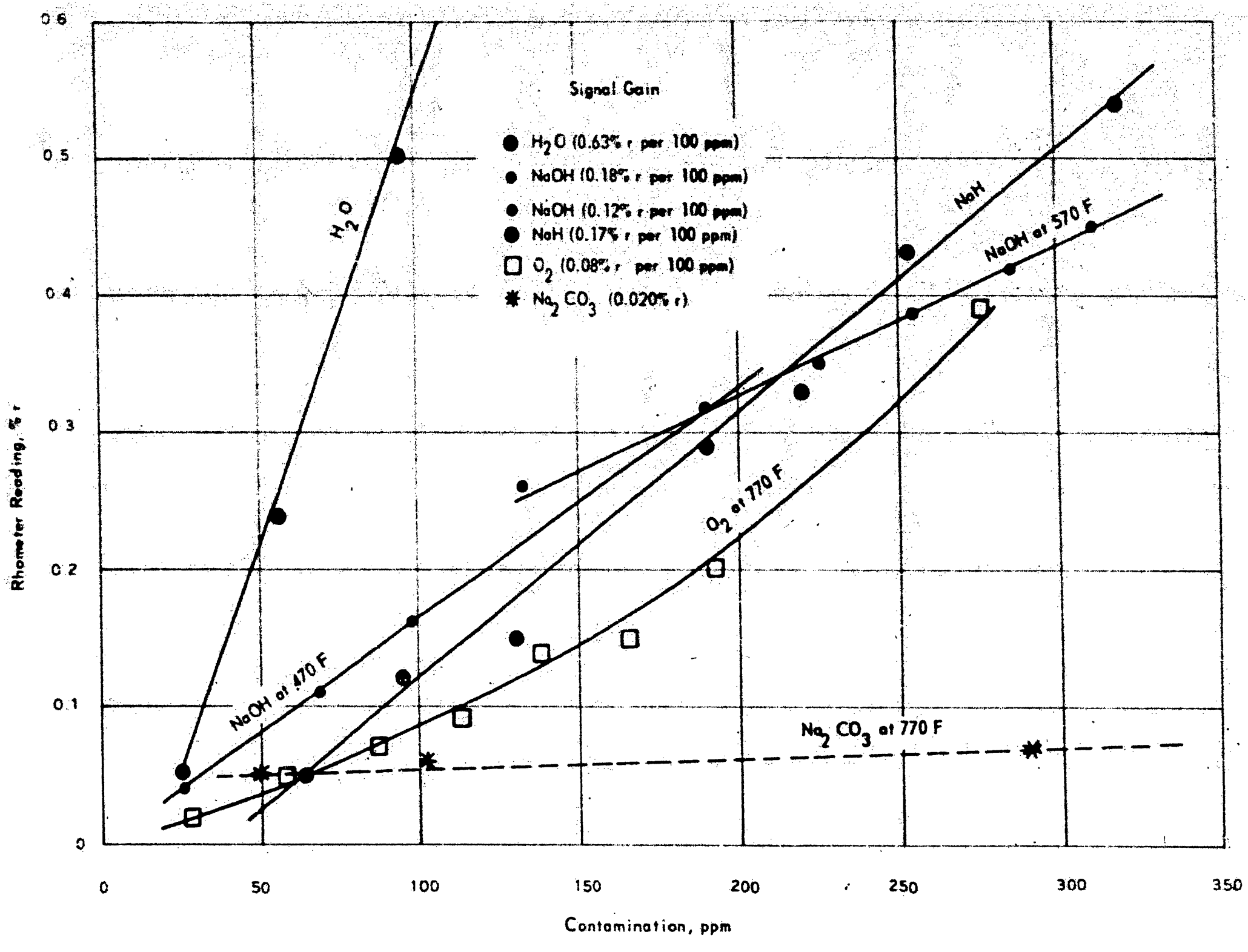


FIG. 8 COMPARISON CURVES OF RHOMETER RESPONSE TO CONTAMINANTS

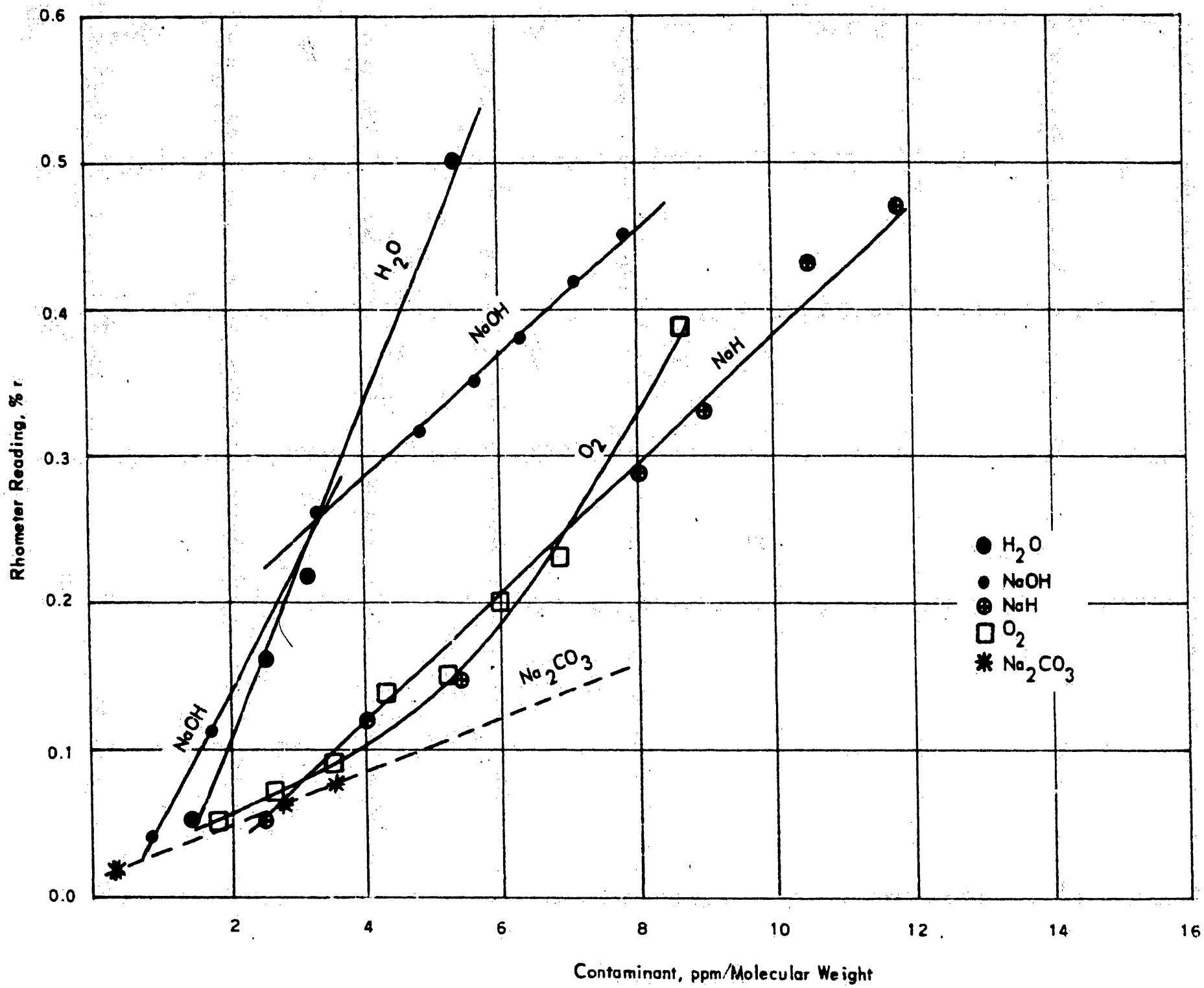


FIG. 9 COMPARISON CURVES OF RHOMETER RESPONSE TO MOLAR CONCENTRATIONS OF CONTAMINANTS

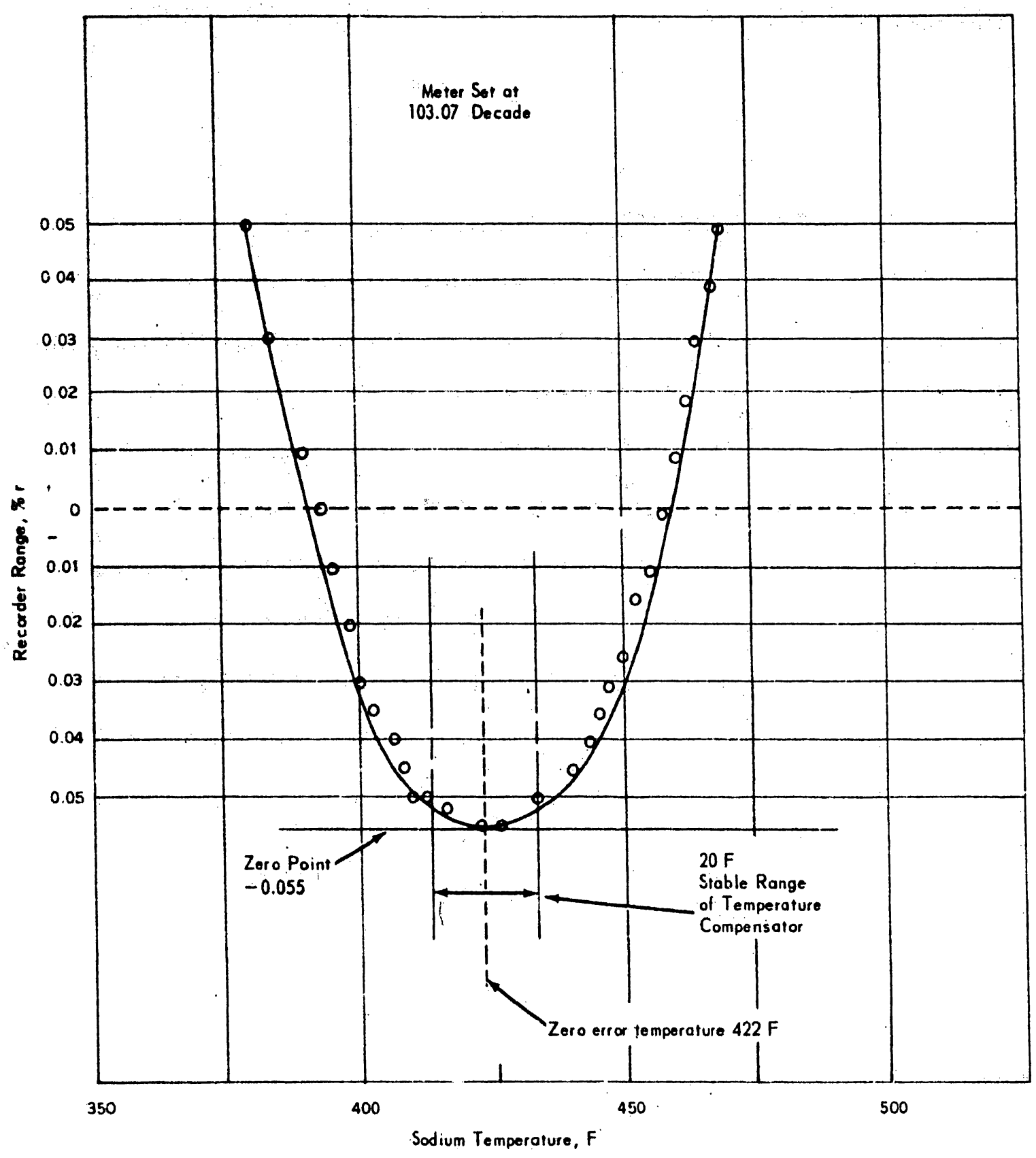


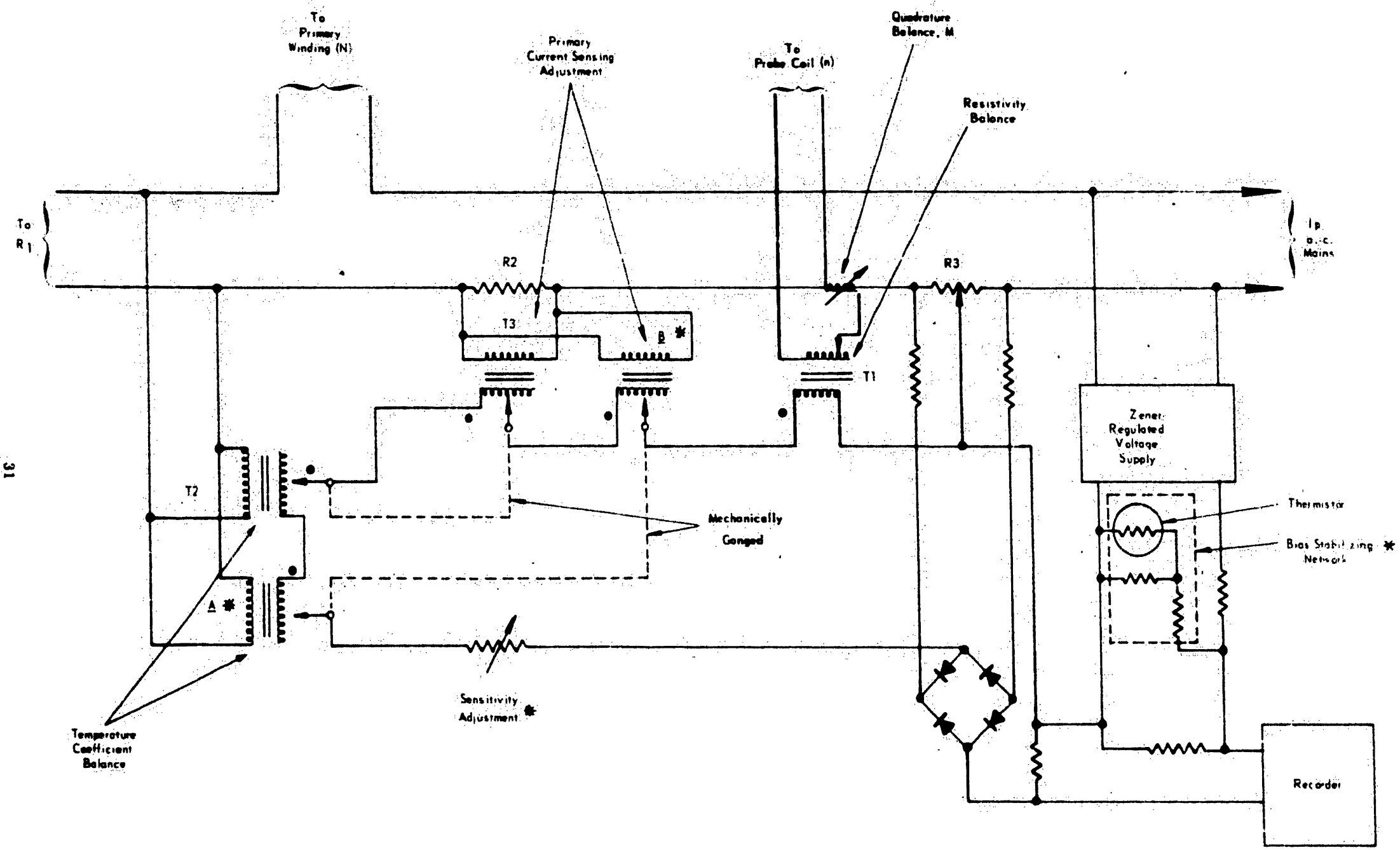
FIG. 10 THERMAL DISTORTION OF RHOMETER SIGNAL

2. The use of a different compensator resistance, such as gold, which has a more favorable temperature coefficient than platinum. This would permit a broader continuous compensation and would be adjustable to 1000 F.

3. Redesign of the compensator to a form employing a resistance thermometer or thermocouple in conjunction with a nonlinear servo for curve fitting to achieve continuous compensation to 1000 F.

Approaches (2) and (3) presented comparatively long-term efforts involving study, hardware design, and functional evaluation. Approach (1) appeared most expeditious for achieving the required operating range, since manual adjustment of compensation could be tolerated. Extension of the original transformer ratios could be implemented by simply switching in auxiliary transformers having the required ratios, and adding their outputs to those of the Rhometer transformers. Operation to 1000 F could be obtained in only three distinct ranges, with some overlap. Since the additional impedance reflected into the signal summation loop would alter the read-out scale factor, provision for sensitivity control would have to be incorporated. This could take the form of a variable resistance in series with the signal summation loop. Figure 11 illustrates the incorporation of the auxiliary transformers, A and B, as well as the sensitivity control.

Auxiliary transformers A and B are a commercially-available, multiple winding, low-loss type. Two voltage ratios for each are sufficient for extension of the range to 1000 F. The primary windings of A and B are connected across R1 and R2, respectively, while their secondary windings are connected in series with the signal summation loop in the same polarity relationship as their respective Rhometer transformers. Voltage ratios for A and B are selected by switching provisions shown schematically in Figure 12. In the original limited meter range, the auxiliary transformer secondaries are removed from the signal summation loop. Their ratios are such that upon selection of the next-higher range, and set-back of the Rhometer compensator coefficient controls to minimum settings, the voltage induced into the signal loop is equal to that introduced with maximum settings in the lower range. This arrangement effectively extends the incremental capability of transformers T4 and T5 of the Rhometer in their relative proportions. The specific ratios provided by A and B are given in Table III.



* Components incorporated by APDA for temperature range extension

● Terminals of like polarity

FIG. 11 RHOMETER CIRCUIT MODIFICATIONS

Note: Indicated Installation Connections pertain specifically to component designations as they appear in Rhometer unit modified by APDA

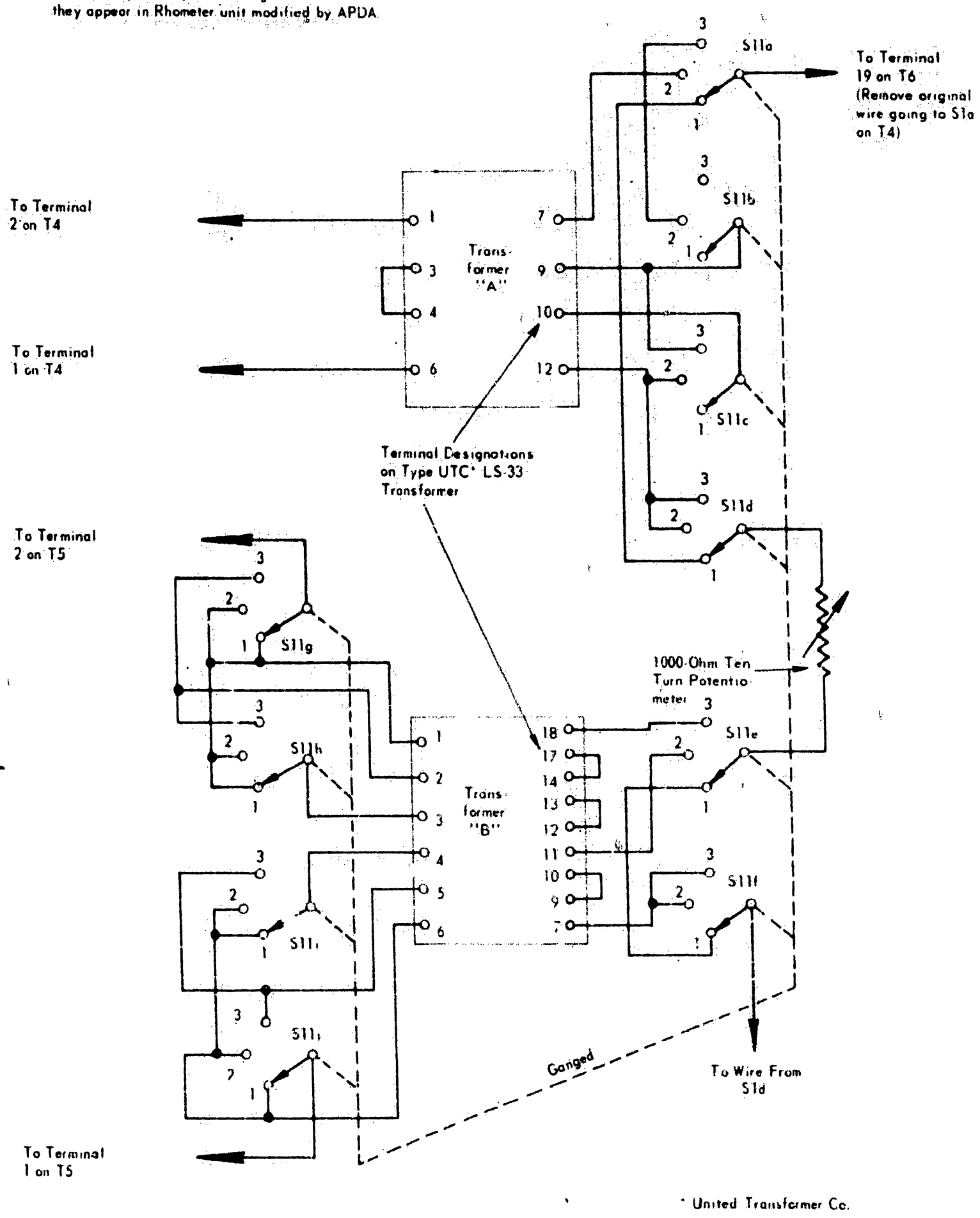


FIG. 12 RHOMETER SWITCHING CIRCUIT FOR AUXILIARY TRANSFORMERS

TABLE III
AUXILIARY TRANSFORMER VOLTAGE RATIOS

Operating Range	Temperature F	Voltage Ratio A	B
1	430 - 580	-	-
2	530 - 860	2.200	1.644
3	855 - 995	2.700	3.254

With theoretically proportioned ratios compensator switching would produce no effect on meter balance; however, some departure from this precision was unavoidable in commercial transformers. It will be noted in Figure 13 that on the low (No. 1) range of the Rhometer in which the auxiliary transformers are out of the circuit some shift of resistivity settings is still introduced by the compensator. Calibration curves for the compensator controls, resistivity balance controls, and the sensitivity control are presented in Figures 13, 14, and 15. Data for these curves were obtained in the course of several temperature ramps from 435 F to 995 F under conditions of high purity and constant flow in the Rhometer, established at 7.5 gpm.

Calibrations for temperature compensation settings in each range were determined by adjusting in sequence the temperature compensator "C", the resistivity balance decades, and the sensitivity adjustment "R". As the loop was ramped up these compensator settings were advanced in steps of about 40 F, through ranges 1, 2, and 3. A null curve similar to Figure 10 was delineated at each 40 F interval on the ramp up and returning. After this data was accumulated, a second temperature ramp was executed with the compensator adjustments preset for null balance. Upon reaching each null median temperature the decade dial settings were confirmed. Immediately after each balance, the decades were offset to the required full scale percentage readout on the recorder ($\pm$ 1.0 % r) and the sensitivity control setting (R) for actual full scale readout was established. In the return ramp down to 435 F all calibration data was reconfirmed.

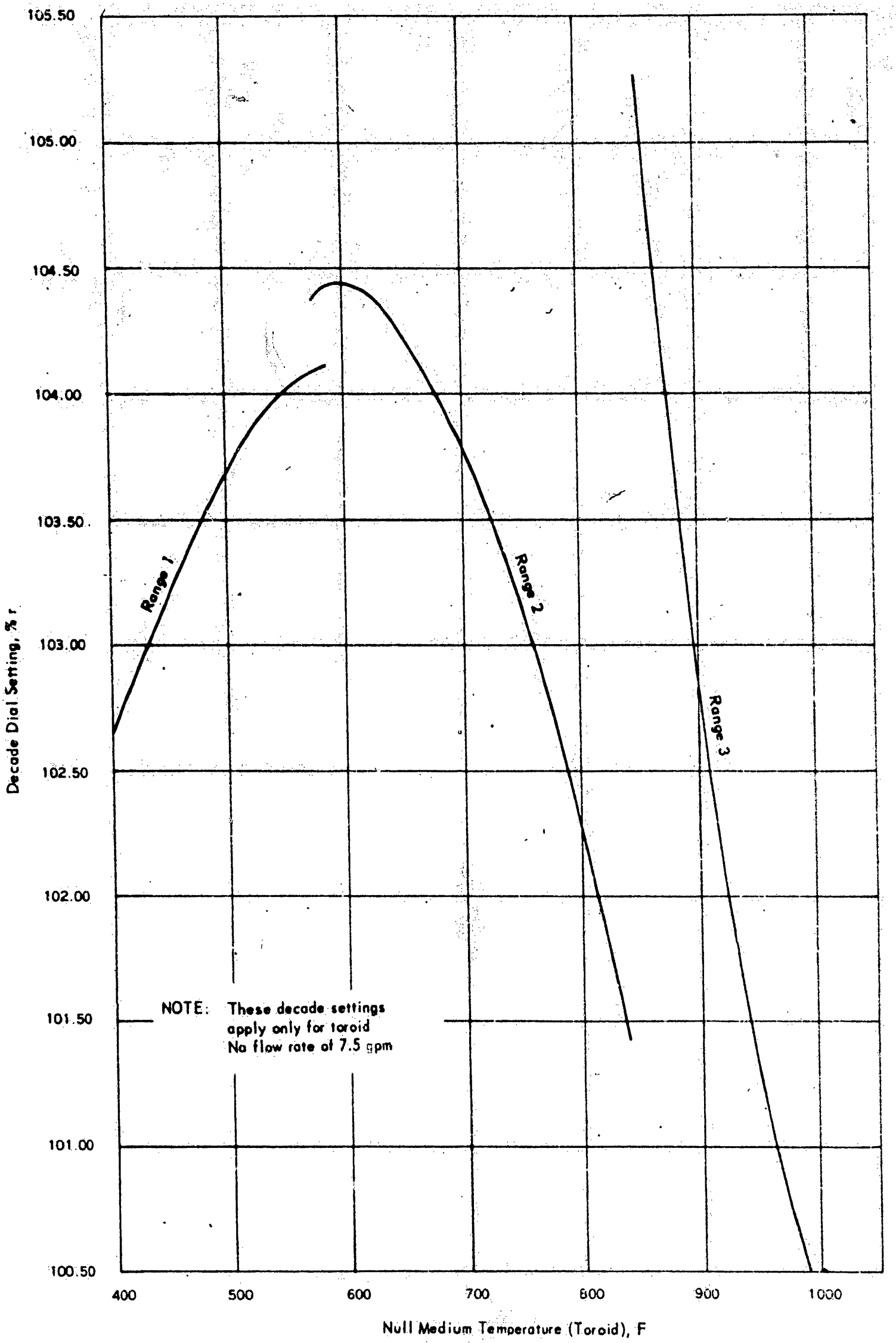


FIG. 13 RHOMETER NULL MEDIAN TEMPERATURE AS A FUNCTION OF DECADE DIAL SETTINGS

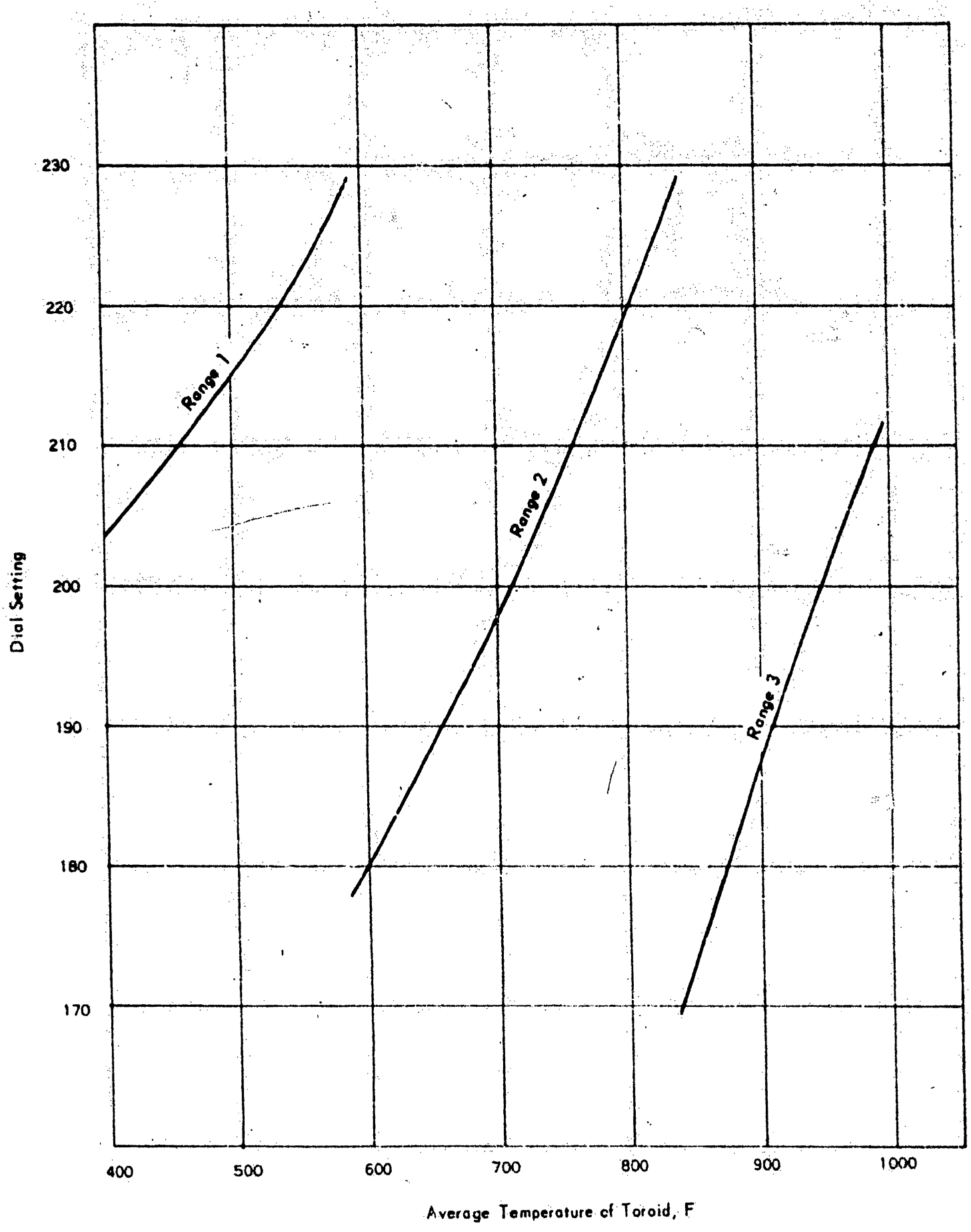


FIG. 14 RHOMETER TEMPERATURE COMPENSATOR DIAL SETTING AS A FUNCTION OF NULL MEDIAN TEMPERATURE

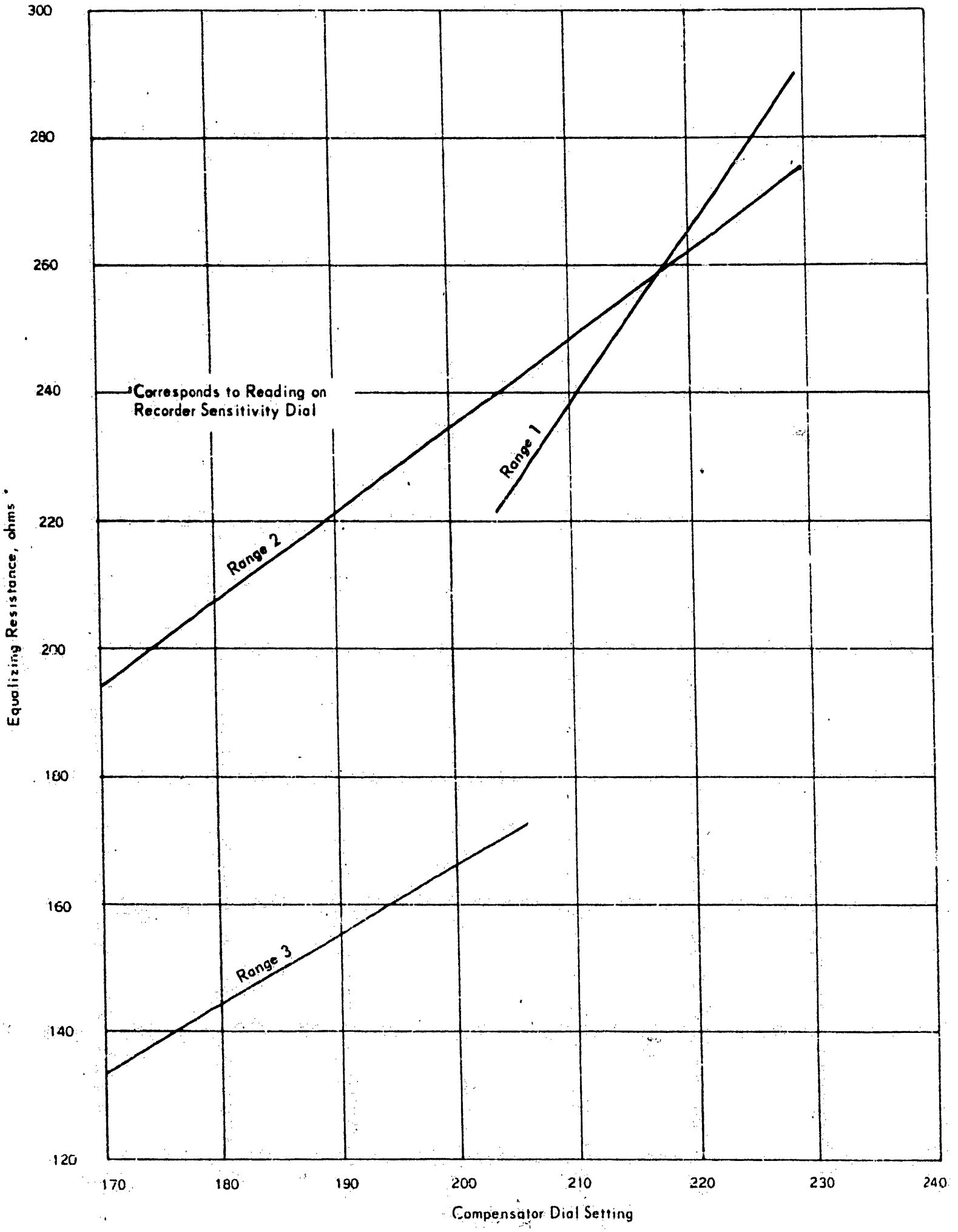


FIG. 15 RHOMETER SENSITIVITY EQUALIZING RESISTANCE AS A FUNCTION OF COMPENSATOR DIAL SETTINGS

During initial operations with the Rhometer, a recorder bias voltage drift to the order of ± 0.02 % r was observed with environmental temperature variations of 50 F to 100 F. The positive polarity effect occurred at high temperature. Instability could not be assigned to ambient temperature effect on any one component of the bias circuit, but appeared to be cumulative. Accordingly a thermistor was incorporated in an adjustable voltage divider network, as shown in Figure 16. Ambient drift of the meter signal was then reduced to about 0.005 % r by trial adjustment of Rx and Ry in this network. The effect of the thermistor is that of counteracting the positive drift of the bias supply voltage by increasing the divide-down ratio as temperature rises, thus producing the effect of a negative temperature coefficient.

A primary concern in operating the Rhometer above 600 F was the limiting temperature of the Mumetal core. Additional thermal insulation in the form of glass fiber was provided in the available void space between the toroid and the transformer core and windings. During subsequent operations at sodium temperatures to 1000 F, the core temperature did not exceed about 510 F, with the ambient air at about 115 F.

Three operational failures occurred during 1963 which point the way to preventive maintenance. Dirty switch contacts materially reduced the sensitivity of the meter. Radio contact cleaner removed the discoloration on these silver contacts and the full meter signal was recovered. The lead wire from the temperature compensator coil broke, causing a shift of -0.275 in the Rhometer signal. This behavior was first thought to be in the temperature coil proper, which would have been very difficult to repair. Even when recognized as a lead break, it was difficult to locate. Finally, the mica insulation on the temperature compensator coil failed in fatigue because of thermal movement during temperature cycles in the loop. This resulted in grounding the coil, and completely erratic signals. Two layers of 1.5 mil mica were used to insulate the Rhometer pipe-section, securing the wound sheet with plastic tape. As the coil was rewound this tape was removed, and finally the coil was sealed with a mud pack of magnesium oxide. After drying, this mud pack was wrapped with glass cloth tape to finish, and the whole encased in aluminum duct work. The repair work is illustrated in Figure 17.

Note: Indicated Part Numbers of Rhometer circuitry are as they appear in Rhometer Unit modified by APDA.

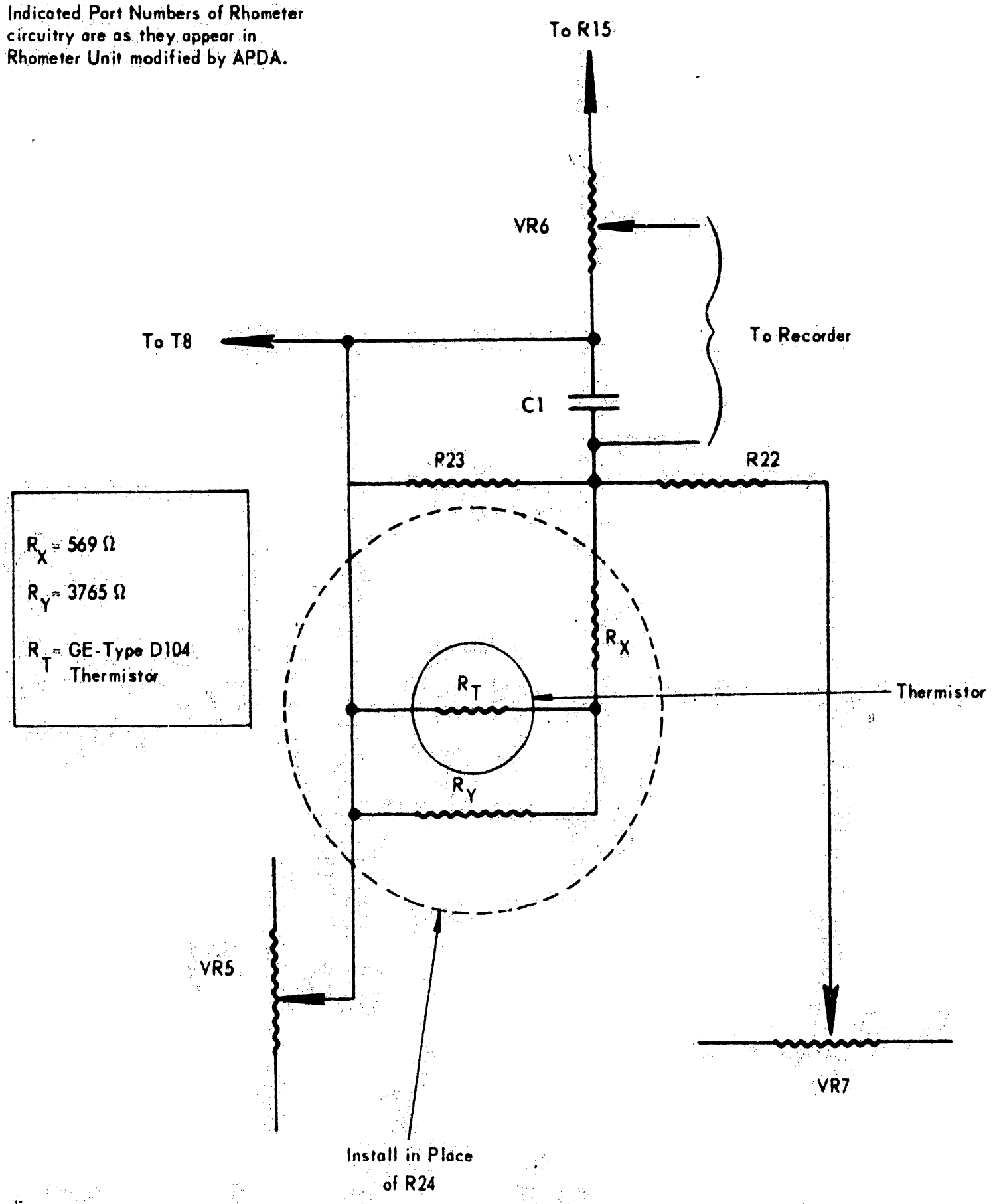
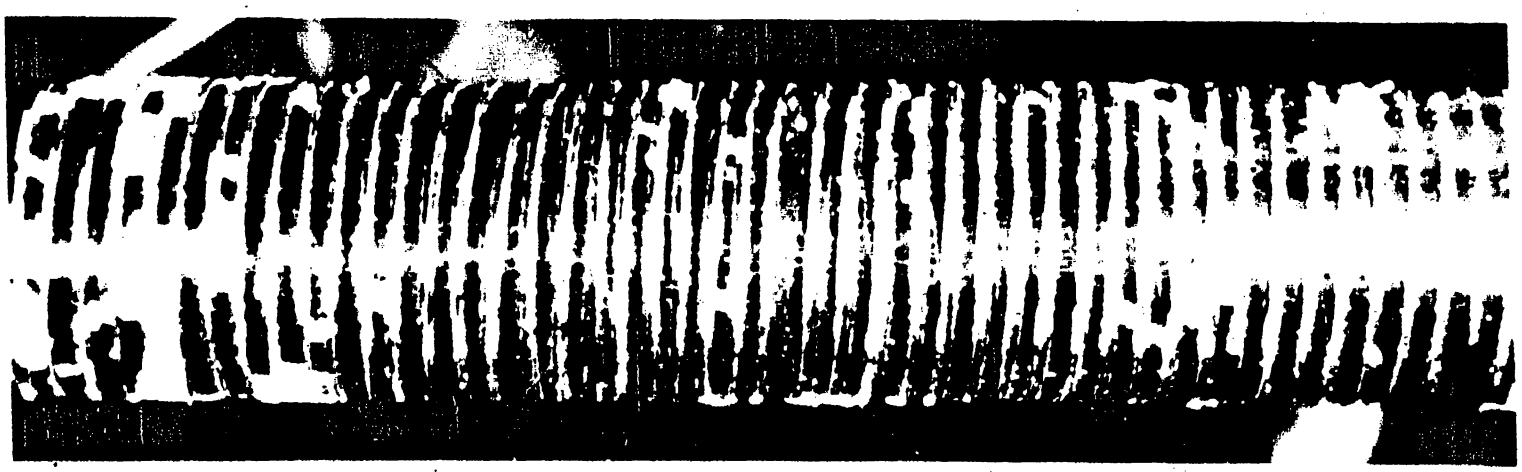
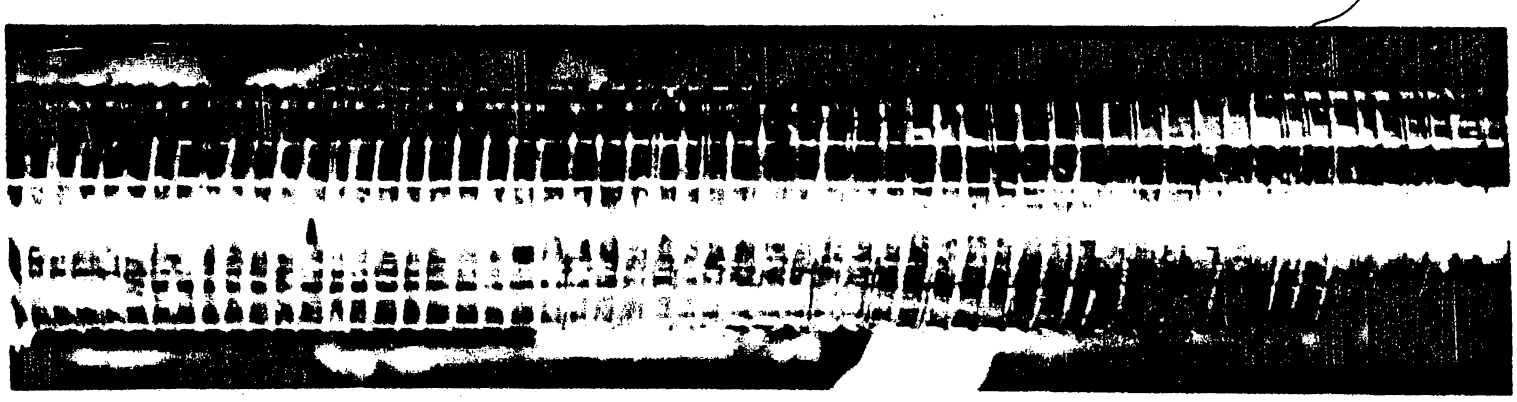


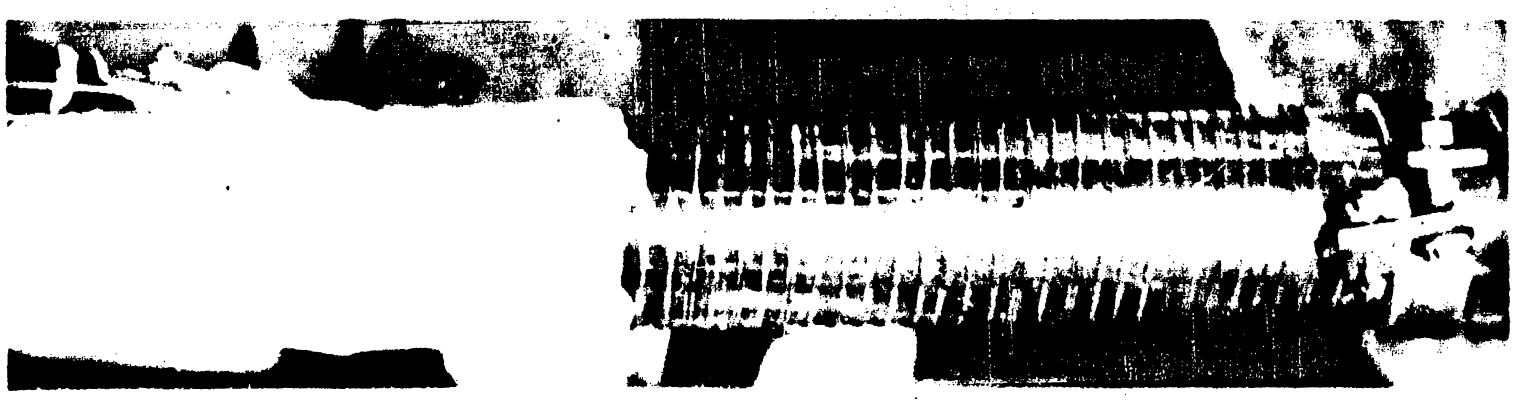
FIG. 16 RHOMETER CIRCUIT MODIFICATIONS FOR TEMPERATURE STABILIZATION OF RECORDER BIAS VOLTAGE



(A) DAMAGED COIL



(B) REWORKED COIL



(C) APPLICATION OF MAGNESIUM OXIDE

FIG. 17 RHOMETER TEMPERATURE COMPENSATOR COIL REPAIR

NICKEL DIFFUSION-TUBE HYDROGEN MONITOR

A nickel diffusion-tube hydrogen monitor was installed in the loop immediately upstream of the plugging meter cooler prior to the water injection run, in order to determine response to sodium-water reaction products at varying concentration levels. This instrument, shown in Figures 18 and 19, was based on the theory of diffusion of hydrogen[9] and a prototype monitor developed by Atomics International[5] in 1960. By regulating flow through the tube to 1/8 gpm and heating to 870 F, it was expected that the escape of hydrogen to the continuously evacuated side of the unit would generate a pressure signal consistent with the total hydrogen concentration in the flowing sodium.

No significant response was observed during the 470 F water injection run, in which loop contamination reached 26 cc or 6 ppm hydrogen. Injections at 570 F also failed to produce a signal. During the 570 F to 770 F ramp, the absolute pressure rose from 5 microns to 22 microns over a 24-hour period, but returned to the 5-micron base point at the conclusion of the ramp. At the end of the 770 F run, with the tube temperature and flow at design levels, a 2-micron signal was generated by a massive injection of 24 cc of water. Loop contamination at this time was at 146 cc or 40 ppm hydrogen. Final injection in the loop of 3 cc at 970 F produced no effect.

During the course of the 570 F injection run, the valve on the vacuum pump was closed, and the rate of pressure increase in the system was observed to be 1 micron per minute. This procedure was repeated at the end of the 770 F run, and the rate of rise had increased to 400 microns per minute. It was concluded that the vacuum pull-down was too vigorous in relation to the rate of hydrogen diffusion and that a cyclic operation of the vacuum system was indicated.

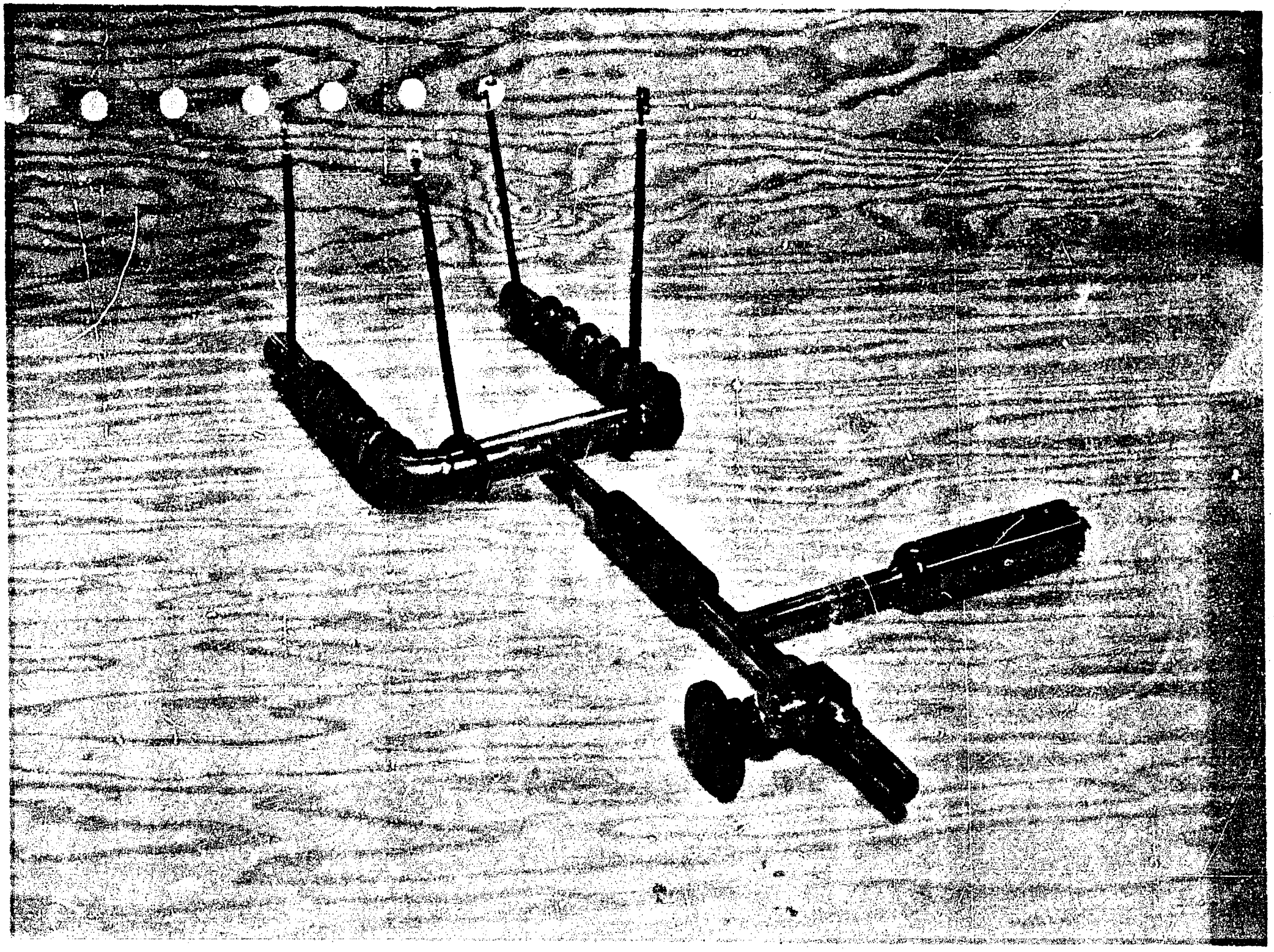


FIG. 18 NICKEL DIFFUSION-TUBE HYDROGEN MONITOR

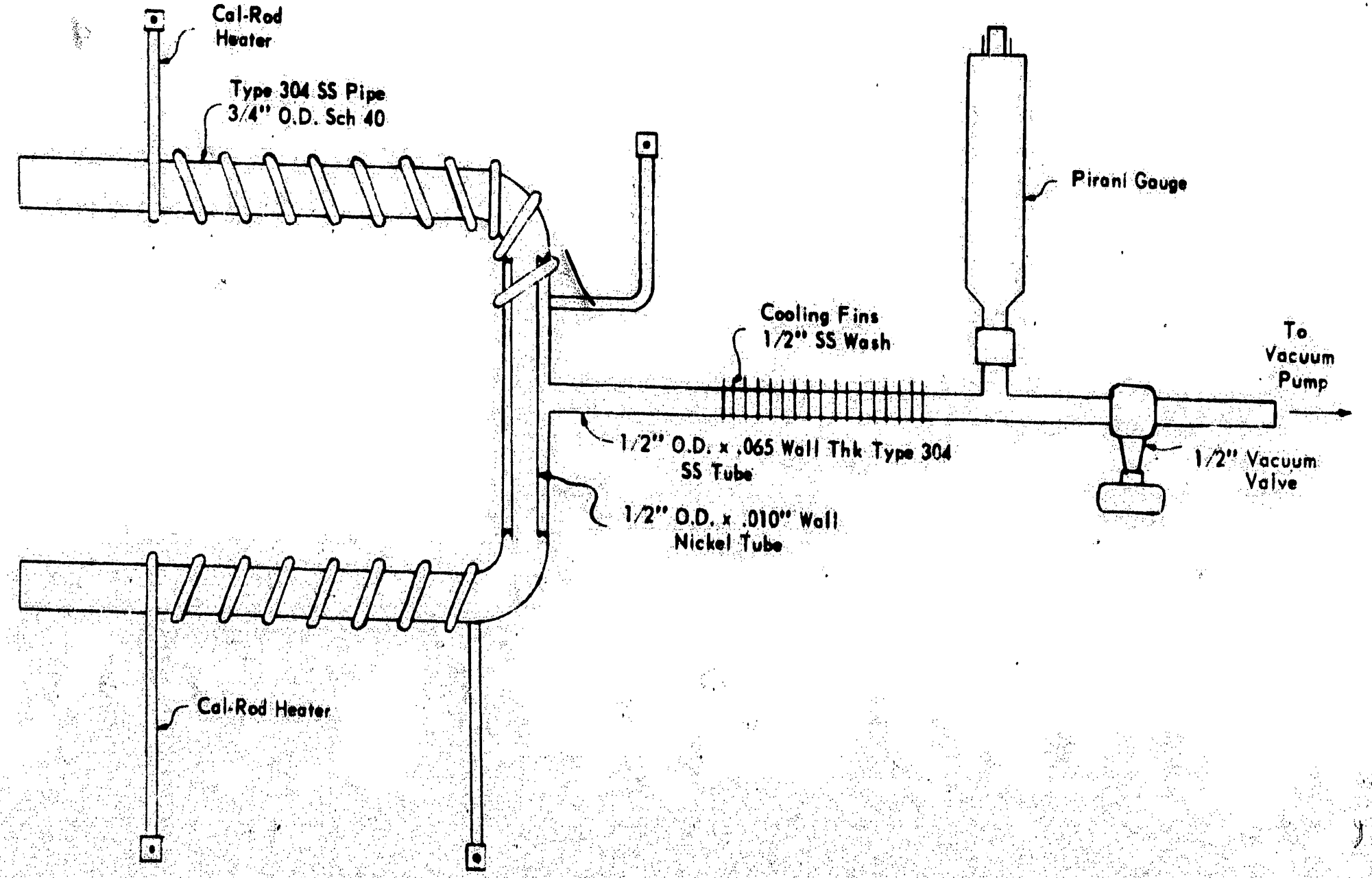


FIG. 19 DIAGRAM OF NICKEL DIFFUSION-TUBE HYDROGEN MONITOR

CONTINUOUS HYDROGEN MONITOR

A continuous hydrogen monitor was evaluated to service argon cover gas systems and provide an early warning signal for leaks in sodium-water systems. The design was based on the comparative thermal conductivity of clean and dirty gas streams. This detector is shown in Figure 20. Sensitivity was specified to 50-ppm hydrogen in the 100-to-2000-ppm range, with a maximum response time of 20 seconds. This value dictated a sample gas flow through the monitor of 10 cc per minute.

The hydrogen monitor was coupled to the loop surge tank during the original hydrogen gas injection run, which afforded an excellent test environment in which hydrogen contamination ranged from 0 to 24,000 ppm. A span gas cylinder was used to zero in the meter signal as required, and a 4-pen, high-speed Sanborn recorder was used to correlate injections and Rhometer signals with the hydrogen monitor output. This output was in turn compared to hydrogen determinations by a Fisher gas partitioner and by an F&M 500 chromatograph. An interior and exterior shot of the meter in Figure 21 shows the flow and pressure regulators and the Gow-Mack conductivity cells. The temperature equalizer coils are enclosed in the insulation cocoons.

Response time proved to be about 25 seconds, and the Gow-Mack cells were overly sensitive, producing an irrational signal above 2000-ppm hydrogen. Otherwise the monitor met specifications. It was also demonstrated that regulation of pressure, temperature, and flow were extremely critical to monitor output, and required almost constant manual supervision.

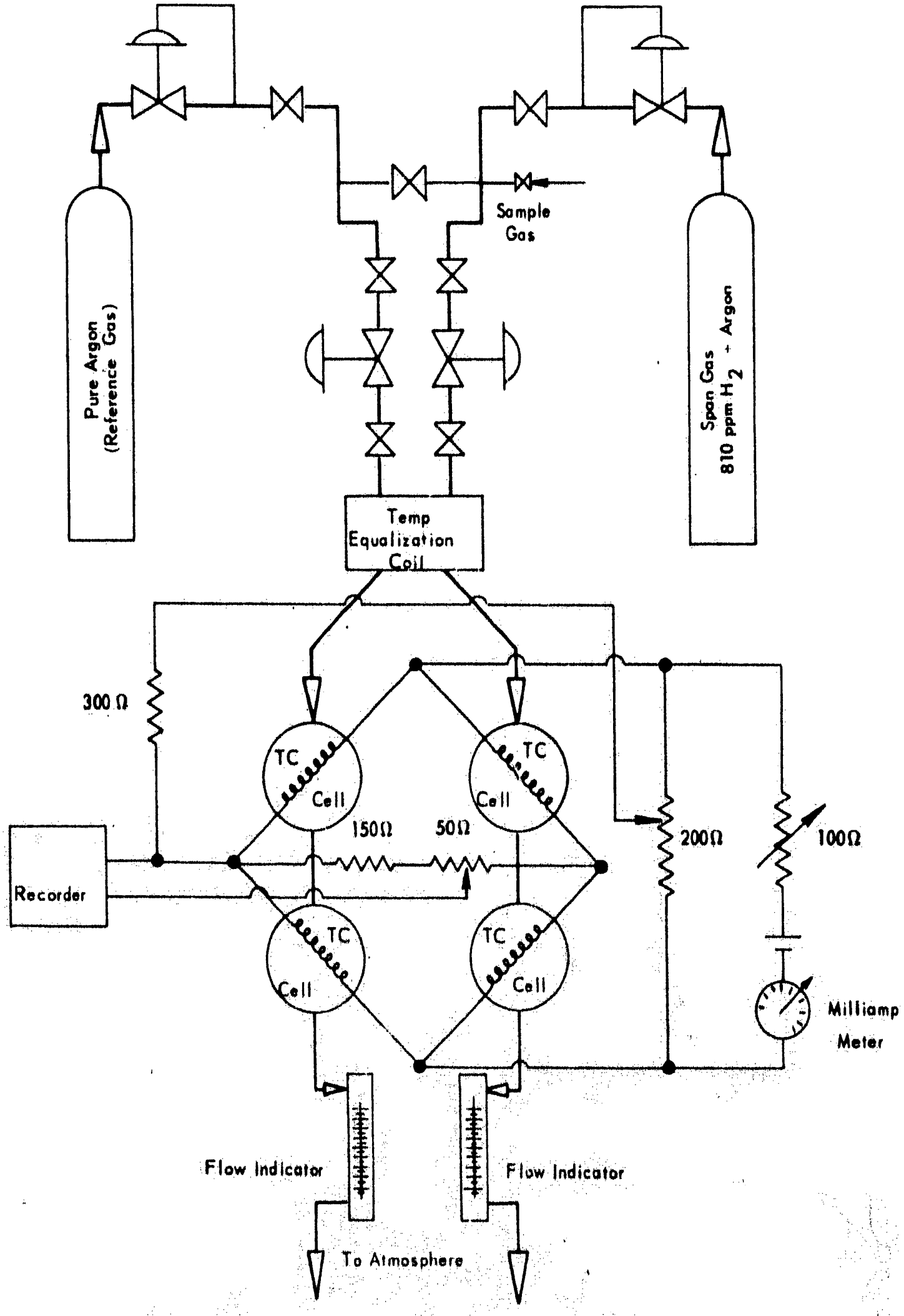


FIG. 20 DIAGRAM OF CONTINUOUS HYDROGEN MONITOR

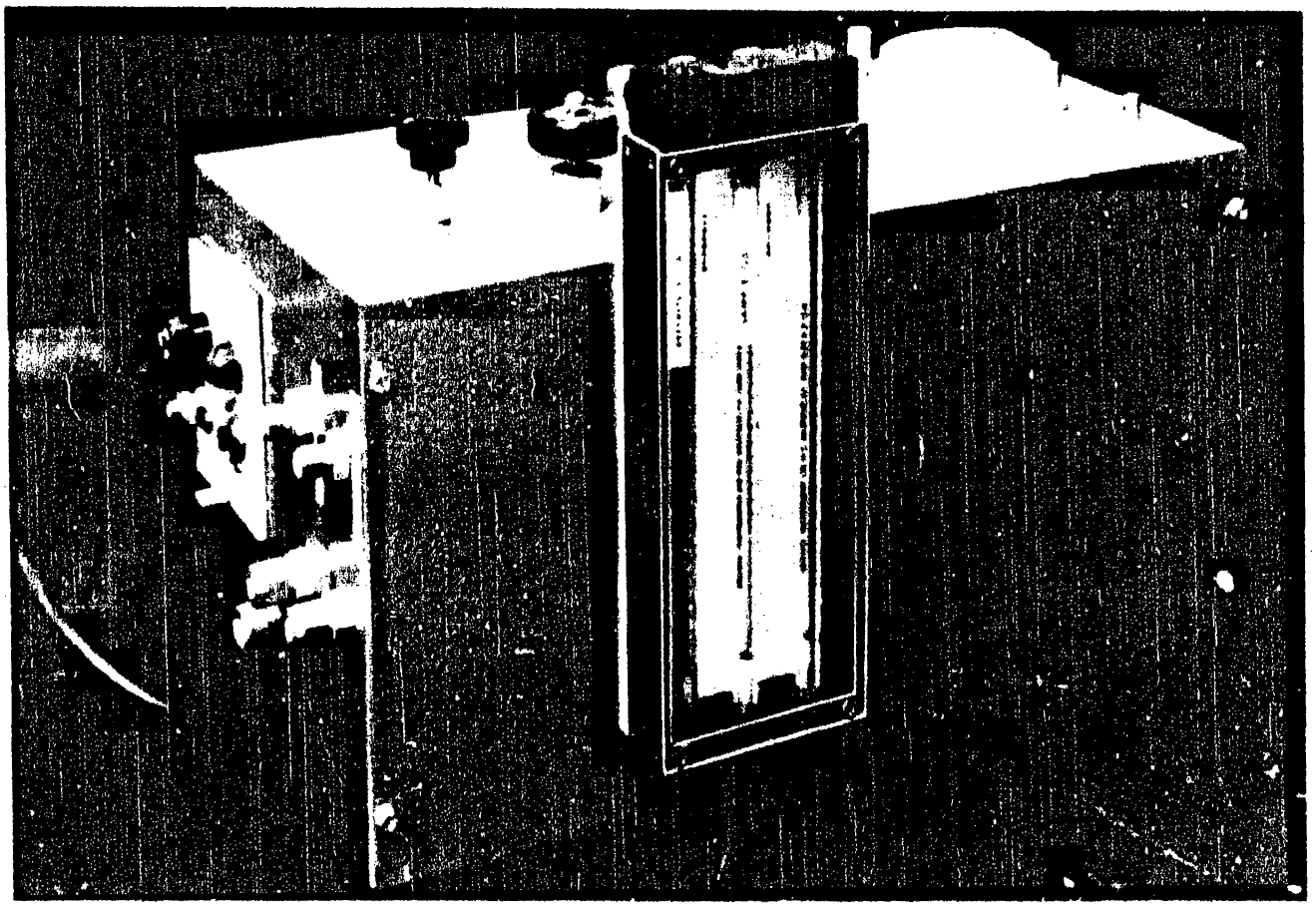


FIG. 21 CONTINUOUS HYDROGEN MONITOR

ORIGINAL HYDROGEN GAS INJECTION RUN

TEST DESIGN

The loop gas injection probe shown in Figure 22 was developed for this initial hydrogen gas injection run, but the Rhometer had not been modified. This limited loop temperature and also the level of contamination that could be attained without risk of plugging the loop. The probability of sodium hydride formation by gas injection was unknown, although thermodynamically the hydrogen-sodium reaction was feasible.

$$Na + 1/2\ H_2 \longrightarrow NaH$$

$$\Delta H = -14\ K\ cal/mol$$

$$\Delta F = -9.3\ K\ cal/mol$$

The injection test was scheduled with the original water-cooled fixed-orifice plugging meter still in service. A Fisher gas partitioner was provided to monitor the loop cover gas for hydrogen, and a continuous hydrogen detector (Figures 18 and 19) was connected to the cover gas system for experimental operation. The Fisher gas partitioner, which is a general gas analyzer designed for display of four or five gases to an accuracy of 1 per cent, was modified to indicate hydrogen in argon to an accuracy of 100 ppm in the 100-to 10,000-ppm range.

The thermal stability of sodium hydride was a major concern, and since no information was available on the probable response of the Rhometer to sodium hydride contamination, test procedures were specified to conform to anticipated dissociation pressures and plugging meter performance, as shown in Table IV.

TABLE IV
PHYSICAL CONSTANTS OF SODIUM HYDRIDE

Sodium Temperature, F	NaH Dissociation Pressure, mm Hg	NaH Solubility, ppm
400	0.1	2.4
500	5.0	52.0
600	26.0	680.0
700	100.0	5600.0
800	760.0	14000.0
850	1200.0	---

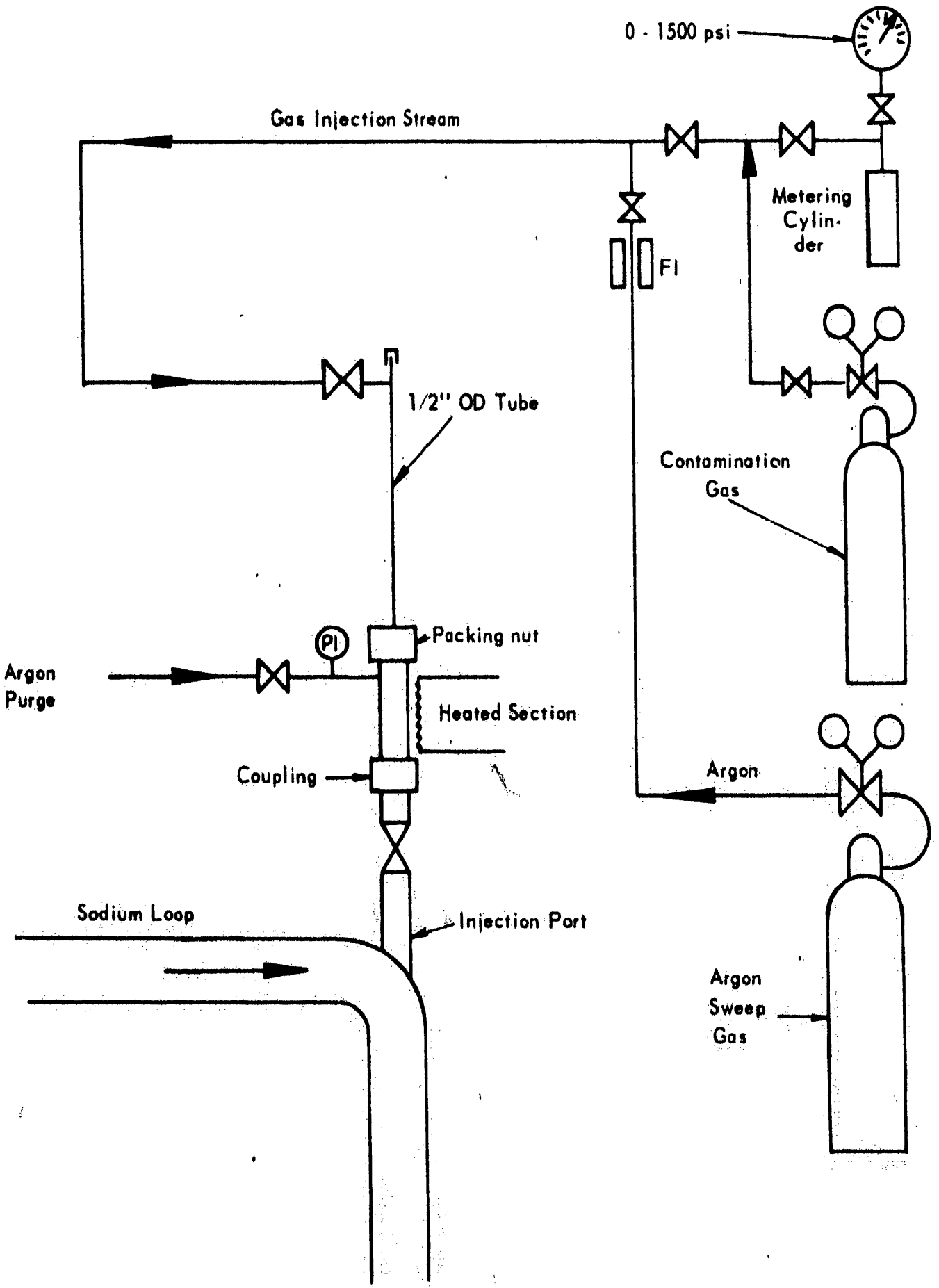


FIG. 22 GAS INJECTION APPARATUS

Dissociation values were based on a two-phase sodium-hydrogen system, and the extent of reported suppression of this dissociation pressure by an argon cover gas was unknown. In order to minimize the expected dissociation losses, an initial injection temperature of 420 F was specified.*

PROCEDURE

Initial injections at 420 F produced no response from the Rhometer or the plugging meter. A significant portion of the injection gas was reported in the cover gas, which failed to react any further in a two hour period. A second attempt was made at 420 F. To favor sodium hydride formation, the loop pressure was increased from 6 psig to 20 psig by throttling back on the surge tank inlet valves (Figure 2). This failed to produce any meter response, and the loop temperature was increased to 570 F which was the maximum operating temperature of the Rhometer at this time. Injections were continued in 0.25-cubic foot increments, to a total of 4.0 cubic feet, according to Table V. With few exceptions, hydrogen increased abruptly in the cover gas after each injection, and then dropped at a rate of 2000-to-4000 ppm per hour as the reaction continued. The exact extent of cover gas loss could not be definitely established. No indication of entrained gas or particulate sodium hydride was observed in the Rhometer signal pattern.[2]

Following injection, loop cleanup was attempted by elevating the loop temperature from 570 F to 870 F in 100 F stages to promote the dissociation of hydride. The cover gas was analyzed at each plateau according to Table VI. After each temperature ramp and gas analysis, the cover gas was thoroughly purged to promote the dissociation of hydride. The 90-hour high-temperature soak consumed approximately 300 cubic feet of clean argon purge gas.

Cold trapping was more effective than the high-temperature soak for loop cleanup. See Table VII. Cover gas was not monitored during cold trapping, but a final sodium sample was taken for verification of cleanup.

DISCUSSION OF RESULTS

From the first and last injections in this series it appears that the hydrogen gas would not react readily beyond the solubility limits of sodium hydride and would not form as a solid particulate in the test loop. Conversely, it was also evident that sodium hydride would not dissociate readily as a solute. This confirms observations in Reference 4

* Note: It was observed in Reference 6 that sodium hydride formation is less vigorous in sodium systems with low oxide impurity levels.

TABLE V
ORIGINAL RHOMETER RESPONSE TO HYDROGEN GAS INJECTION*

Injections, Cumulative Cubic feet	NaH, Cumulative ppm	Cover Gas, ppm H_2	Cumulative Correction	NaH, Net ppm	Rhometer Reading, % r	Plugging Temperature, F
0.00	0.0	100	0.0	0.0	-0.01	215
0.25	33.5	6040	6.4	27.1	+0.01	-
0.50	67.0	320	6.7	60.3	0.06	438
0.75	100.5	300	7.0	93.5	0.10	423
1.00	134.0	300	7.3	126.7	0.12	425
1.25	167.5	1500	8.8	158.7	0.14	422
1.50	201.0	7900	17.3	183.7	0.16	422
1.75	234.5	11750	29.8	204.7	0.20	430
2.00	268.0	3570	33.6	234.4	0.26	430
2.25	301.5	9930	44.3	257.2	0.34	435
2.50	335.0	1690	46.1	288.9	0.37	435
2.75	368.5	20960	68.5	306.0	0.39	427
3.00	402.0	1770	70.4	331.6	0.43	433
3.25	435.5	20900	92.7	342.8	0.47	432
3.50	469.0	540	93.3	376.5	0.53	438
3.75	502.5	17670	112.1	390.4	0.61	429
4.00	536.0	24240	137.9	398.1	0.65	500

* Sodium Inventory 1000 pounds = 454,000 grams
NaH Yield (1/359) (2 x 24 x 454) = 61 grams per cubic foot of H_2
Cover Gas Volume 8 cubic feet
NaH loss equivalent to 1000 ppm H_2 gain in the cover gas
$(1000 \times 8/10^6)(61) = 0.488$ grams NaH
$(0.488)(10^6/454,000) = 1.07$ ppm NaH

TABLE VI

RHOMETER RESPONSE TO HYDROGEN GAS INJECTION CLEANUP

HIGH TEMPERATURE SOAK

ORIGINAL RUN

Running Time, Hours	Loop Temperature, F	Cover Gas, ppm H_2	Plugging Temperature, F	Rhometer Reading, % r
0	570	5000	500	+0.65
40	670	5000	495	-
0	770	5000	475	-
42	870	3000	440	-
10	570	2500	475	+0.48

TABLE VII

RHOMETER RESPONSE TO HYDROGEN GAS INJECTION CLEANUP

COLD TRAPPING

ORIGINAL RUN

Running Time, Hours	Loop Temperature, F	Cold Trap Temperature, F	Plugging Temperature, F	Rhometer Reading, % r
0	570	570	475	+0.48
11	575	277	-	+0.35
6	570	257	-	+0.02
15	570	253	386	0.00

that sodium hydride dissociation is inhibited by an argon cover gas system, and that sodium hydride must first sublime to escape the liquid phase before dissociation can take place. It also appears that hydrogen present in the cover gas does react slowly with the system, and is not totally lost by purging action. The charted response of the Rhometer to injection is shown in Figure 23.

In summation, it can be said (1) that some hydrogen losses were sustained, (2) that system equilibrium reaction was probably not reached between injections, and (3) that the metered injections of hydrogen probably did not result in quantitative increments of sodium hydride in the loop. *

Plugging temperatures were not consistent with contamination build up; however, this inconsistency was not of material significance since it was at this time that trouble developed with the water-cooled exchanger in the plugging meter, and the concept of a variable orifice valve led to complete replacement of the unit. The plugging meter used for this injection run served its purpose in signaling the approach of loop saturation by plugging at 500 F. This determined the safe limit of contamination for the experiment.

The Rhometer demonstrated an over-all signal gain of 0.166 % r per 100 ppm of hydride, which compares favorably with response to other contaminants.

* Note: In theory, the 1000-pound sodium loop would be saturated by 0.38 pounds or 380 ppm of sodium hydride at 570 F. The 4 cubic feet cumulative injection of hydrogen should have produced 0.534 pounds of sodium hydride.

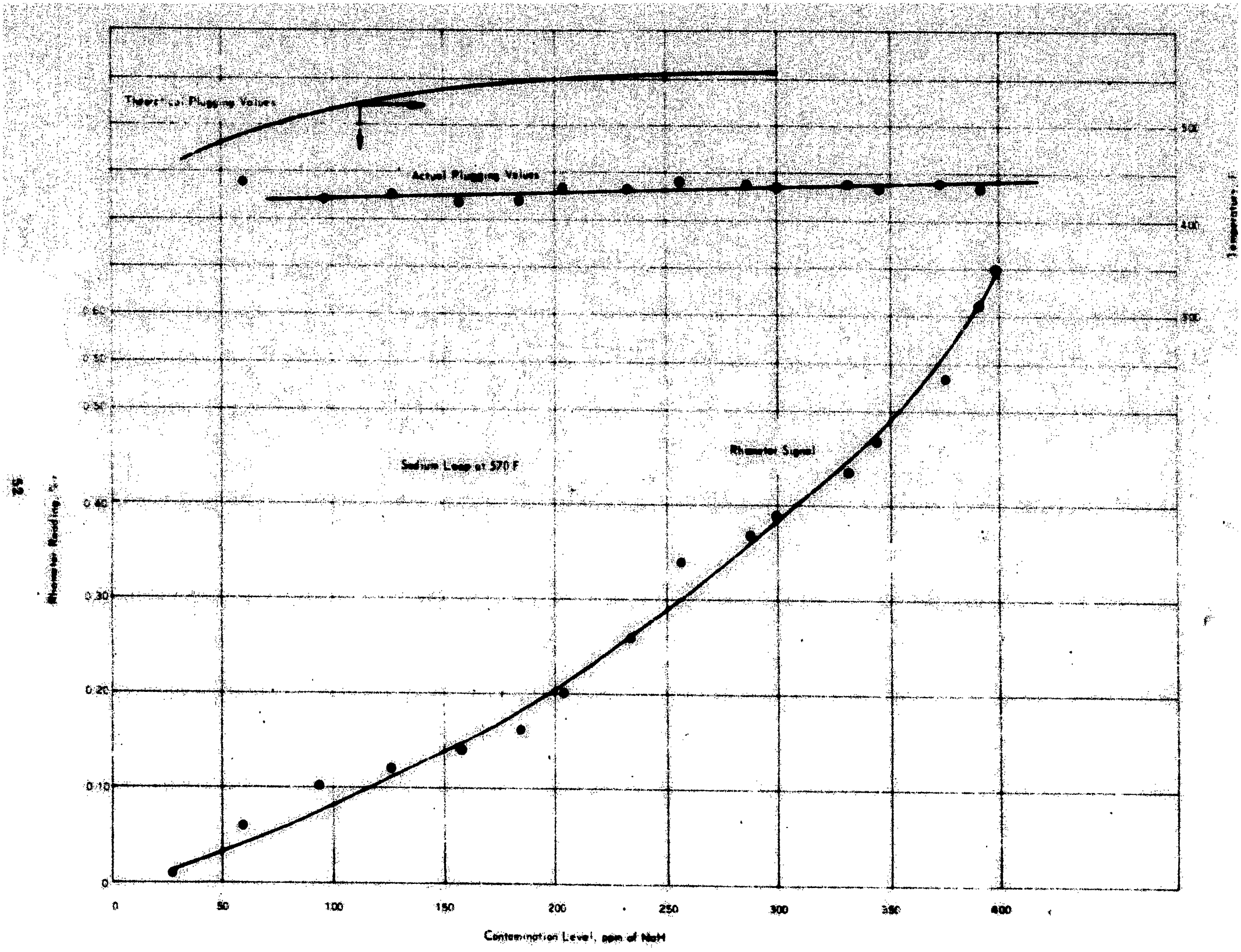


FIG. 23 RHOMETER AND PLUGGING METER CALIBRATION CURVES FOR THE INITIAL H_2 GAS INJECTION TEST

SODIUM HYDRIDE TEA BAG INJECTION

TEST DESIGN

The sodium hydride tea bag injections were planned to supplement the original hydrogen gas injection run for calibration of the Rhometer and plugging meter. For this first attempt at tea bag injection, three types of tea bags were fabricated. The 165-micron stainless-steel frit unit and the 11-mil slotted type 304 stainless-steel tubing unit are shown in Figure 24. A third bag was fabricated of reinforced 325-mesh wire cloth. This bag was destroyed in one handling, and did not appear to be rugged enough for sodium service.

The test schedule provided for initial cold trapping and operation of the loop to steady state at 570 F, continuous operation of the Rhometer, periodic operation of the plugging meter, and sampling of the sodium and cover gas at appropriate intervals during injection and cleanup. A log of argon consumption was also maintained to determine the sweep rate in the cover gas. The operating log sheet was posted every 2 hours on a 24 hour basis, with special notations as required during critical periods. Major items of record included: power loads and voltage; Rhometer set points and signal; system pressures such as pump discharge, pump seal, and cover gas; flow through all loop components; and 32 temperature check points.

PROCEDURE

The sodium hydride run was made after modifications to the Rhometer, and installation of the variable-orifice plugging meter, both previously described in this report. A nickel diffusion-tube hydrogen monitor (Figures 20 and 21) was also installed in the loop immediately upstream of the plugging meter cooler. For inspection of the cover gas a new F&M 500 chromatograph was procured to replace the Fisher gas partitioner used in the earlier hydrogen gas injection run. Dry box atmosphere was also monitored with this new instrument.

Sodium hydride obtained for the test was in a 50 per cent mineral oil dispersion, and assayed 2 per cent free sodium. A nitrogen filled dry box was outfitted with a soxhlet apparatus for extraction with hexane, and a cooling system of isopropyl alcohol installed to service the soxhlet condenser. A special balance with a silicone filled dash pot was obtained for operations within the dry box. The sodium hydride extract was stripped and stored in a vacuum desiccator mounted in the dry box. Finally, a pellet machine was installed to facilitate handling and weighing the

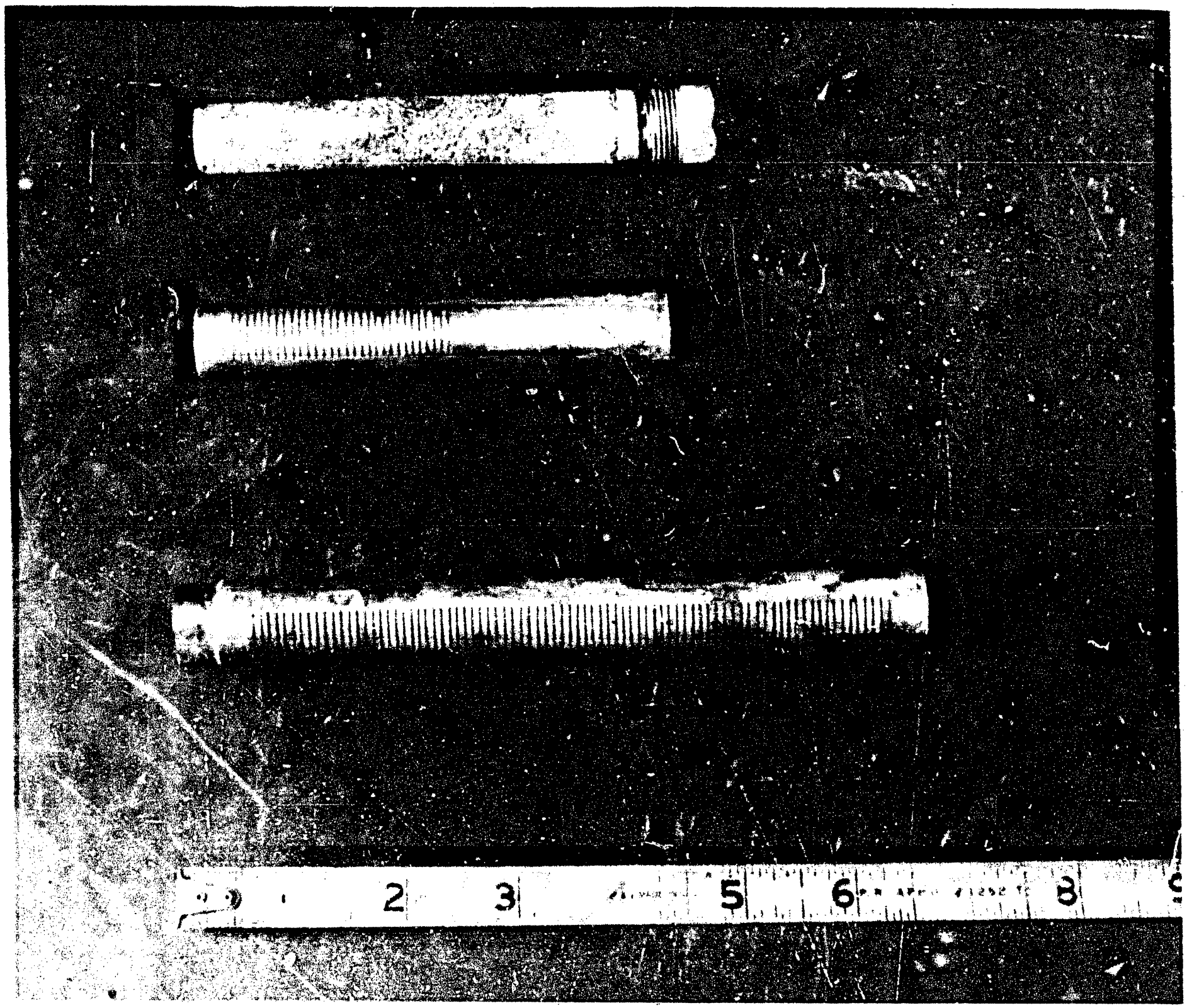


FIG. 24 INJECTION TEABAGS

sodium hydride powder. The tea bag and probe, Figure 25, were attached in the dry box and protected in transfer to the loop with a gas filled plastic bag. After injection, this assembly was transferred back into the dry box, examined for residual deposits, and cleaned.

In all, ten injections totaling 56.1 grams were made at 570 F, and five injections totaling 26.6 grams at 770 F. Cleanup by cold trapping followed. To insure a clean system the loop was ramped to 1000 F before trapping. After an apparently effective cleanup at 570 F, the loop was again ramped to 1000 F and the loop meters indicated a small contamination pick up. The third ramp-and-trap cycle was successful.

DISCUSSION OF RESULTS

Operation charts and calibration curves for the sodium hydride run and cleanup are not included in this report. This is omitted because several limitations were inherent in the tea bag technique which largely obscured the results of the experiment. In most cases, solution of the sodium hydride was incomplete. Submersion of the tea bag at the ambient temperature of the probe port produced a cold finger effect, and deposits trapped on the surface of the tea bag sealed off the openings, blocking solution of the charge. When the tea bags were preheated in the loop probe port before submersion, the sodium hydride load partially dissociated forming a deposit inside the tea bag which further resisted solution. A consistent increase in the Rhometer signal was observed after the tea bag was removed from the loop and during positive temperature ramps. It was postulated that particles of sodium hydride escaping from the tea bag remained in the solid state, dissolving slowly at higher temperatures. All of these variables disqualified the results of the run for meter calibration.

Although loop contamination increments could not be established, most of the injections resulted in a gain which was reflected by the meter readings. Typical results in Tables VIII and IX illustrate the rationality of the readings of both meters. Some intermediate values were not rational, reflecting a net loss from the injection probably due to the cold finger effect. During cleanup the Rhometer signal and plugging temperature did not always shift in the same direction. This inconsistency was ascribed to unsteady state in the loop produced by temperature changes.

Sodium hydride demonstrated high thermal stability in loop environment (submerged) and did not dissociate to any significant degree during injection, or during temperature ramps.

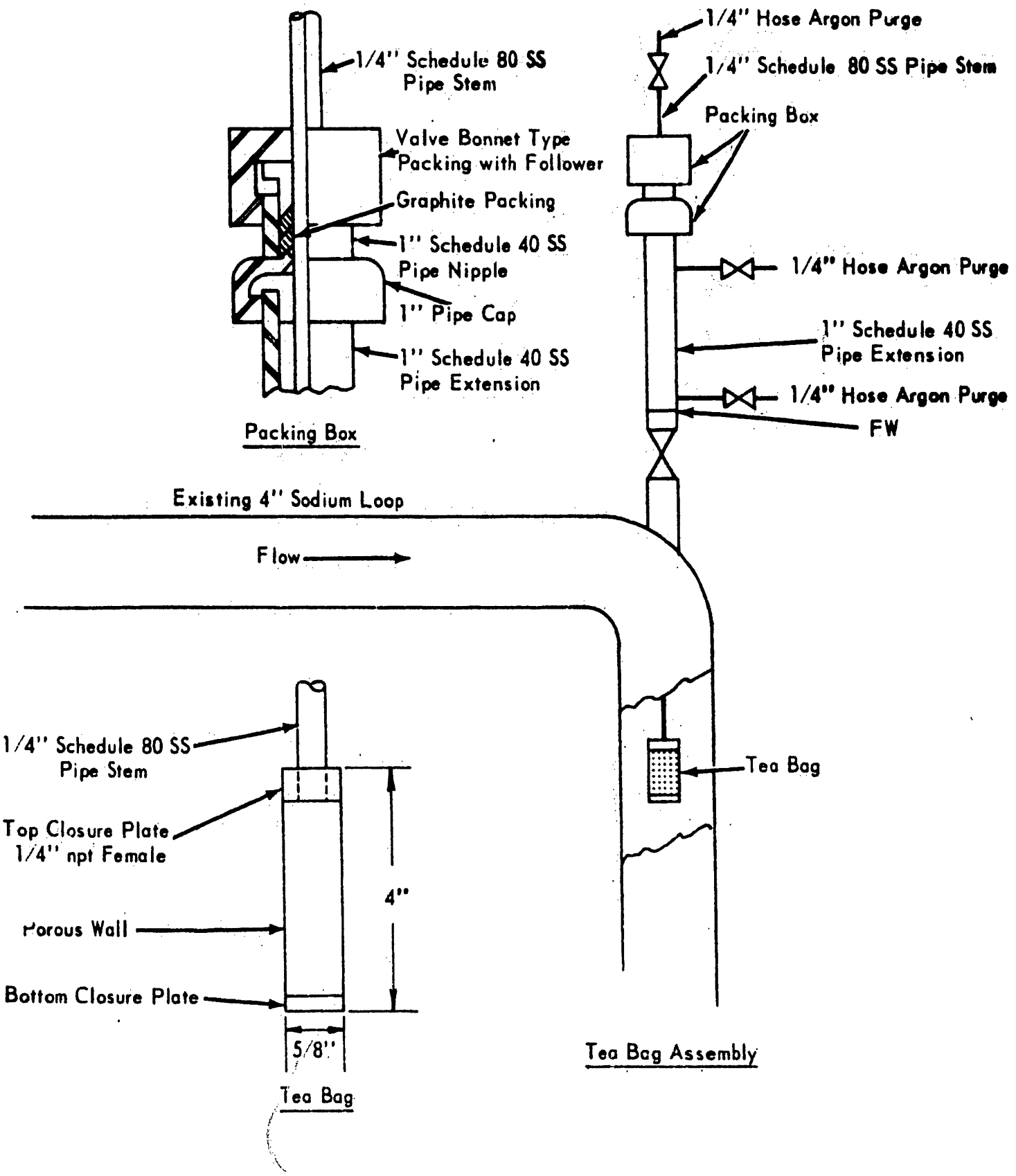


FIG. 25 TEABAG INJECTION APPARATUS

TABLE VIII
RHOMETER RESPONSE TO SODIUM HYDRIDE TEA BAG INJECTION

Injection, grams	Plugging Temperature, F	Rhometer Reading, % r
	215	-0.02
17	387	+0.14
25	424	+0.16
61	480	+0.26
78	525	+0.36

TABLE IX
TYPICAL COVER GAS ANALYSIS DURING SODIUM HYDRIDE INJECTION AND CLEANUP

Loop Operation	Hydrogen, ppm Before	After
Inject 5.91 gm	820	860
Inject 5.25 gm	1075	1160
Ramp 885 F - 970 F	1495	1535

HYDROGEN GAS INJECTION RERUN

TEST DESIGN

The hydrogen injection rerun was undertaken to correct Rhometer calibrations made in an earlier experiment. These earlier calibrations were thought to be biased by a material imbalance resulting from loss of hydrogen to the cover gas. The rerun also afforded an opportunity to calibrate the variable-orifice plugging meter which was installed in the loop after the original hydrogen injection run. Finally, it was intended to investigate the thermal dissociation rate of the sodium hydride and, if possible, to obtain an expression of dissociation rate as a function of temperature.

In this hydrogen injection series, it was planned to add the maximum amount of gas necessary to form an equivalent of 330 ppm sodium hydride at 570 F. These conditions were chosen because previous runs at 570 F indicated that the hydride forms readily until saturation is approached and remains stable in the loop environment at that temperature. Following the injections, a step-wise progression of 50 F ramps to a maximum of 970 F were scheduled, and provisions were made to monitor the cover gas closely for evidences of dissociation during the ramp. In order to reduce the error in material balance, a complete purge of the cover gas was specified as soon as hydrogen gain was recorded for each injection. As before, hydrogen injections were designated in 0.25-cubic foot increments, and injections were to be terminated at a 500 F plugging temperature. A constant 570 F loop was also specified.

PROCEDURE

A total of 2.5 cubic feet of hydrogen gas were injected during this rerun (Figure 26). After the 12 injections were completed the sodium hydride dissociation ramp was initiated. The loop temperature was raised in increments of 50 F to a maximum of 970 F. A sweep rate of 0.0125 cfm of clean argon was established in the cover gas during this ramp. The observed changes in the hydrogen level of the cover gas during this operation were considered insignificant (Figure 26).

DISCUSSION OF RESULTS

Meter calibrations (Figure 27) show that both the Rhometer and the plugging meter responded consistently to progressive contamination levels. The Rhometer signal gain was linear with respect to contamination level, with a signal index gain of 0.17 % r per 100 ppm sodium hydride.

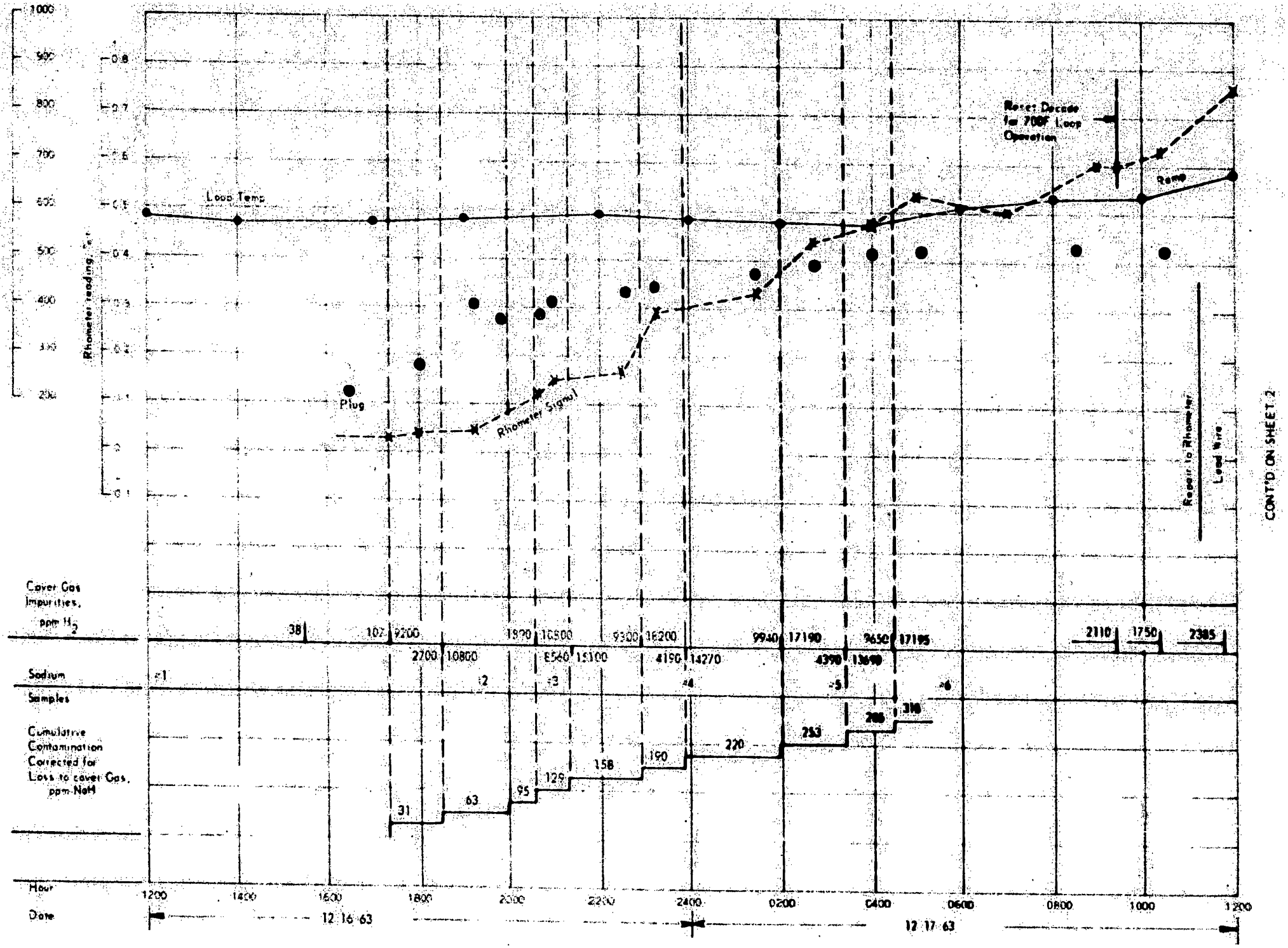
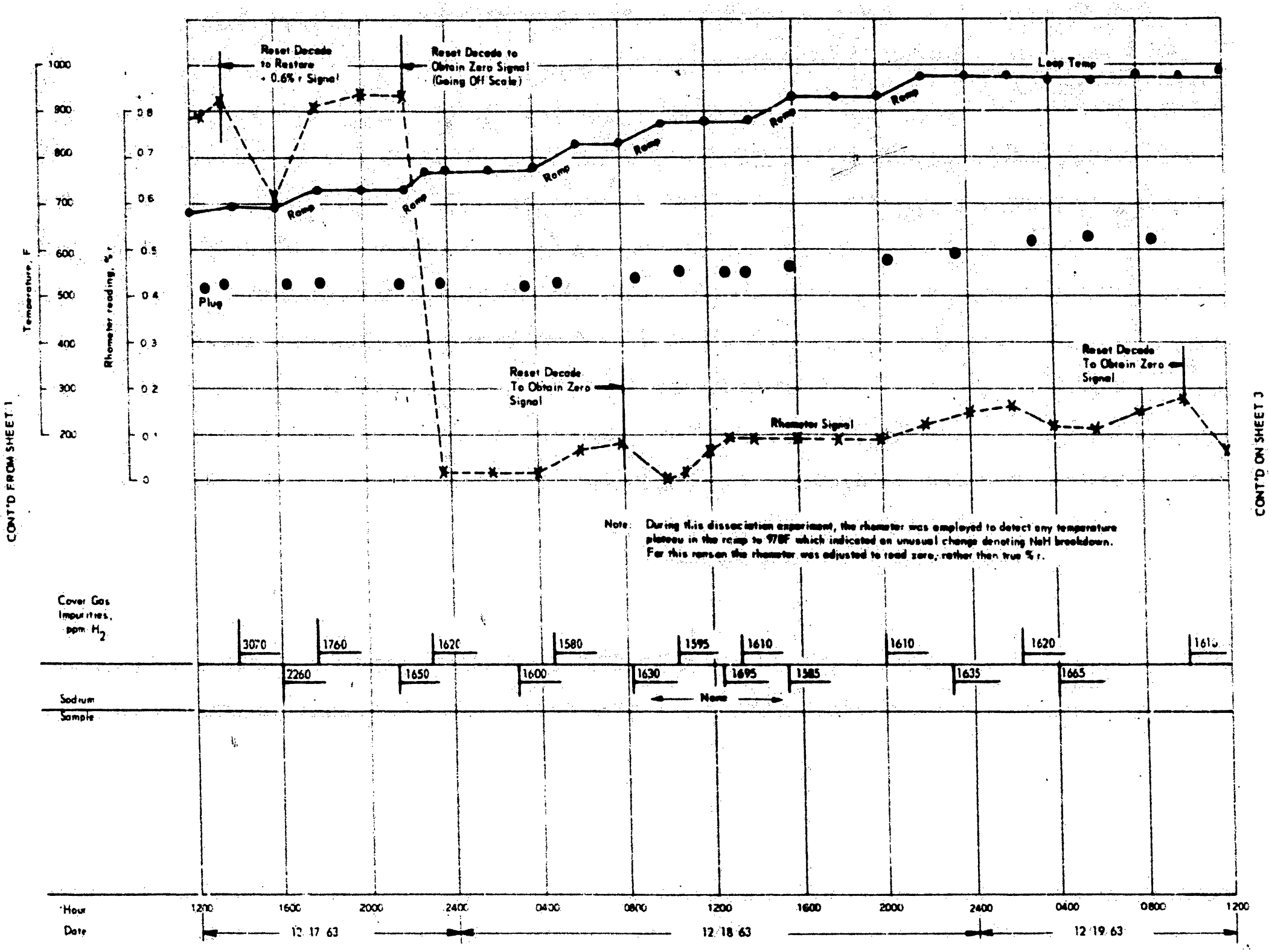


FIG. 26 LOOP LOG OF H_2 GAS INJECTION RERUN AND THERMAL DISSOCIATION OF NaH (Sheet 1 of 3)

CONT'D FROM SHEET 1



CONT'D ON SHEET 3

FIG. 26 LOOP LOG OF H_2 GAS INJECTION RERUN AND THERMAL DISSOCIATION OF NaH

CONT'D FROM SHEET 2

Temperature, F

Rhometer reading, ft

Loop Temp

Plug

Rhometer Signal

Cover Gas Impurities, ppm H_2

1565 1800 1770 1610 1140

1860 1670 1775

Sodium Sample

Hour 1200 1600 2000 2400 0400 0800 1200 1600 2000 2400 0800 1200 1600

Date 12 19 63 12 20 63 12 23 63

Closed Contacts on Rhometer Temp.

Compressor Switches

Start Cold Trap

FIG. 26 LOOP LOG OF H_2 GAS INJECTION RERUN AND THERMAL DISSOCIATION OF NaH

(Sheet 3 of 3)

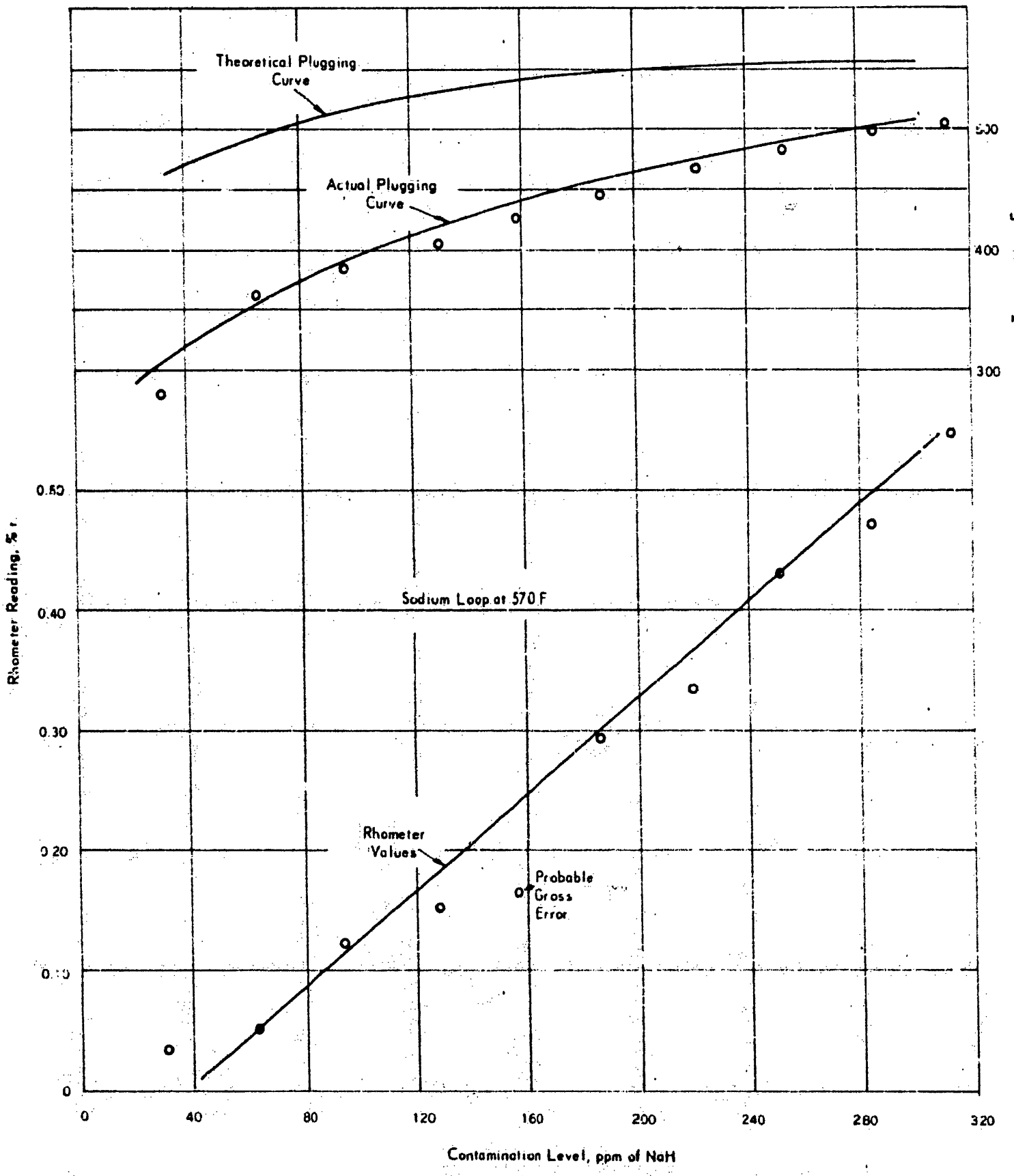


FIG. 27 RERUN CALIBRATION CURVE OF RHOMETER AND PLUGGING METER FOR CONTAMINATION BY H_2 GAS INJECTION

This response was slightly greater than the 0.166 signal index gain evidenced in the original run, according to Table I.

Inconsistent plugging temperatures during the dissociation run caused no great concern since the temperature changes were generating an unstable condition. The disparity between predicted and experienced plugging values during the injection run are not easily explained. Solubilities given in Figure 28 were based on values in Reference 7 and Reference 8. These sources are subject to a constant error implicit in the technique of the original solubility experiments. It is entirely possible that the solubilities given in these references do not apply to the present loop environment. Plating action in the plugging meter cooler section located upstream of the orifice could have introduced a bias in this direction; however, such a mechanism should become more evident as contamination increased, and such was not the case. The data for the hydrogen injection rerun are shown in Table X.

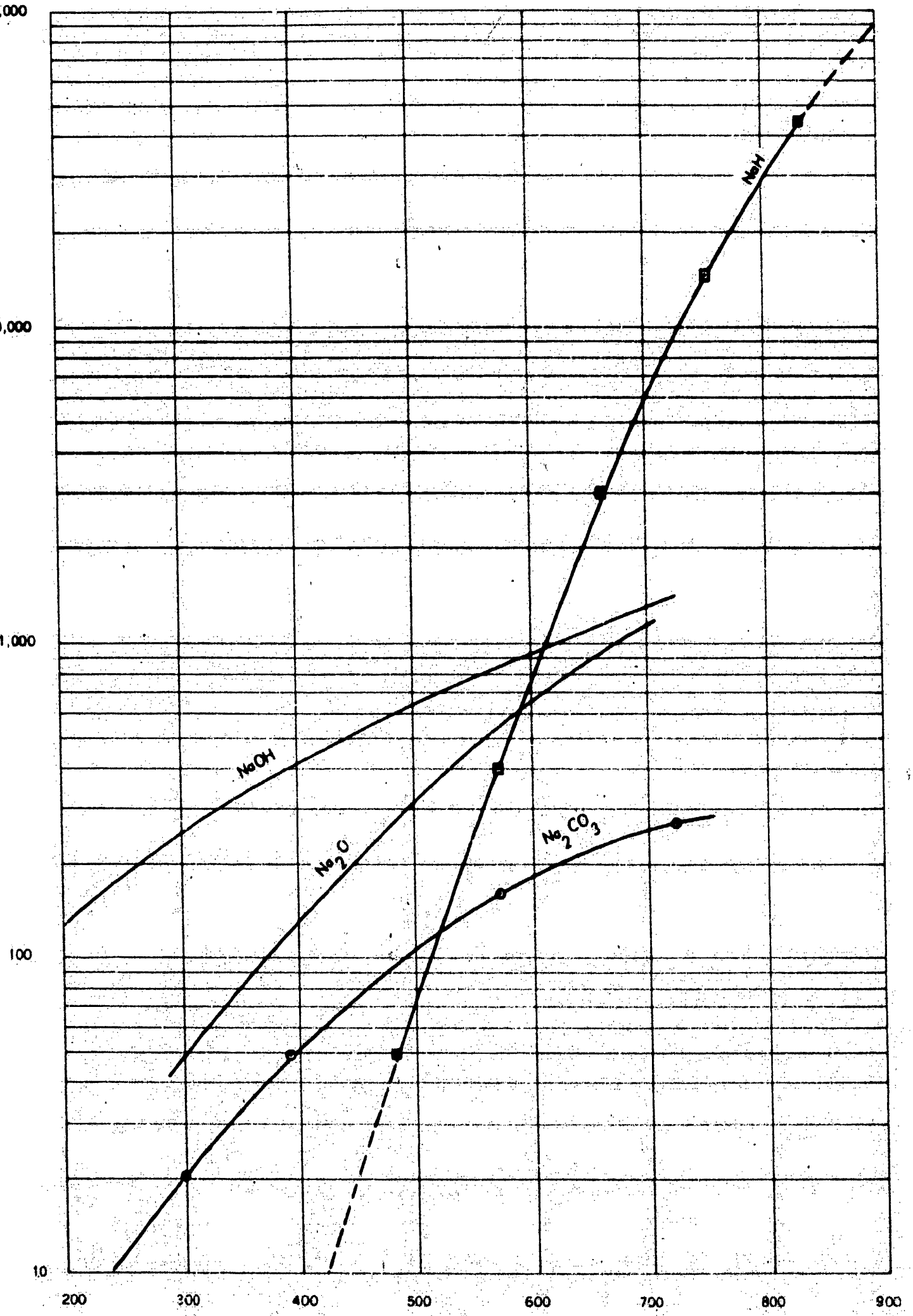


FIG. 28 SOLUBILITY OF MATERIALS IN SODIUM

TABLE X
HYDROGEN GAS INJECTION RERUN DATA*

Injections, Cumulative Cubic Feet	NaH, Cumulative ppm	Cover Gas, ppm H_2	Cumulative Correction	NaH, Net ppm	Rhometer Reading, % r	Plugging Temperature, F
0.0	--	--	--	--	--	220
0.25	42	9100	10.8	31.2	+0.03	280
0.50	84	8100	20.4	63.6	0.05	365
0.75	126	8900	31.0	95.0	0.12	388
1.00	168	6500	38.7	129.3	0.15	408
1.25	210	10700	51.5	158.5	0.16	432
1.50	252	8900	62.1	189.9	0.29	449
1.72	294	10000	73.0	220.1	0.33	471
2.00	336	7200	82.4	253.6	0.43	490
2.25	378	9300	93.4	284.6	0.47	503
2.50	420	7500	102.3	317.7	0.54	509

* The loop retention tank was removed just before the hydrogen injection rerun, resulting in a loss of 30 gallons of inventory sodium and a one cubic foot reduction in cover gas volume. Sodium inventory became 360,000 grams, and a 1000 ppm hydrogen gain in the cover gas indicated a sodium hydride loss of 1.185 ppm.

SODIUM MONOXIDE TEA BAG INJECTION

PROCEDURE

In preparation for the sodium monoxide calibration run (Figure 29), loop operations were stabilized at 770 F and the circulating sodium cold-trapped until the Rhometer signal was 0.00 % r and the plugging meter showed "No Plug" at 215 F. The cold trap was then secured. To confirm the Rhometer temperature compensator "zero-reading" set points (as seen in Figures 13, 14, and 15) over the 520 F to 770 F range, the loop was ramped down to 520 F and returned to 770 F. These chart set-points were validated at 770 F, 700 F, and 570 F, according to Table XI.

TABLE XI
VALIDATION OF RHOMETER SET POINTS

Hour, 10-14-63	Temperature, F		Calibration Chart				Rhometer Reading, % r
	Loop	Meter	Range	Decade	"C"	"R"	
1400	779	770	2	102.800	214	254	-0.01
1500	701	-	2	103.800	199	234	-0.01
1724	570	-	1	104.075	226	281	0.00
2200	774	764	2	102.800	214	254	+0.02

The calibration chart zero settings for the 570 F to 700 F range were not as precise as the foregoing check-point settings, partly because operations were not at a steady state during the ramp and partly because of the meter range shift which occurs at approximately 600 F.

Two slotted tea bags (Figure 24) with approximately 50-gram capacities were loaded with sodium monoxide for alternate injection into the loop, employing the dry-box facilities previously described. The cover gas was sampled at appropriate intervals throughout the run. Cover gas analyses were made to monitor contamination introduced inadvertently during the injection. Cover gas analyses by chromatograph were satisfactory. Ten successive injections of approximately 50 grams each brought the loop sodium contamination level to 489.8 grams of sodium monoxide and to a plugging temperature of 670 F. For each injection, the tea bag was pre-heated to 800 F in the loop injection port before submersion to avoid the

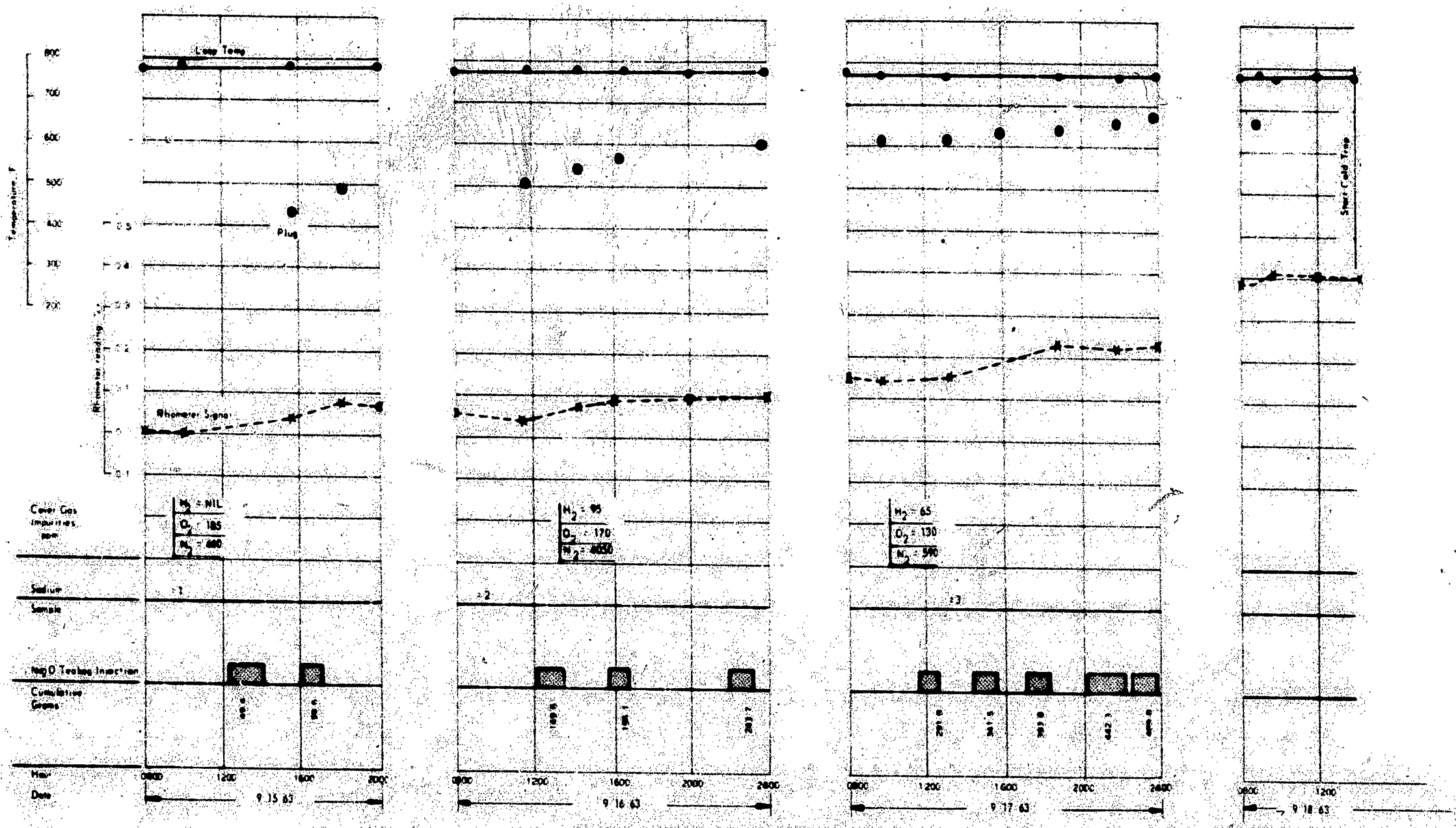


FIG. 29 LOOP LOG OF Na_2O TRACER INJECTION

"cold finger" effect. Solution rate was satisfactory, and upon withdrawal from the loop the tea bags were observed to be empty and free from residues. It was therefore unnecessary to apply any correction to the weighed increments of sodium monoxide.

DISCUSSION OF RESULTS

Previous attempts to calibrate the Rhometer for oxygen contamination are described in Reference 2. Contamination was accomplished by incremental unloading of a cold trap into the flowing sodium loop at 570 F, and it was assumed that the trap discharge was exclusively sodium monoxide. At 570 F, sodium monoxide contamination was limited to a maximum of approximately 80 ppm, reported as oxygen. The Rhometer signal gain was 1.0 % r per 100 ppm oxygen which is equivalent to 0.25 % r per 100 ppm sodium monoxide. The calibration was made against an unimproved plugging meter and against cold trap equilibrium values employing solubility data slightly at variance with the more recent values shown in Figure 28.

The present Rhometer calibration run was conducted at 770 F, to approximate commercial loop conditions and to permit higher contamination levels. Weighed increments of sodium monoxide were introduced by tea bag injection into the flowing sodium stream, Figures 25 and 26. These increments checked closely with concentrations indicated by the variable-orifice plugging meter, particularly in the high contamination range (Figure 30). This confirmed the accepted solubility values shown in Figure 28. Plugging temperatures were reproducible to $\pm$ 5 F. A comparison of the calibration curves of weighed increments versus plugging meter values is shown in Figure 31. Periodic monitoring of the cover gas indicated no spurious contamination from this source during the run.

The Rhometer response to sodium monoxide contamination was observed to be non-linear, varying with the sodium monoxide level. Below 80 ppm oxygen the signal gain was less than 0.02 % r per 100 ppm sodium monoxide and increased to 0.07% r per 100 ppm sodium monoxide over the last two injections. This non-linear response does not militate against the usefulness of the Rhometer when employed in conjunction with a plugging meter, since the change in signal gain is gradual, and can be indexed to the appropriate range of contamination as indicated by the plugging meter.

Interpretation of the disparity between the present run and previous meter calibrations necessarily involves a critical analysis of possible errors introduced by operating technique. It is very possible that the earlier runs were biased by the nature of the contaminants, which could have contained materials other than sodium monoxide. This circumstance would produce an error in the Rhometer response, further compounded by an error in plugging meter values or cold trap equilibrium temperatures

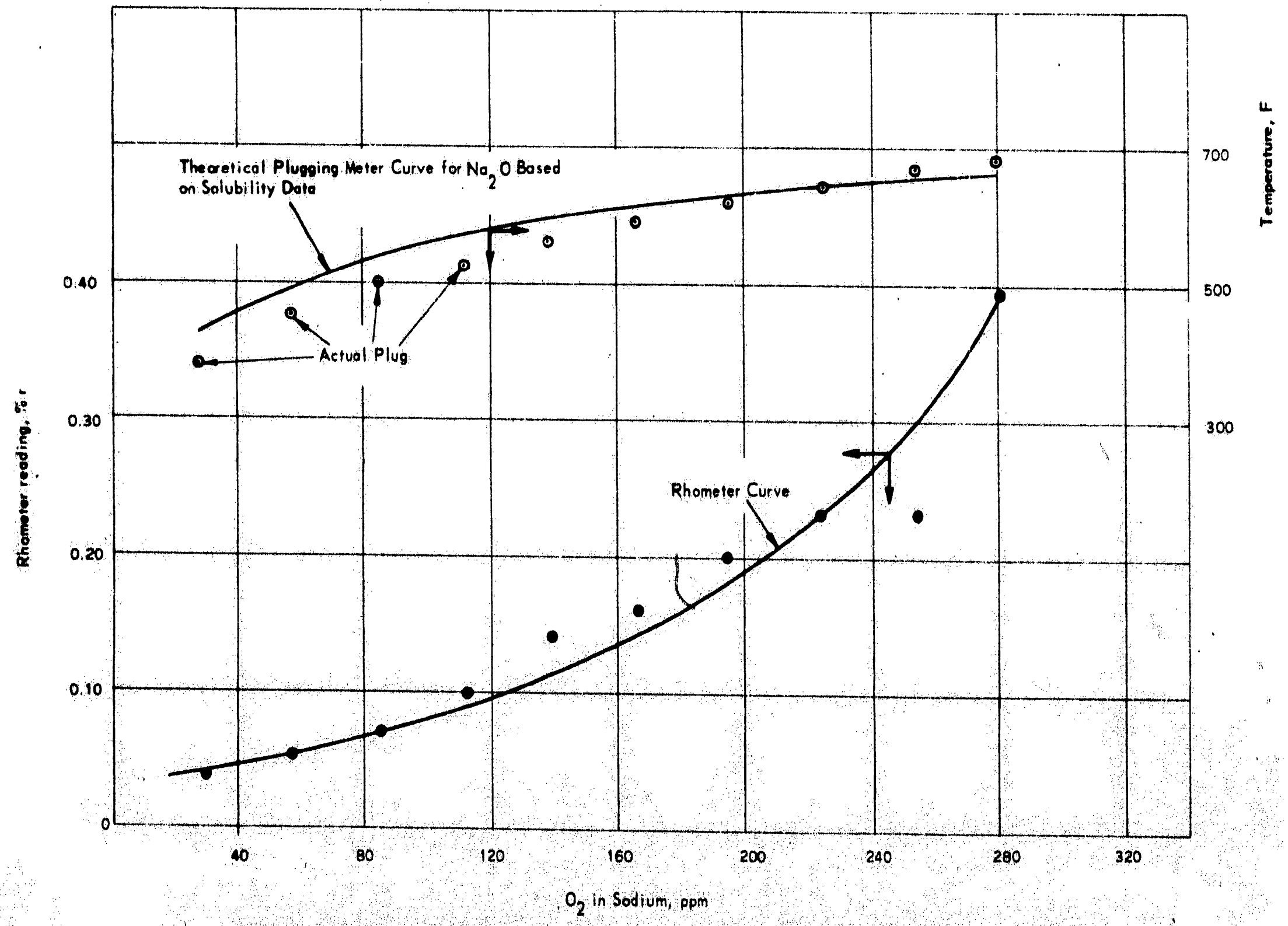


FIG. 30 RHOMETER AND VARIABLE ORIFICE PLUGGING METER CALIBRATION CURVES FOR CONTAMINATION BY TEABAG INJECTION OF NA_2O AT 770 F

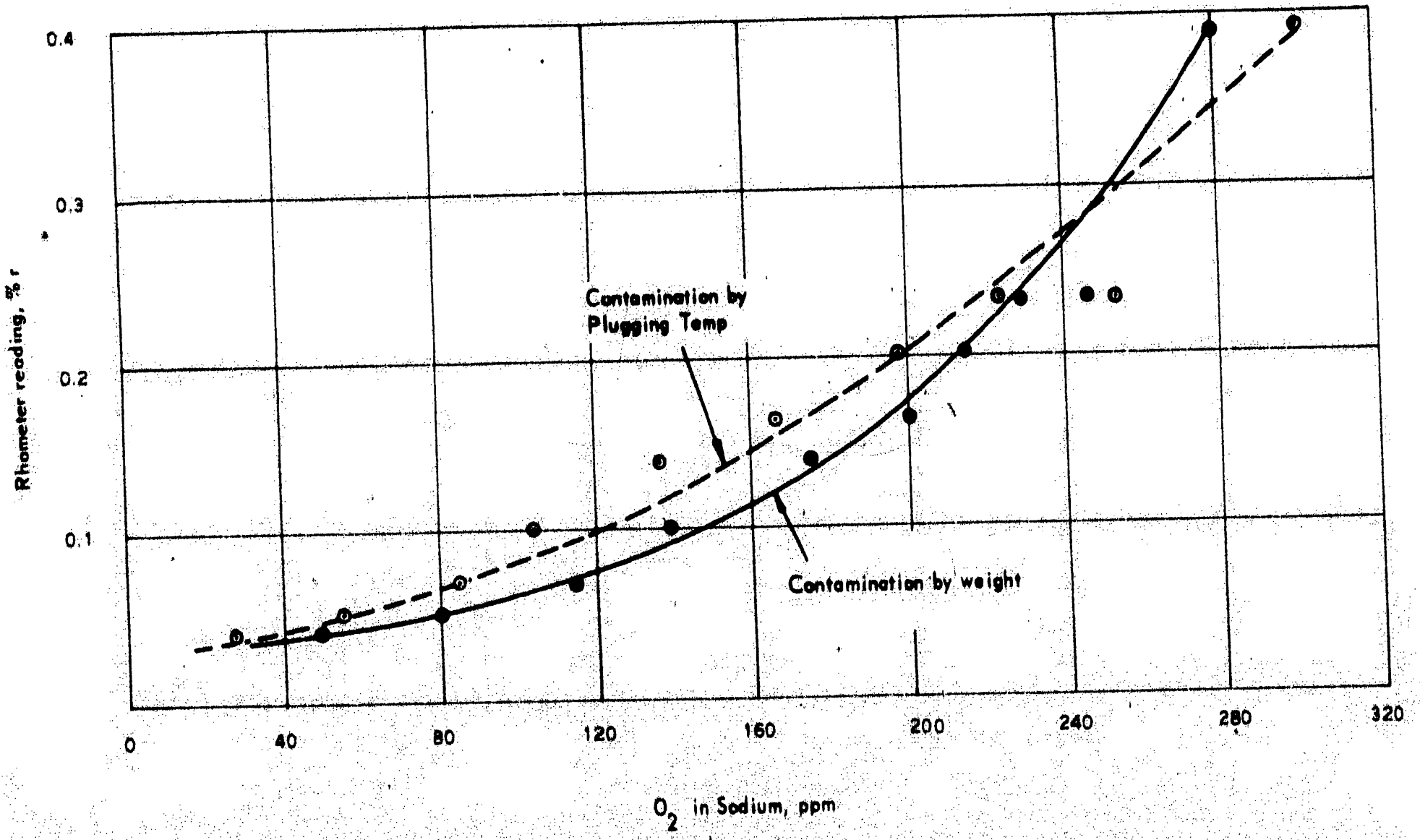


FIG. 31 RHOMETER CALIBRATION CURVE FOR CONTAMINATION BY TEA BAG INJECTION OF NA_2O AT 770 F

against which the calibration was made. It is remotely possible that the tea bag injection technique produces a partial suspension of undissolved particulates which persist in the sodium loop and do not register on the Rhometer, however, the plugging meter values would be expected to be similarly distorted in this environment, and no such distortion was observed. By the same reasoning, it is unlikely that any substantial amounts of sodium monoxide were inadvertently trapped out of the loop by cold spots. Table XII represents the tea bag injection data for the sodium monoxide run.

TABLE XII

SODIUM MONOXIDE INJECTION DATA AT 770 F

Injections, Cumulative Grams	Cumulative ppm O_2	Rhometer Reading, % r	Plugging Temperature, F
0	--	0.00	<220
49.4	28	0.04	370
99.6	56.5	0.05	450
149.6	85	0.07	500
196.1	111	0.09	530
243.7	139	0.14	560
291.8	165	0.15	600
341.5	194	0.20	610
393.8	222	0.23	627
442.3	243	--	641
489.8	277	0.39	670

WATER INJECTION

TEST DESIGN

The water injection experiment was designed with a threefold purpose: (1) to calibrate the response of the Rhometer and the plugging meter to concentrations of sodium-water reaction products; (2) to determine whether the Rhometer could be used to furnish an early warning of water leaks in a sodium steam generator facility; and (3) to apply previous meter calibrations for known single contaminants to determine whether a Rhometer and plugging meter operating in conjunction with each other could discriminate between the mixed water reaction products and other impurities. This last study suggested two corollary areas of interest: (1) a second investigation of the thermal stability of sodium hydride and sodium hydroxide in sodium loop environment; and (2) whether hydrogen injections could be used to simulate a water leak in a commercial sodium loop for the purpose of checking out leak monitor instruments.

It was assumed that an injection rate of 2 cc per hour; was a practical threshold sensitivity for simulation of leak detection. Injections were scheduled at 470 F in order to avoid the range of thermal decomposition of sodium hydroxide. It was decided to use parallel observations of the earlier hydrogen gas injection series by posting results at 6 cc intervals for comparative evaluation.

1/4-cubic foot hydrogen x 2/359 x 18/2 = 0.0125 pounds water
0.0125 x 454 = 5.7 grams water

Solubilities are limited at 470 F, and it was anticipated that saturation would be reached at a very low level of contamination. In order to build up contamination to a significant level for this study, provisions were made to continue water injections at 570 F, and at an accelerated rate. The "first order" sodium water reaction was assumed for operations at 570 F and below (Reference 6).

$$H_2O + 2\,Na \longrightarrow NaOH + NaH$$

When approach to saturation was indicated by plugging temperatures a 570 F to 770 F ramp was specified, followed by a temperature soak at 770 F to assure a steady state condition. This procedure was designed to confirm the decomposition reaction,

$$NaOH + 2\,Na \longrightarrow Na_2O + NaH$$

and to determine the rate of this reaction at 770 F. By thus disposing of the sodium hydroxide component, it was hoped to eliminate the bias which would have been introduced by continued breakdown of residuals in the loop as injections of water continued at the higher temperature.

In the 770 F injection series that followed, the "second order" sodium-water reaction was assumed.[10]

$$H_2O + 4\ Na \longrightarrow Na_2O + 2\ NaH$$

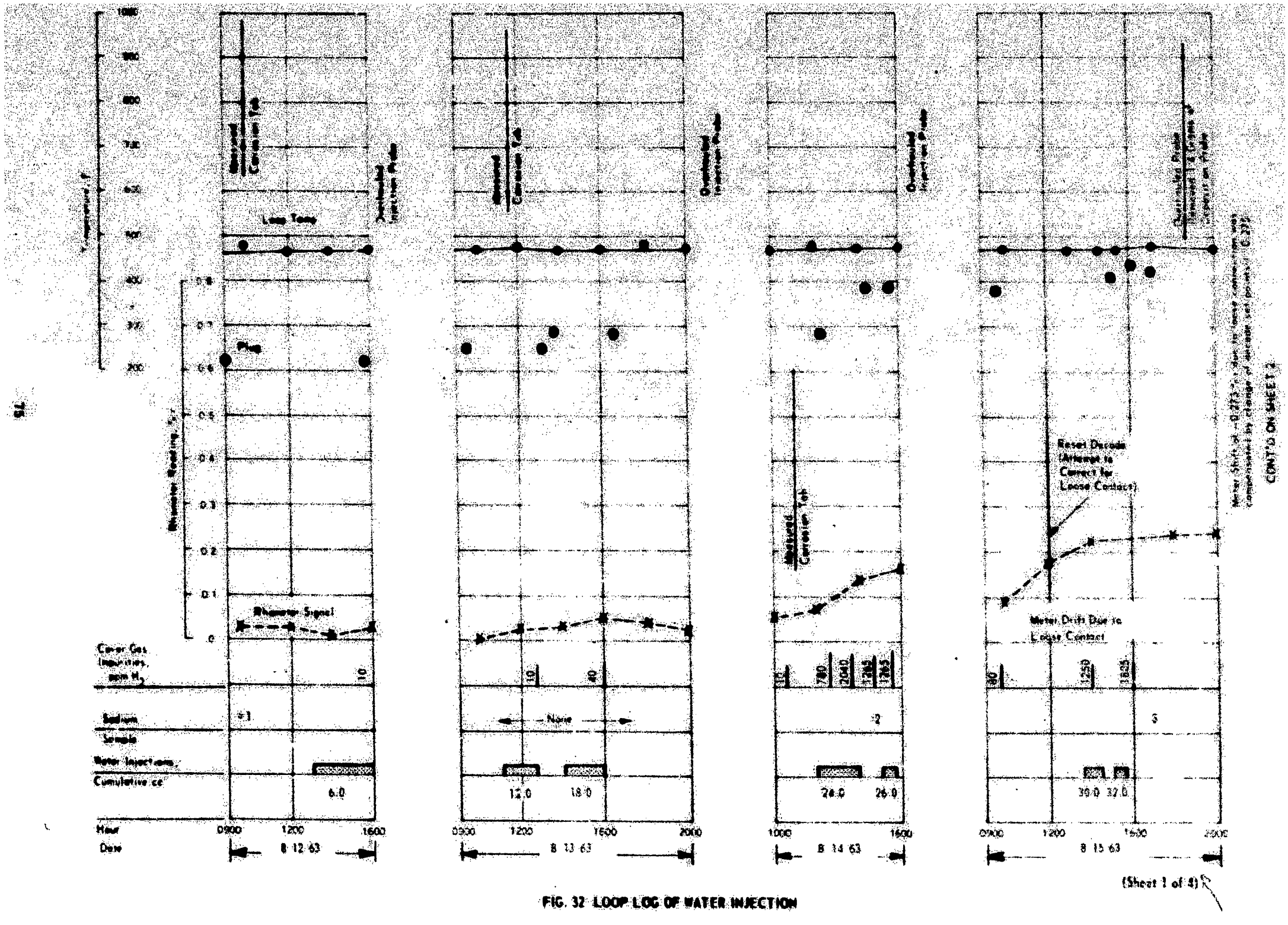
On the theory that there was a relation between molar concentrations of any impurity mix and Rhometer response, the interval of observation for injections at 770 F was changed to 4 cc to allow for the increased molar yield of the second order reaction.

A final ramp to 970 F was prescribed to study the thermal stability of sodium hydride in mixed contamination environment. This would insure the complete decomposition of sodium hydroxide and would facilitate the cold trap cleanup to follow. If the hydride was successfully dissociated at 970 F,[4,11] it was planned to plateau the cold trap cleanup at appropriate intervals, to obtain confirming data for an earlier Rhometer oxide calibration run.

PROCEDURE

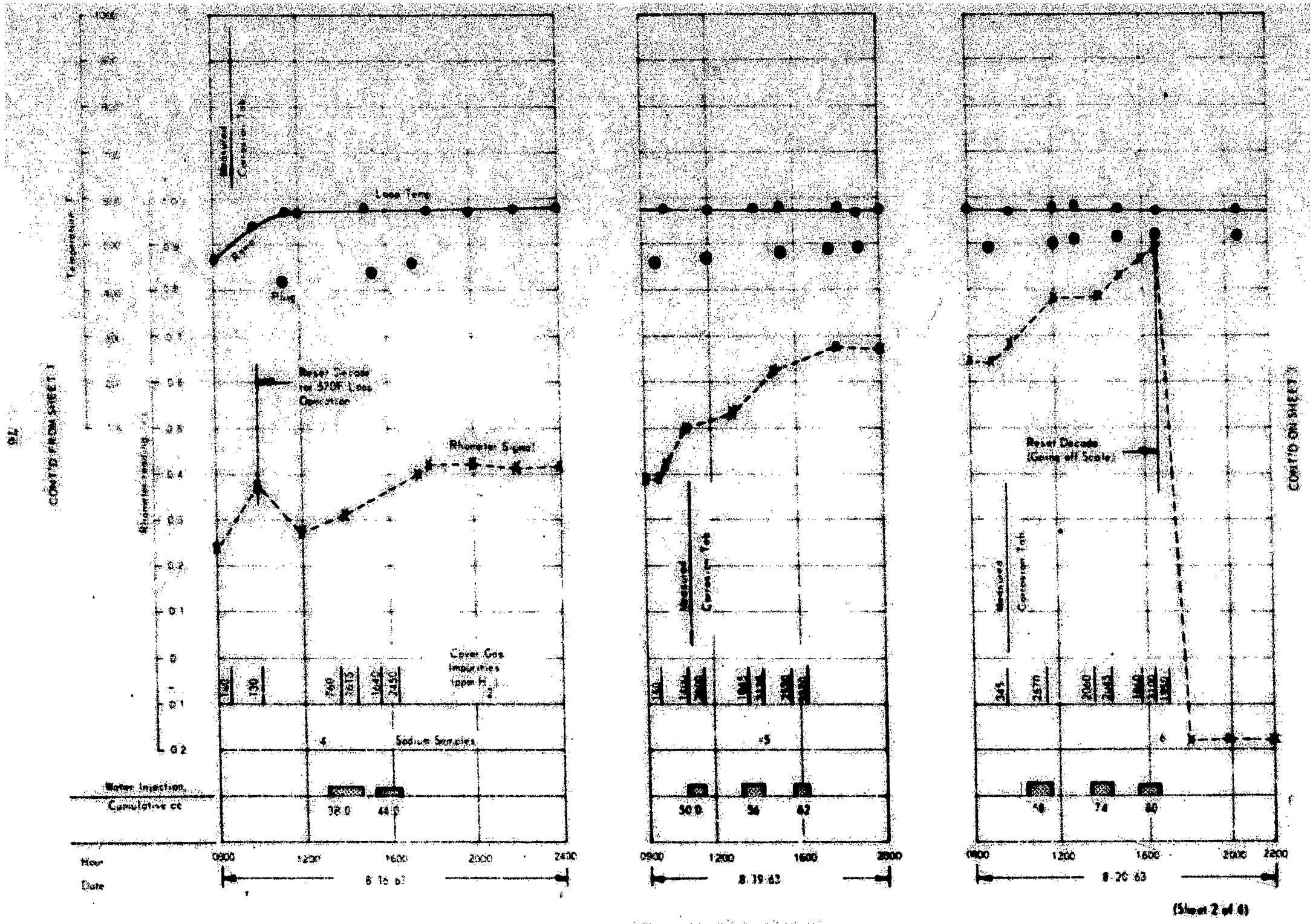
Water injections (Figure 32) were carried out in the loop with the apparatus shown in Figure 33. Argon gas was purged through the injection probe at a rate of 400 cc per minute. Over a period of one minute, this purge was accompanied by a 1/2-cc injection of water from a hypodermic. To clean the probe of residual water vapor, purging was continued for 2-to 3-minutes after discharge of the hypodermic. This operation was repeated at 15 minute intervals to simulate a specific leak rate of 2 cc per hour. After the first 6 cc increment, hypodermic charges were increased to 1 cc and the interval between injections increased.*

* Note: Before loop start up, a series of water injections were carried out with this apparatus in an outdoor pressure pot filled with liquid sodium covered with an argon blanket. No violent reaction was observed, but the deposits formed were extensive and showed clearly the danger of fouling the loop if contamination were to exceed saturation levels.



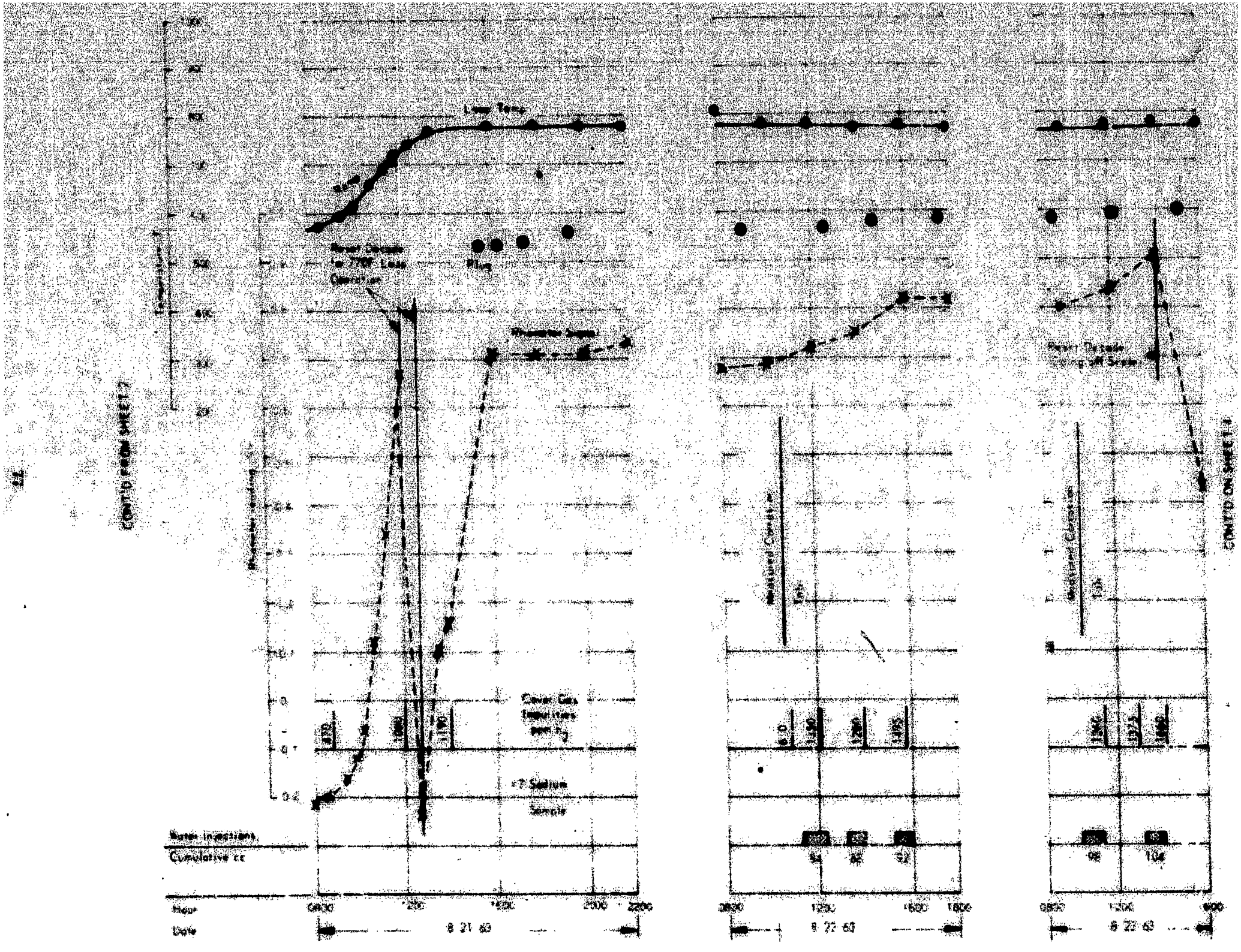
(Sheet 1 of 4)

FIG. 32 LOOP LOG OF WATER INJECTION



(Sheet 2 of 6)

FIG. 32 LOOP LOG OF WATER INJECTION



(Sheet 3 of 4)

FIG. 32 LOOP LOG OF WATER INJECTION

CONT'D FROM SHEET 3

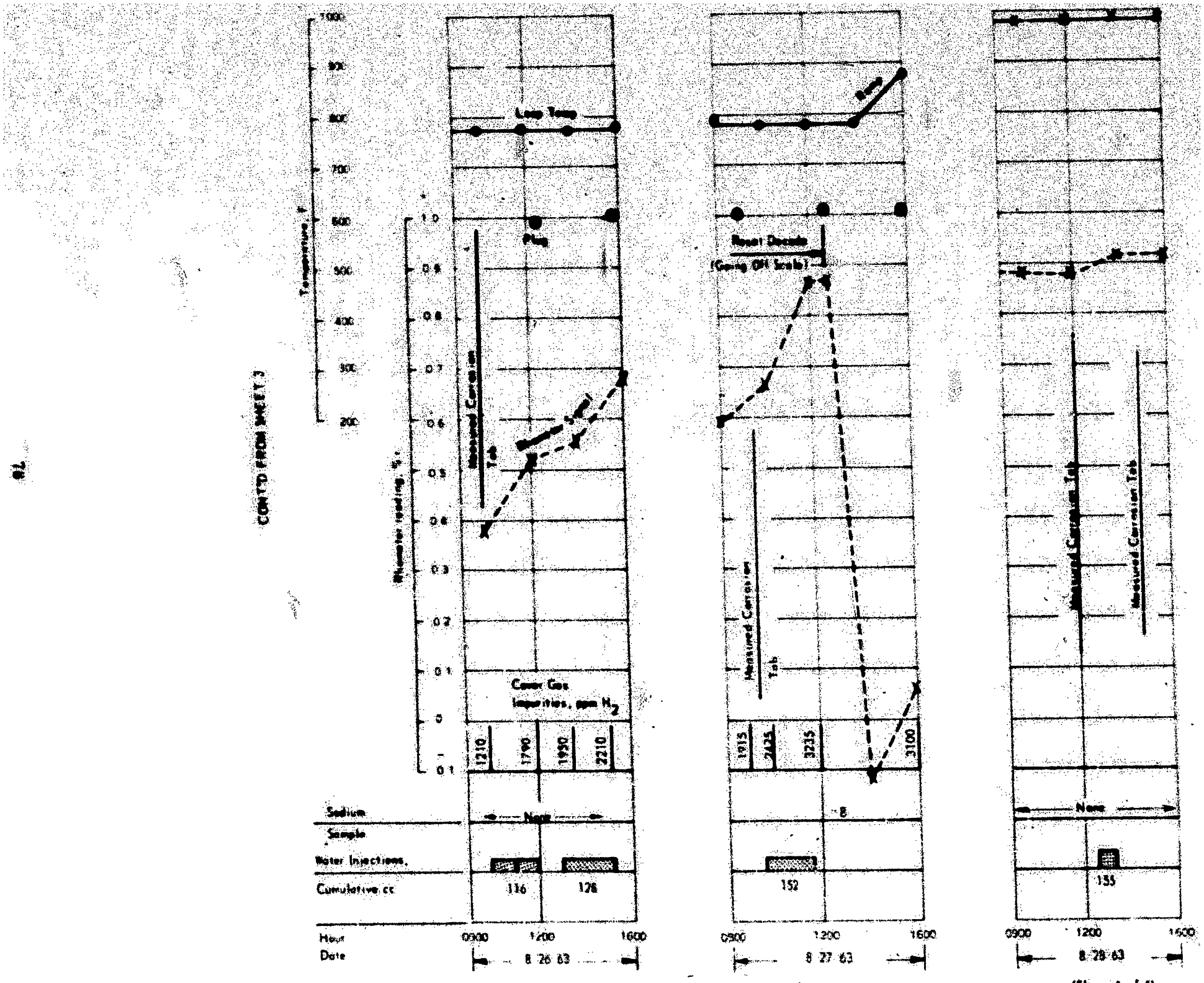


FIG. 32 LOOP LOG OF WATER INJECTION

(Sheet 4 of 4)

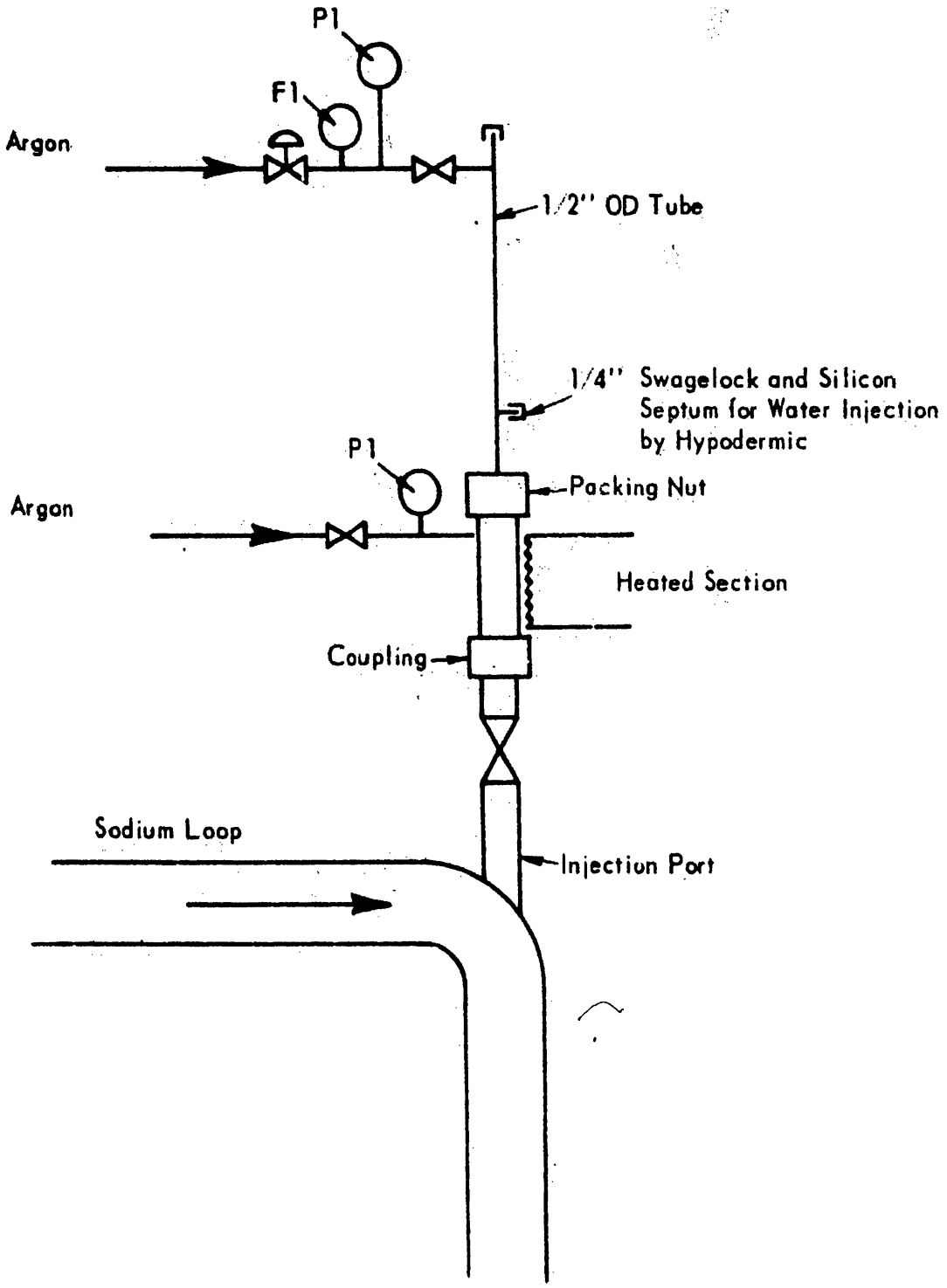


FIG. 33 WATER INJECTION APPARATUS

During the entire test run the cover gas was monitored, sodium samples were taken at appropriate intervals, and the injection probe was periodically removed and examined for deposits. A corrosion tab of 2-1/4 Cr - 1 Mo steel tubing was fixed to the injection tube outlet to observe the effects of direct exposure to a sodium-water reaction zone. This specimen was miked in the course of each examination of the probe.

Hydrogen evolution into the cover gas was not detected above the background level during the initial injection at 470 F. The average background increased to 1200 ppm as contamination increased during the 570 F run. A progression of twelve 1-cc injections in this series pushed the hydrogen contamination up to 2500 ppm. During the 770 F injection run, hydrogen increased briefly to a maximum level of 3000 ppm following a massive (24 cc) water injection. Another significant gain occurred during the 570 F to 770 F ramp, when hydrogen increased from 400 ppm to 1200 ppm in four hours. Oxygen and nitrogen were also monitored for housekeeping control, but no significant changes in level were observed throughout the experiment.

A shift of -0.275 % r occured in the Rhometer signal during the initial 470 F operations which persisted throughout the experiment. It was later determined that the shift was caused by a break in the temperature compensator lead wire.

Injections were terminated at the 320 ppm level with a small (3 cc) injection at 970 F, which was made for the sole purpose of observing meter response to water injections at high temperatures.

The 570 F to 770 F ramp was of special interest (Figure 34). As the loop temperature was increased, the plugging temperature increased and the Rhometer signal decreased. Both meter readings showed a steady state in 48 hours from the start of the ramp. Figure 34 also indicates that the Rhometer was more responsive to contamination at 570 F than at 770 F. No appreciable change in the meter readings were produced during the 470 F to 570 F ramp or the 770 F to 970 F ramp. During the final soak at 970 F, no reaction was observed in 8 days. With no evidence that the sodium hydride was dissociated, the plan to confirm sodium monoxide contamination data at various plateaus during loop cleanup was abandoned, and cold trapping was continued down to the initial loop purity level.

DISCUSSION OF RESULTS

Assumptions made regarding the sodium-water reactions were confirmed. The Rhometer response to water injections at 570 F was consistent with a signal gain of 0.6 % r per 100 ppm water (Figure 34). At 770 F, the Rhometer sensitivity was reduced to 0.45 % r. The change in sensitivity and the linear response of the meter at 770 F were

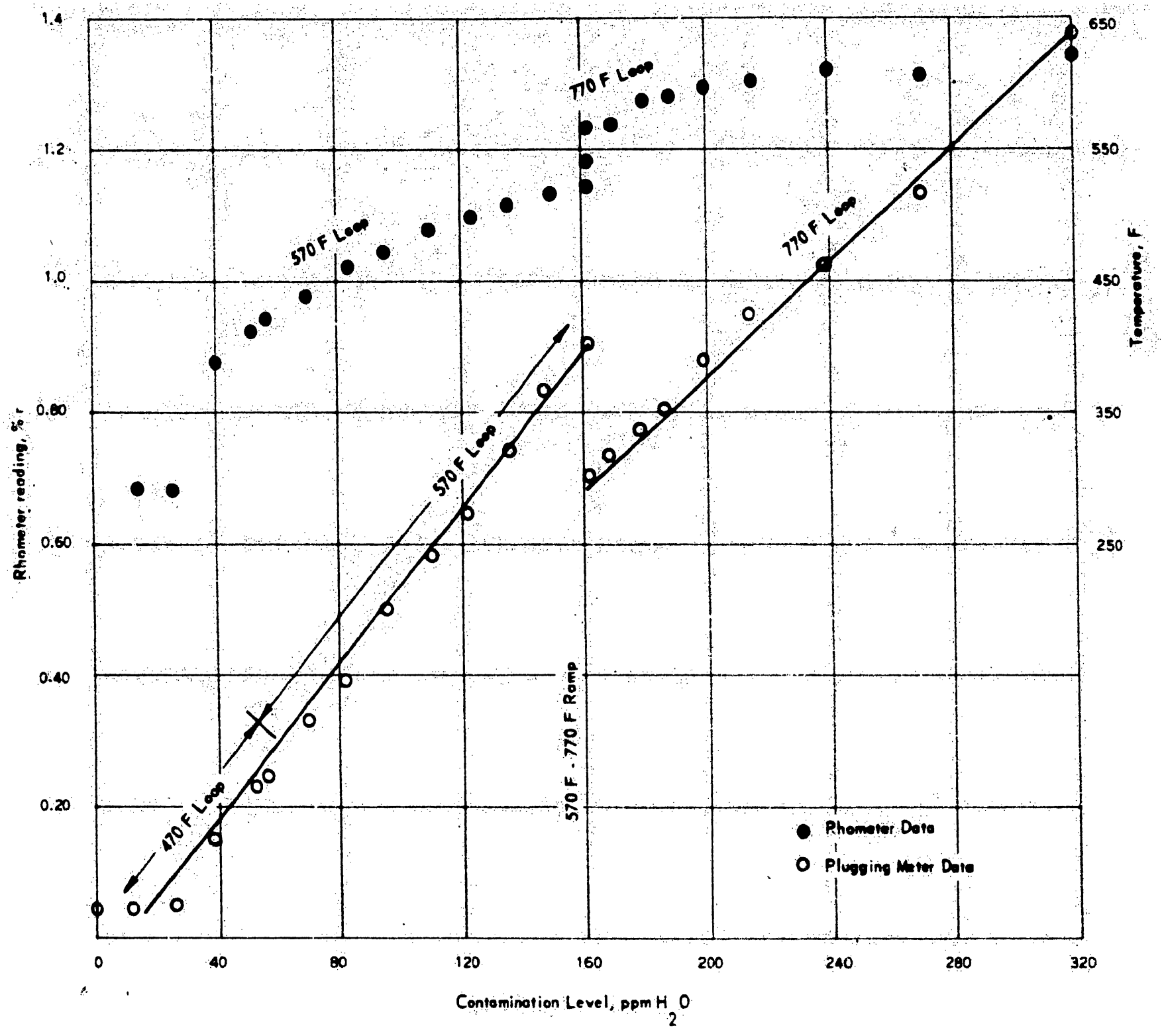


FIG. 34 RHOMETER AND PLUGGING METER CALIBRATION CURVES FROM THE WATER INJECTION TEST

evidence that no sodium hydroxide remained or was being formed at 770 F; therefore, the second order sodium-water reaction postulated for 770 F was applicable. Conversely, the first order sodium-water reaction was applicable at 570 F, as indicated by uniform sensitivity in the 470 F and 570 F operation and linear response to contamination level. Supporting evidence was the steady state reached after the 570 F to 770 F ramp which indicated that the sodium hydroxide decomposition reaction went to completion in 48 hours.*

The preconcept that Rhometer response bore some relation to the molar concentration of the contaminants present was not confirmed in the water injection series. It was demonstrated in Figure 34 that the 770 F water injection run generated less signal gain than the 570 F run although a greater molar yield is assumed for the 770 F run. This contradiction may have been caused by a thermal effect. The individual studies shown on Figure 9 indicate no correlation between resistivity and molar concentration, except as concentrations apply to a given contaminant.

An increase in the rate of water injection accelerated the release of hydrogen to the cover gas. This effect was probably magnified by the system geometry or contact time of the test loop, and would be greatly reduced by a longer path from the point of injection to the point of gas release. Assuming that hydrogen evolution is a genuine system reaction to accelerated water injection, an instrument such as the continuous hydrogen monitor would be most effective in detecting water leaks in the early stages. Unfortunately, a temperature ramp might produce the same signal from this instrument.

Threshold response of the plugging meter to water injection was reported at 6 cc (13 ppm water) and the Rhometer signal was first evident at 12 cc (26 ppm water). The response of both meters was consistent with contamination levels (Figure 34). Plugging temperatures could not be related to a cumulative effect of the various contaminants present, however, such a summation could be postulated for the Rhometer signal, for which the signal gain from water contamination was approximately equal to the total effect of the sodium-water reaction products as predicted by Table I. The plugging temperatures plotted in both the 570 F run and the 770 F run (Figure 34)

* Note: In a later experiment, injections of pure sodium hydroxide by tea bag appeared to decompose at 570 F. This suggests that the decomposition of sodium hydroxide is supressed by the presence of the decomposition products present in the water injection experiment. Minor irregularity may be due to the mutual solubility of these contaminants in each other.

approximate the expected plugging temperatures for sodium monoxide alone. It may be that the plating action of the plugging meter is selective (analogous to a crystallization separation process), and favors the least soluble component present at plugging meter temperatures.

The 570 F to 770 F ramp was of special interest. Theoretically, plugging temperatures should be increased by the decomposition of the highly soluble sodium hydroxide; and they did increase. Assuming the same decomposition reaction, the Rhometer signal would decrease as shown in Table I. The Rhometer signal actually dropped 0.2 % r. From observation of the cover gas, no great loss of hydrogen was sustained to explain this signal loss. The same decrease in Rhometer signal was observed to a lesser degree during the sodium hydroxide injection run following a 470 F to 570 F ramp. Therefore, it was assumed that the observations indicate a genuine mechanism of the sodium-water system. To understand this system mechanism more completely, it would be appropriate to consider the effects produced by mutual solubility of sodium-water reaction products.[4] It should also be noted in this connection that all of the solubility curves for sodium-water reaction products in sodium cross in the 570 F to 770 F range (Figure 28).

Attack on the corrosion tab fixed to the water injection probe was fairly uniform, with no particular radial or longitudinal bias. No unusually severe service condition was noted. In appearance the tab became granular, and after some 300 minutes of direct exposure to a sodium-water reaction zone had lost 1.5 mils of wall thickness. A thermocouple attached to the tab indicated no temperature rise during the entire water injection run, and it was concluded that the corrosion on the tab is representative of the effect of a slow leak over any similar exposure period.

Water injection data are shown in Table XIII.

TABLE XIII
WATER INJECTION DATA

Injections, Cumulative Grams	Cumulative ppm	Rhometer Reading, % r	Plugging Temperature, F	Loop Temperature, F
0	--	0.00	--	470
6	13.1	0.04	288	470
12	26.2	0.05	--	470
18	39.3	0.143	385	470
24	52.4	0.23	410	470
26	56.8	0.24	419	470
32	70	0.33	439	570
38	83	0.39	457	570
44	96	0.50	469	570
50	110	0.58	485	570
56	123	0.64	495	570
62	136	0.74	504	570
68	149	0.83	511	570
74	162	0.90	517	570
74	162	0.68	560	770
78	170	0.73	564	770
82	179	0.77	580	770
86	188	0.80	585	770
92	200	0.87	595	770
98	216	0.94	600	770
110	240	1.02	605	770
122	270	1.12	--	770
146	320	1.37	622	770

SODIUM HYDROXIDE TEA BAG INJECTIONS

TEST DESIGN

A series of sodium hydroxide injections were planned to better understand the sodium-water reactions that were discussed in an earlier loop experiment involving water injections. The second purpose of the sodium hydroxide injection run was to demonstrate whether this decomposition reaction

$$NaOH + 2\,Na \longrightarrow Na_2O + NaH$$

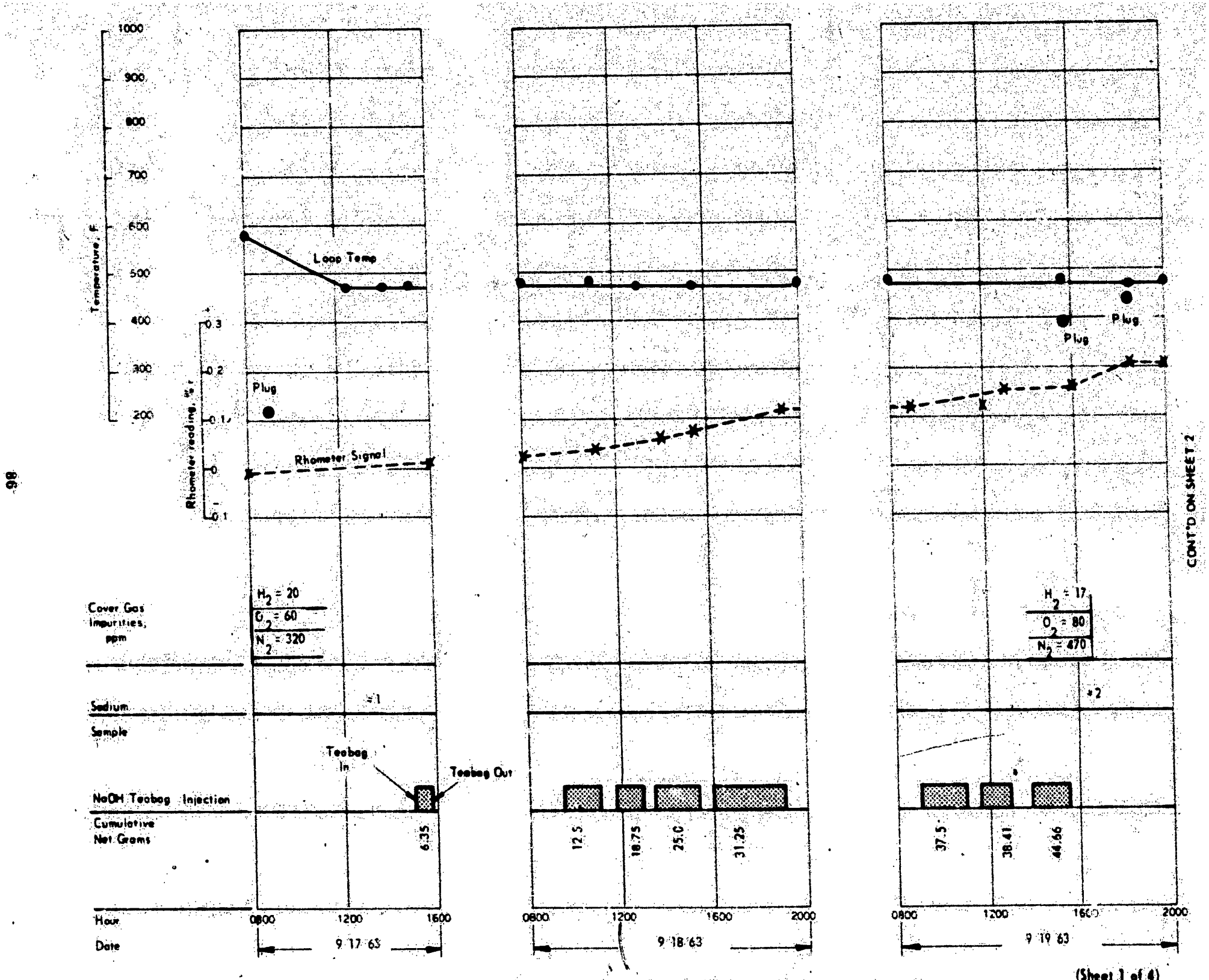
could be controlled to facilitate loop cleanup. The high solubility of sodium hydroxide, Figure 28, imposes a limit on cold trapping, whereas the decomposition reaction products are relatively insoluble at cold trapping temperatures and consequently easy to crystallize out.

A low plugging temperature is generally accepted as an indication of low contamination level. The high solubility of sodium hydroxide results in low plugging temperatures also, and can thus be misleading. The rhometer signal response to sodium hydroxide contamination is relatively high. It was therefore anticipated that sodium hydroxide contamination could be identified by this difference in meter responses.

From the water-injection experience and various statements made in the literature,[6] it was expected that sodium hydroxide would become unstable in sodium solution at its melting point (600 F). A loop temperature of 570 F was considered too near the melting point of sodium hydroxide for stable operation; therefore, 470 F was selected as the temperature for the initial tea bag injections.

PROCEDURE

The sodium hydroxide tea bag injection run employed the dry-box facilities developed for the earlier sodium hydride tea bag injection and the injection hardware illustrated in Figures 25 and 26. Injection operations were conventional, as shown on the loop log, Figure 35. Cover gas inspection was provided for. The cover gas monitoring operations using the F&M 500 chromatograph were satisfactory, but failed to indicate any significant change in impurity level during the injection run or during the subsequent



(Sheet 1 of 4)

FIG. 35 LOOP LOG OF NaOH TEA BAG INJECTION AND THERMAL DISSOCIATION

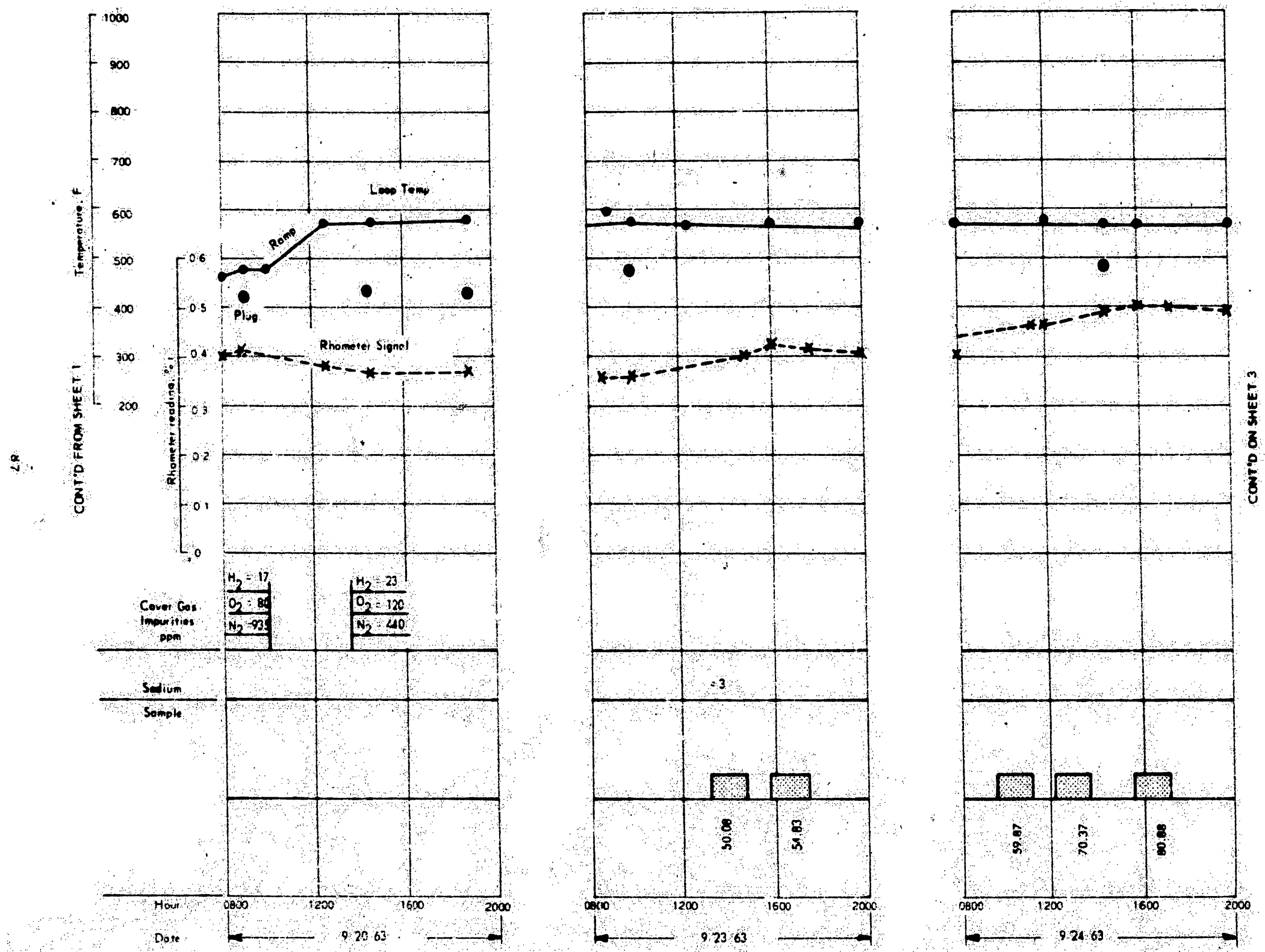
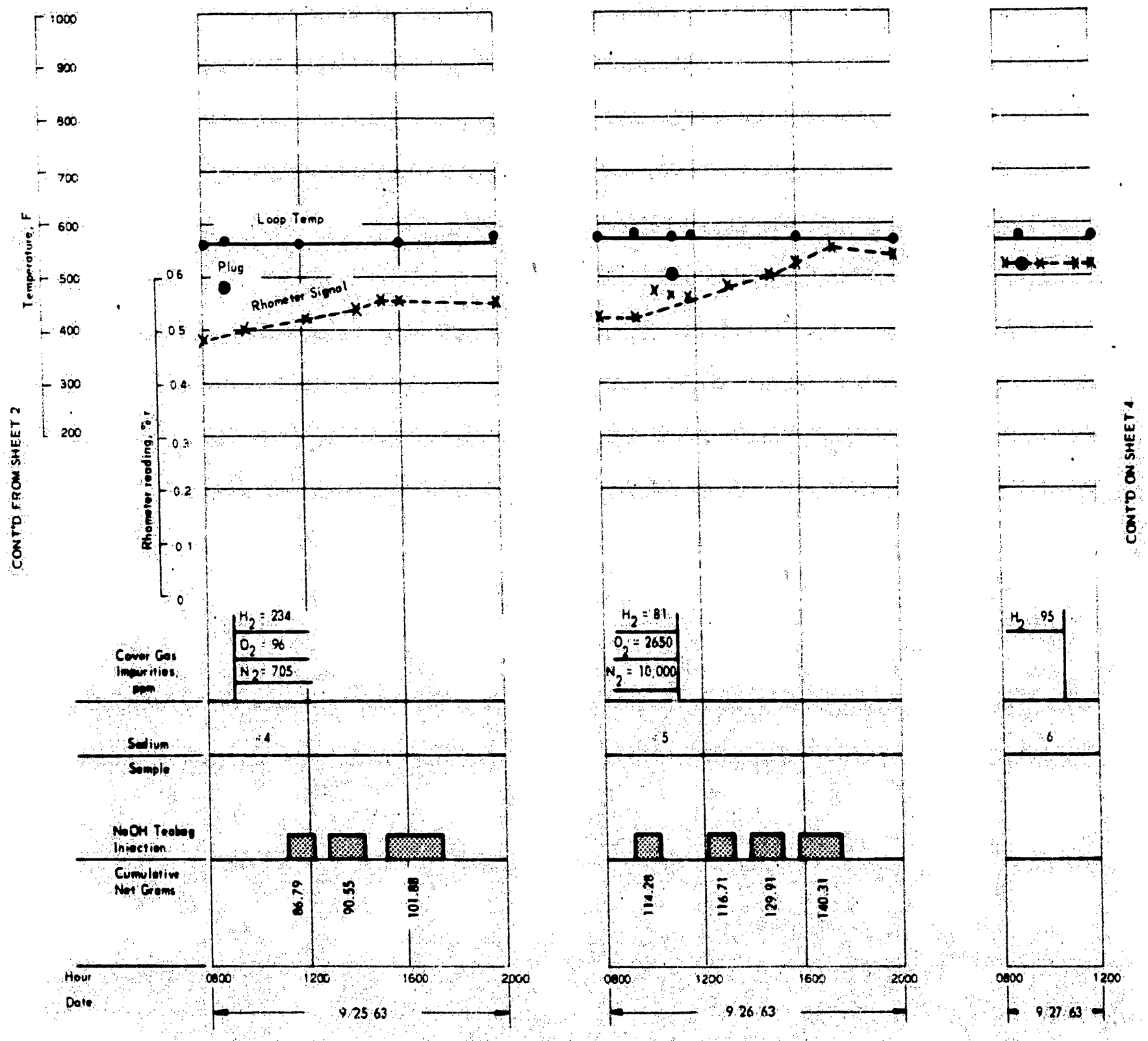


FIG. 35 LOOP LOG OF NaOH TEA BAG INJECTION AND THERMAL DISSOCIATION

(Sheet 2 of 4)

CONT'D FROM SHEET 2



CONT'D ON SHEET 4

FIG. 35 LOOP LOG OF NaOH TEA BAG INJECTION AND THERMAL DISSOCIATION

CONT'D FROM SHEET 3

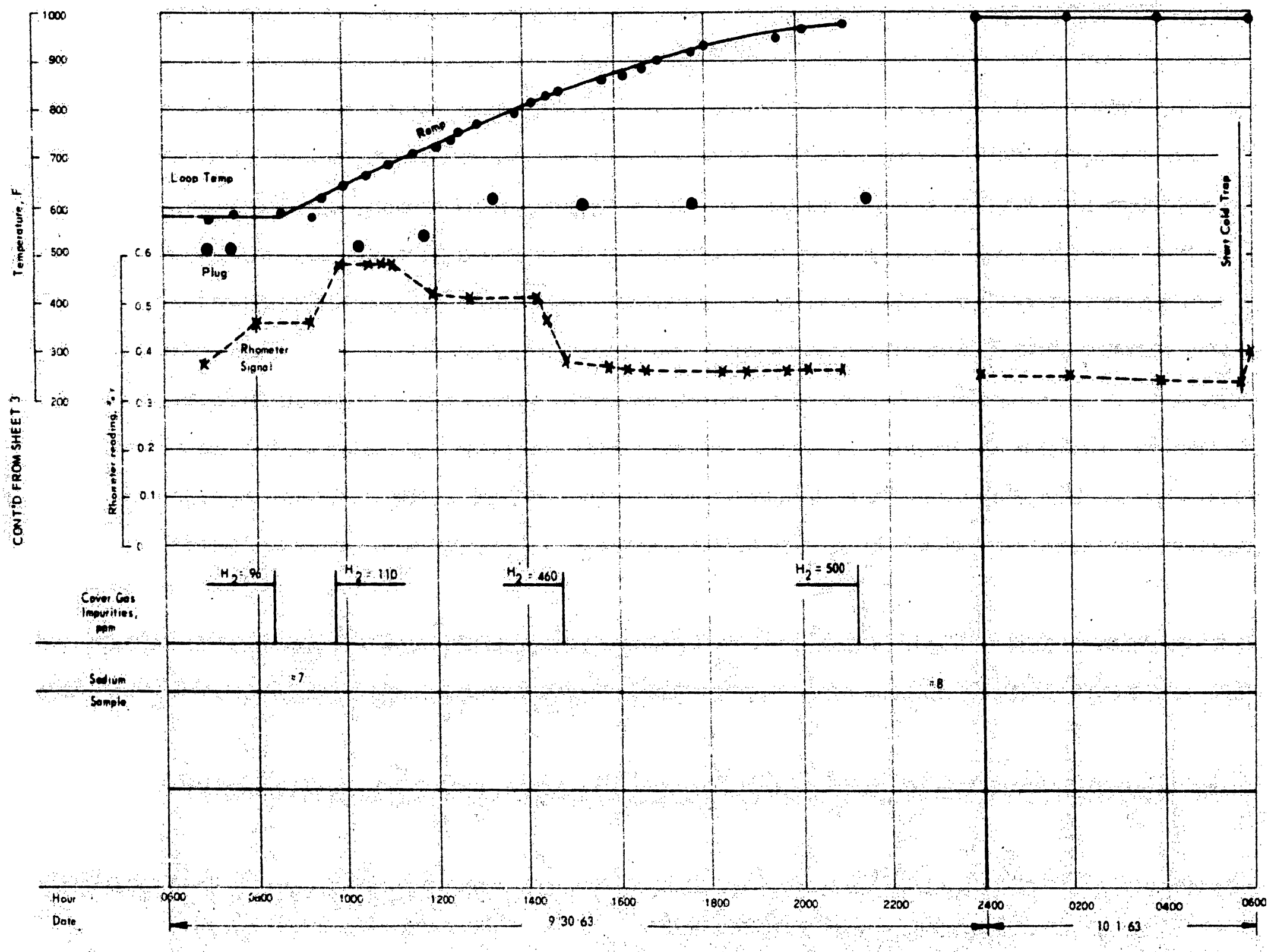


FIG. 35 LOOP LOG OF NaOH TEA BAG INJECTION AND THERMAL DISSOCIATION

(Sheet 4 of 4)

loop cleanup. As before, the tea bags were preheated to avoid the cold finger effect noted in the earlier sodium hydride run, but special precautions were adopted in order to remain below the melting point of sodium hydroxide. Provision was made to backweigh tea bags in the event that complete solution was not obtained, and 10 of the 20 weighed increments charged to the loop were corrected for residual deposits in the tea bags.

After 8 injections totaling 98 ppm sodium hydroxide, the loop was ramped to 570 F because of difficulty experienced in attaining further solution. Contamination was then carried to 308 ppm sodium hydroxide, with no apparent loss of impurity to the cover gas. The consistent pattern of responses from the Rhometer and the plugging meter are shown in Figures 36 and 37. The overall signal gain of the Rhometer was approximately +0.15 % r per 100 ppm sodium hydroxide. The actual plugging temperatures were much higher than expected from accepted solubility data, but they did conform to the theoretical curves for decomposition products as indicated on Figure 36. It was also observed that following the 470 F to 570 F ramp, the Rhometer signal decreased and the plugging temperature increased, paralleling the pattern established by the 570 F to 770 F ramp executed during the water injection experiment.

Loop cleanup by cold trapping was preceded by a ramp to 970 F, closely monitored at 15 F intervals. The purpose of this ramp, as stated, was to complete the decomposition of the sodium hydroxide to facilitate cold trapping. Close monitoring was specified to detect any critical temperature or breakpoint in the process of the hydroxide decomposition reaction or of the dissociation of reactant hydride. No critical point was evidenced.

Cold trapping followed the 970 F ramp, and the loop was returned to a 213 F plugging temperature and a +0.02 % r Rhometer signal after 2 days of trapping.

DISCUSSION OF RESULTS

The fact that no significant reaction* was detected during the 570 F to 970 F ramp can be interpreted in two ways: (1) the sodium hydroxide remained stable during the run, or (2) the sodium hydroxide was already decomposed when the ramp was initiated. The behavior of

* The increase in hydrogen in the cover gas from 110 ppm to 500 ppm during the 970 F ramp is not considered significant.

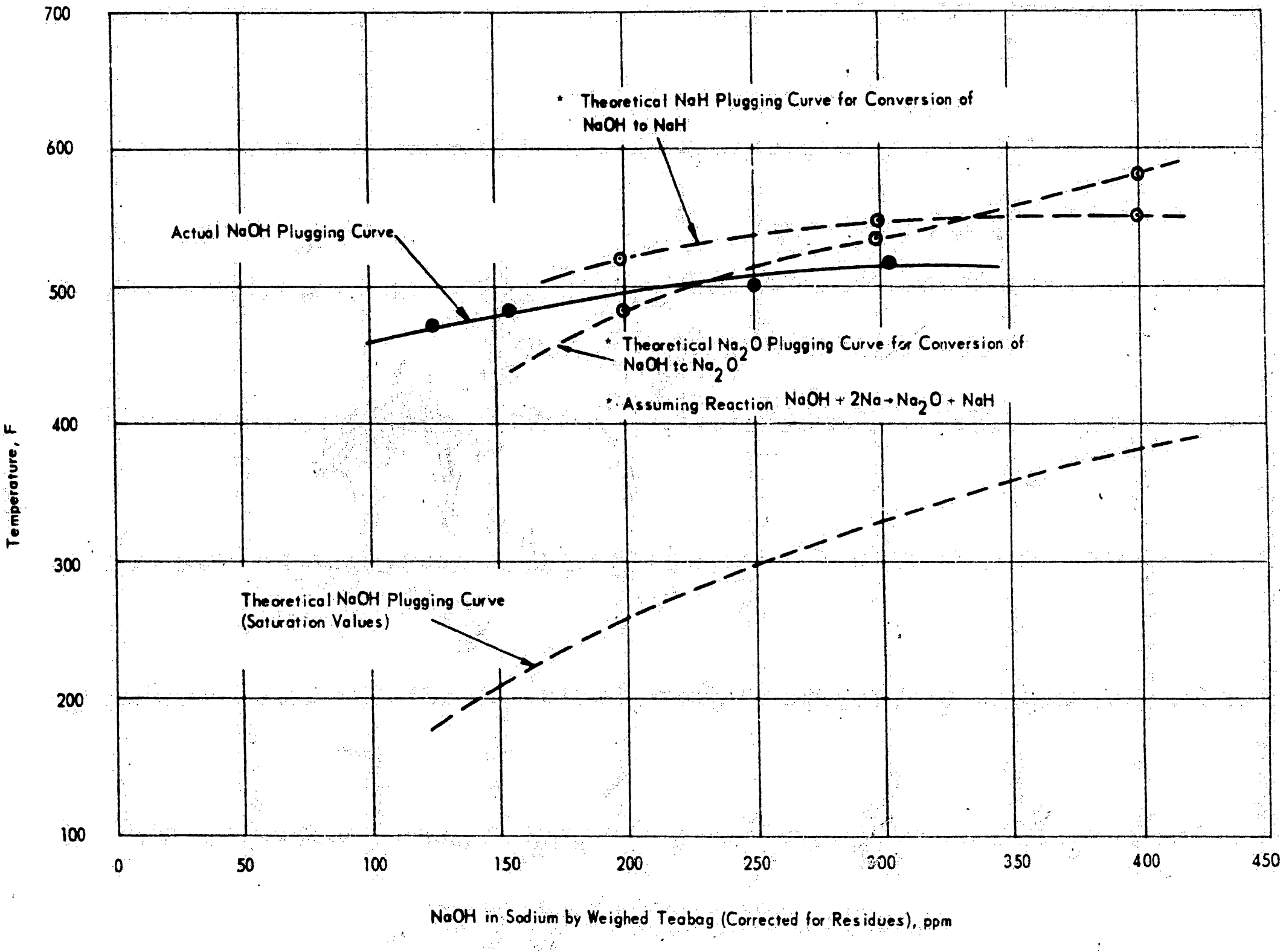


FIG. 36 PLUGGING METER CALIBRATION CURVE FOR NaOH CONTAMINATION BY TEA BAG

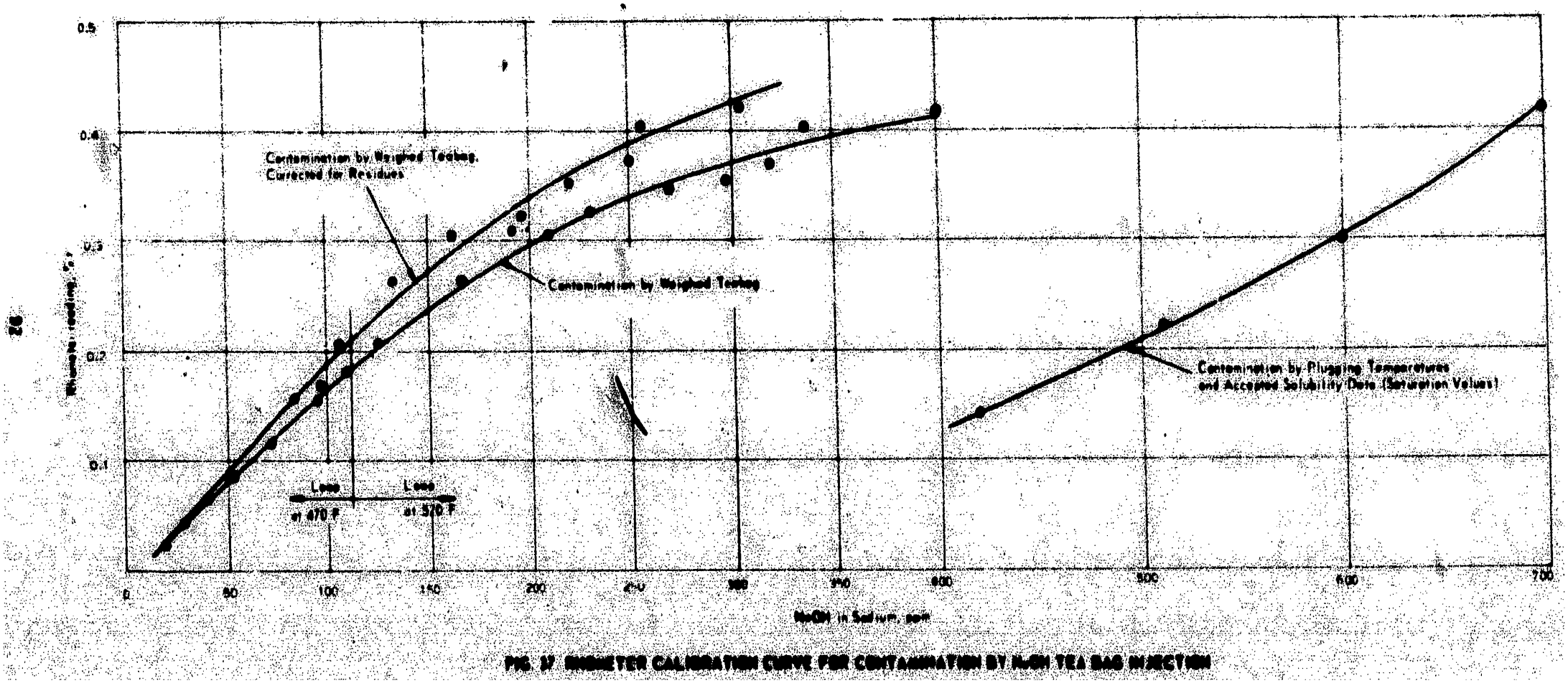


FIG. 27 RHEOMETER CALIBRATION CURVE FOR CONTAMINATION BY HIGH TEA BAG INJECTION

the Rhometer signal and plugging temperature during and after the 470 F to 570 F ramp supported the conclusion that the sodium hydroxide was already decomposed. Also in evidence is the fact that subsequent cold trapping brought the Rhometer signal down to zero. It has been stated previously that the Rhometer does indicate small concentrations of sodium hydroxide, although the plugging meter does not. There is ample evidence that the decomposition products of sodium hydroxide are stable in loop environment at 970 F, and there is much evidence in the literature that sodium hydroxide is not thermally stable. This probably accounts for the higher Rhometer signal index gain for sodium hydroxide during the 470 F loop operation, and less signal response in the 570 F run,

The data for the sodium hydroxide tea bag injections are shown in Table XIV.

TABLE XIV
SODIUM HYDROXIDE INJECTION DATA*

Injections, Cumulative Grams	Cumulative ppm	Rhometer Reading, % r	Plugging Temperature, F	Loop Temperature F
0.00	--	0.00	--	470
6.35	14	0.01	--	470
12.50	27.5	0.04	--	470
18.75	41	0.06	--	470
25.00	55	0.08	--	470
31.25	69	0.11	--	470
37.50	82.5	0.125	--	470
38.41	85	0.15	--	470
44.66	98	0.16	--	470
50.08	112	0.20	418	470
54.83	121	0.22	472	570
59.87	132	0.26	--	570
70.37	155	0.30	--	570
80.88	177	0.31	486	570
86.79	190	0.32	--	570
90.55	200	0.34	--	570
101.88	225	0.35	--	570
114.28	250	0.37	500	570
116.71	255	0.38	--	570
129.91	285	0.42	--	570
140.31	310	0.45	518	570

* Corrected for Residues

SODIUM CARBONATE TEA BAG INJECTIONS

PROCEDURE

Injections of sodium carbonate by tea bag followed established procedure, with preliminary loop cleanup and periodic inspection of cover gas during the run. The sodium carbonate loop log is shown in Figure 38. The loop was operated at 770 F, and injection in 10 to 15 gram increments was accomplished by the mechanisms shown in Figures 24 and 25.

Although the tea bags were systematically preheated before submersion, considerable difficulty was experienced in obtaining complete solution of the charge, and some 16.5 grams of residues were reported. Tea bags were back-weighed to correct for residues; however, a significant error must be assumed, since in addition to residual carbonate the deposits in the tea bag also contained sodium and sodium compounds resulting from reaction with the atmosphere after withdrawal from the loop.

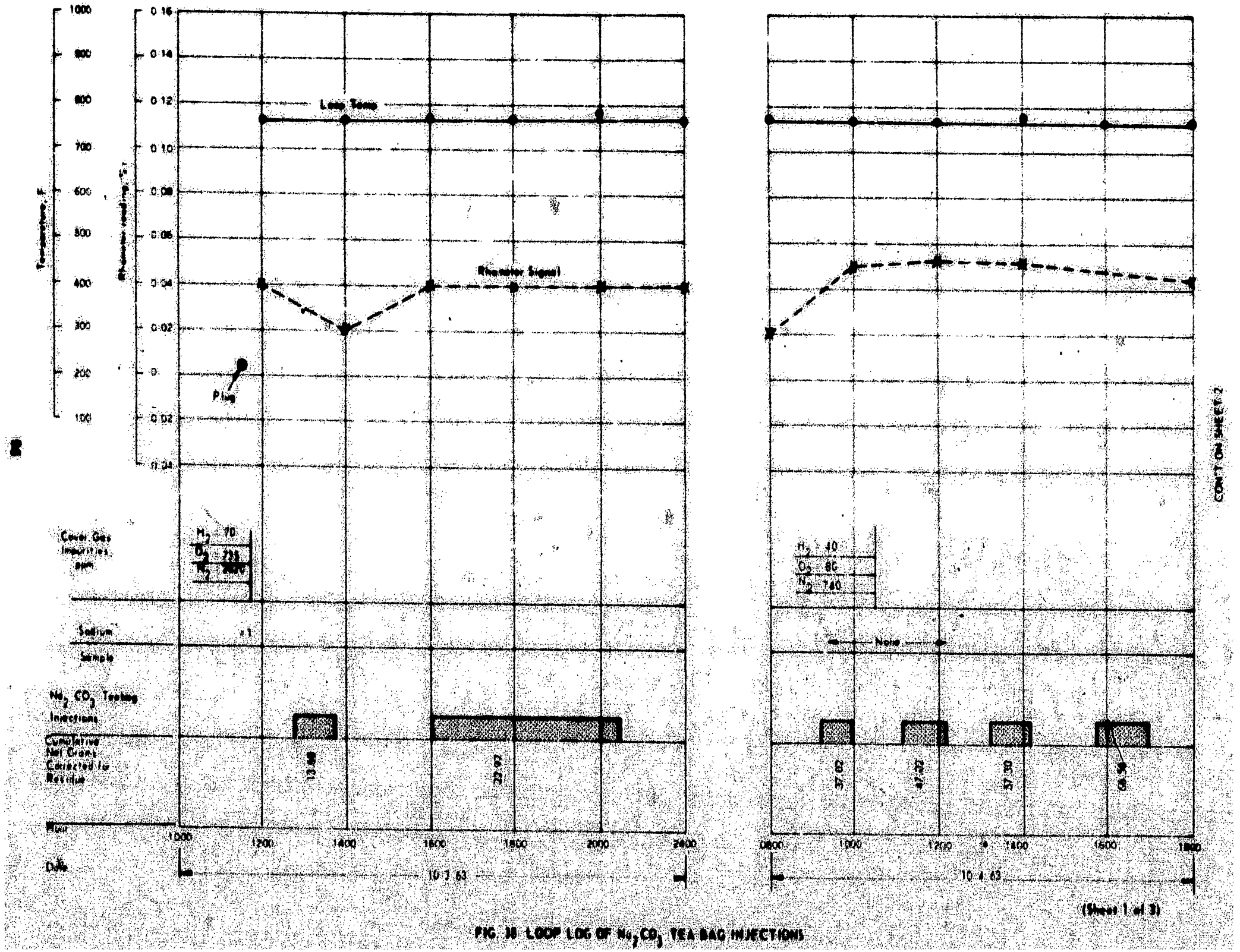
It was anticipated from published solubility data, Figure 28, that saturation would be approached at 270 ppm sodium carbonate; however, since plugging meter temperatures were consistently below expected values the injections were continued to the 425-ppm level. Following the contamination run, the loop was cold trapped for 24 hours and both the Rhometer and plugging meter returned to their original signal values.

It should be noted that at contamination levels below 100 ppm, plugging meter temperatures were not sharply defined. The flow pattern through the meter showed a constant decrease throughout the 5 F/minute temperature ramp, with no sharp break during the plugging run.

DISCUSSION OF RESULTS

Although the Rhometer showed a trend toward signal gain during the sodium carbonate injection, results were widely scattered and the signal relatively weak and erratic, as seen in Figure 39. A total gain of 0.08% r was indicated at the 425 ppm sodium carbonate level.

The pattern of the variable-orifice plugging meter showed less scatter, but the signal gain was not much bettern than that of the Rhometer, and no plugging temperature could be determined below the 100 ppm level. Plugging temperatures were consistently below expected values based on solubility data (Figure 28). No significant change in cover gas contamination was observed during the run, and it was concluded that no loss of sodium carbonate was sustained by thermal dissociation.



(Sheet 1 of 3)

FIG. 38 LOOP LOG OF Na_2CO_3 TEA BAG INJECTIONS

CONT'D FROM SHEET 1

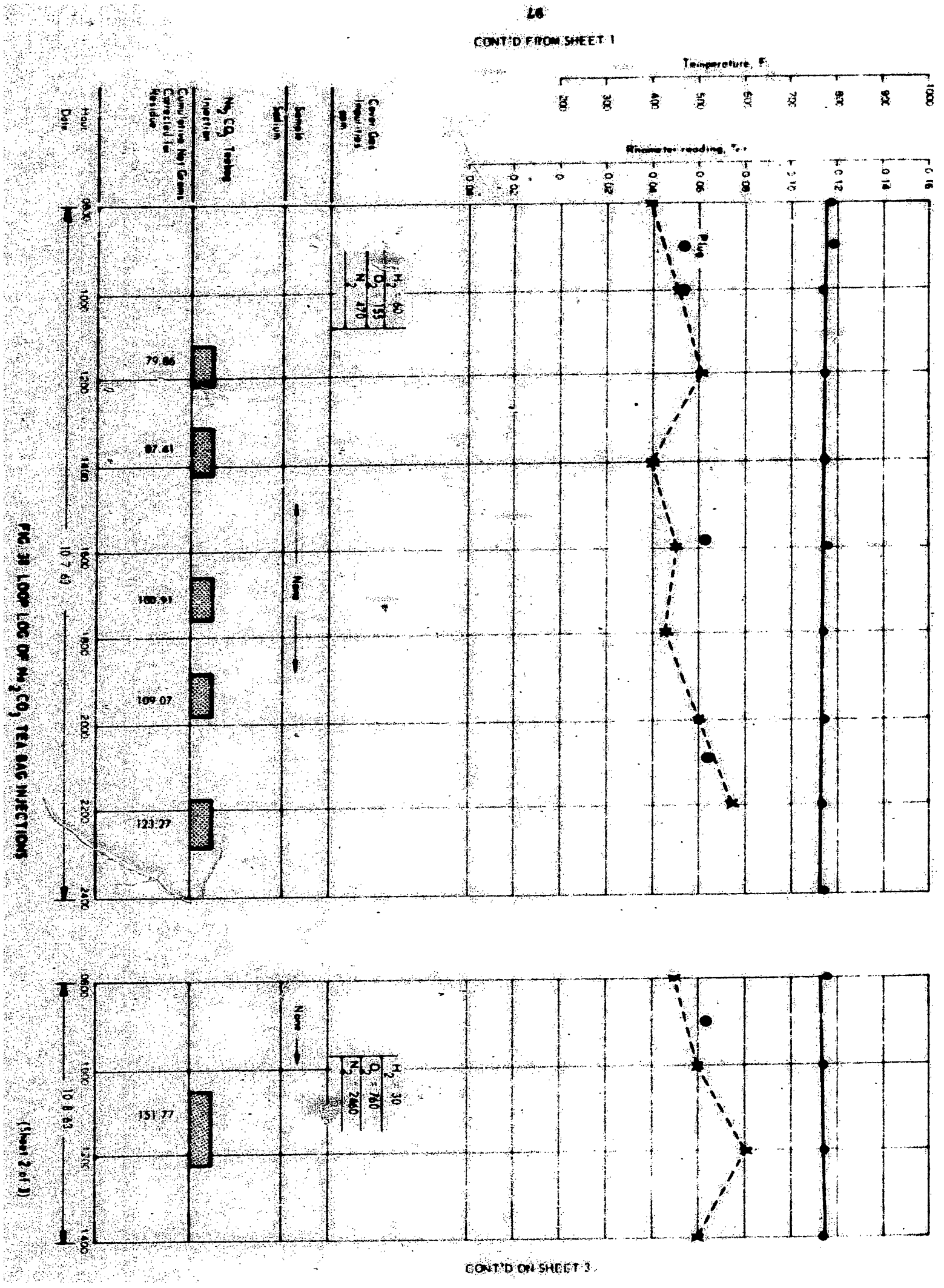


FIG 31 LOOP LOG OF N_2CO_3 TEA BAG INJECTIONS

(Sheet 2 of 3)

CONT'D ON SHEET 3

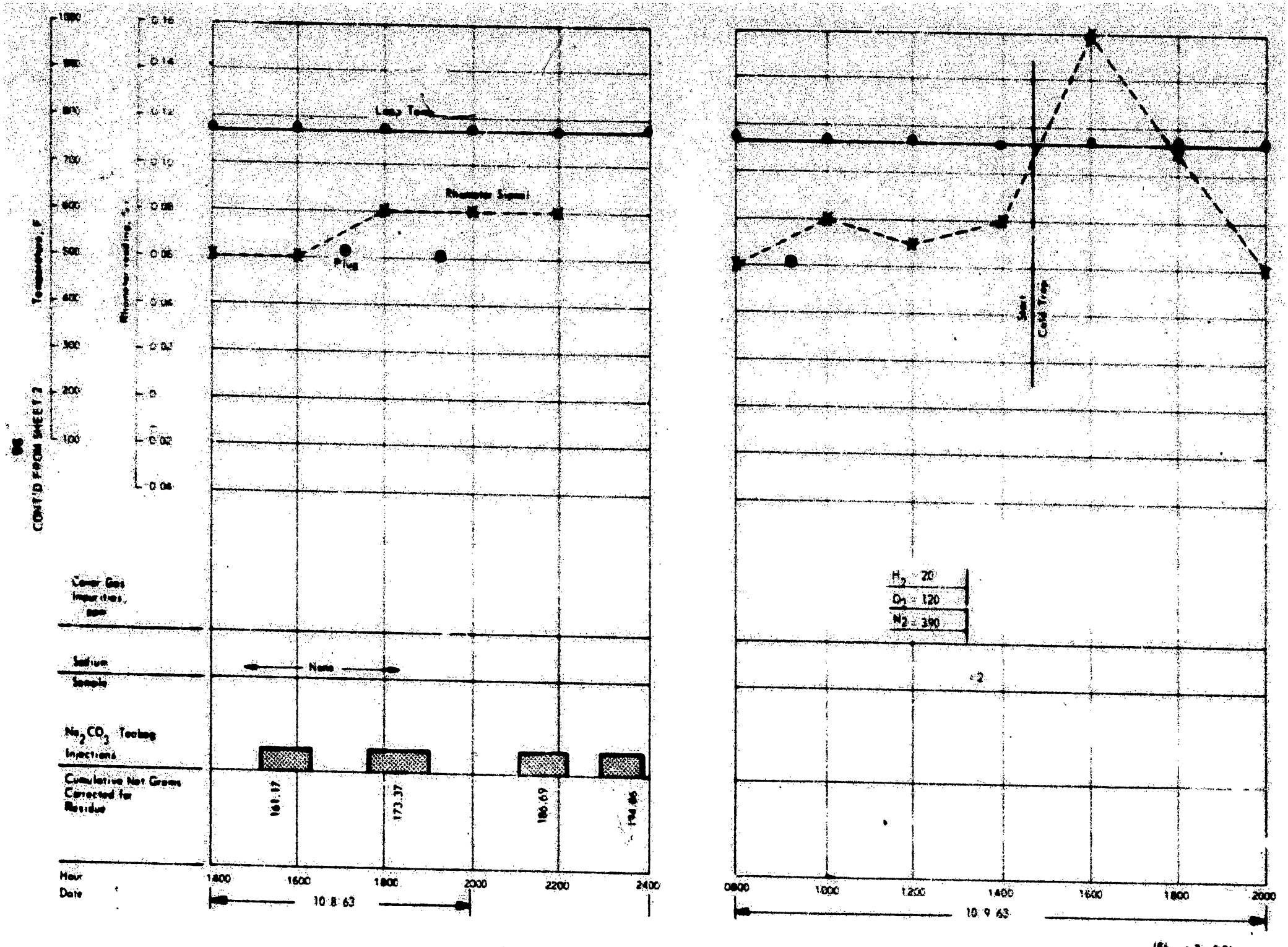
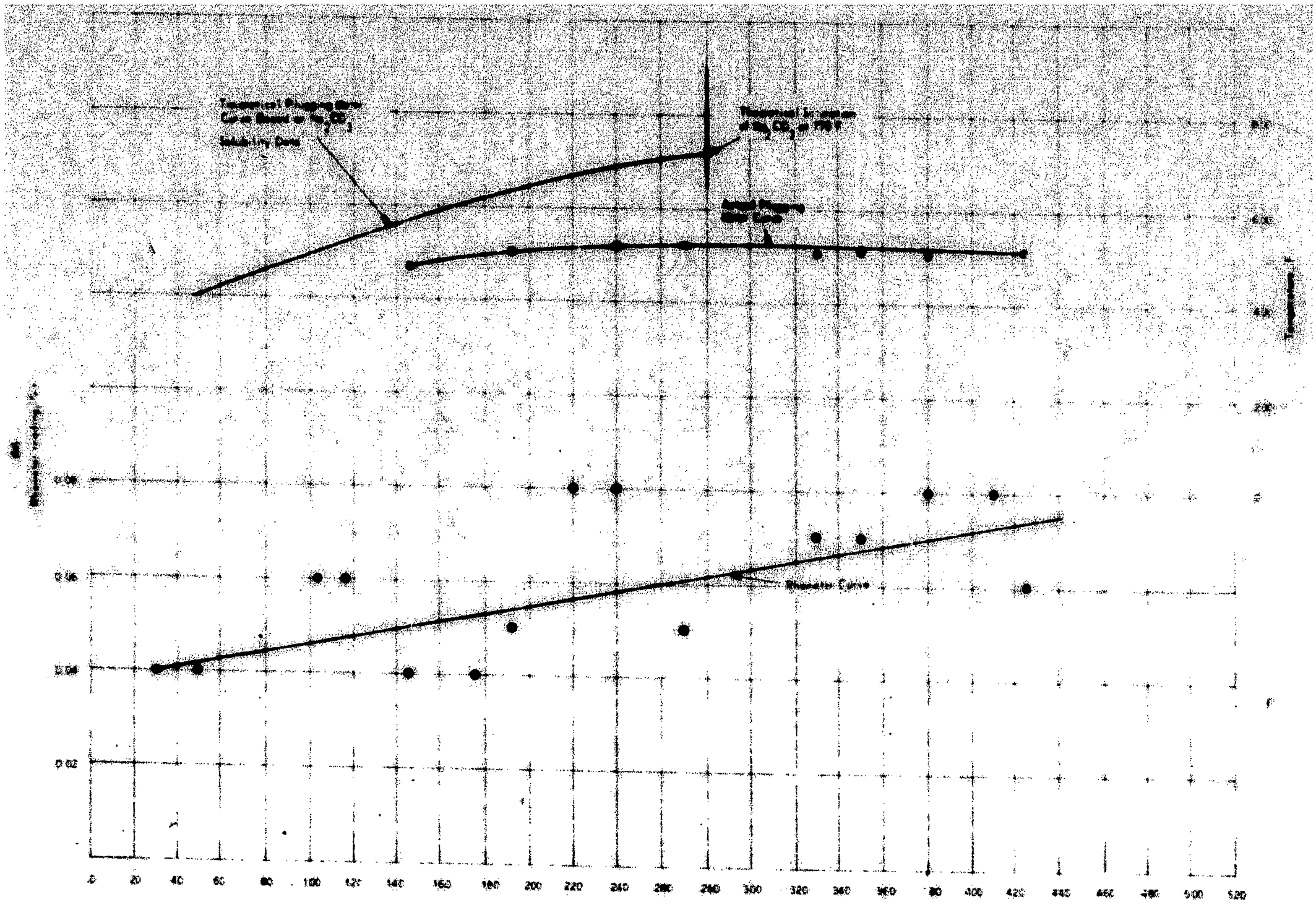


FIG. 38 LOOP LOG OF Na_2CO_3 TEA BAG INJECTIONS

(Sheet 3 of 3)



Na_2CO_3 in Sodium (Corrected for Residue), ppm

FIG. 39 RHEOMETER AND PLUGGING METER CALIBRATION CURVES FOR Na_2CO_3 CONTAMINATION BY TEA BAG INJECTION

Several interpretations of the behavior of sodium carbonate in the loop are tenable. Contaminates may have settled out of solution in cold spots; however, this is unlikely in view of the successful loop cleanup that followed. The departure from expected plugging meter values could be an indication that sodium carbonate does not remain stable at 770 F, but converts to a complex.* It is also possible that the sodium carbonate particles escaping from the tea bag remained in solid suspension, but the characteristic "blips" that would be expected on the Rhometer recorder sheet from the amount of carbonate introduced did not appear. The most feasible explanation for the failure of the plugging meter to confirm accepted solubility data and for the erratic performance of the Rhometer is that the sodium carbonate-sodium system in the loop environment of this experiment is not a simple solution, and that solubility data for sodium carbonate in sodium do not apply in all temperature ranges (Figure 28). The data for the sodium carbonate injection run are shown in Table XV.

* There has been some speculation to this effect in the literature on hot trapping of carbon with stainless steel.

TABLE XV

SODIUM CARBONATE INJECTION DATA AT 770 F

Injections, Cumulative Grams	Cumulative ppm	Rhometer Reading, % r	Plugging Temperature, F
0.00	--	0.00	213
13.68	30	0.02	--
22.92	50	0.04	--
37.02	60	0.05	--
47.02	104	0.06	--
57.30	128	0.06	--
66.30	147	--	468
79.63	175	--	--
87.18	192	--	501
100.68	220	--	--
108.84	236	--	513
123.04	293	0.07	512
151.54	332	--	502
160.94	375	0.08	510
172.81	380	--	500
187.03	412	--	--
195.20	430	0.06	508

CARBON DIOXIDE GAS INJECTION

PROCEDURE

Following loop cleanup, the carbon dioxide gas injections (Figure 40) were initiated at 450 F in the loop. This relatively low operating temperature was selected to reduce the possibility of thermal decomposition of the reaction product sodium carbonate assuming the reaction:

$$4\ Na + 3\ CO_2 \longrightarrow 2\ Na_2CO_3 + C$$

$$\Delta H = -256\ K\ cal/mol\ (calculated)$$

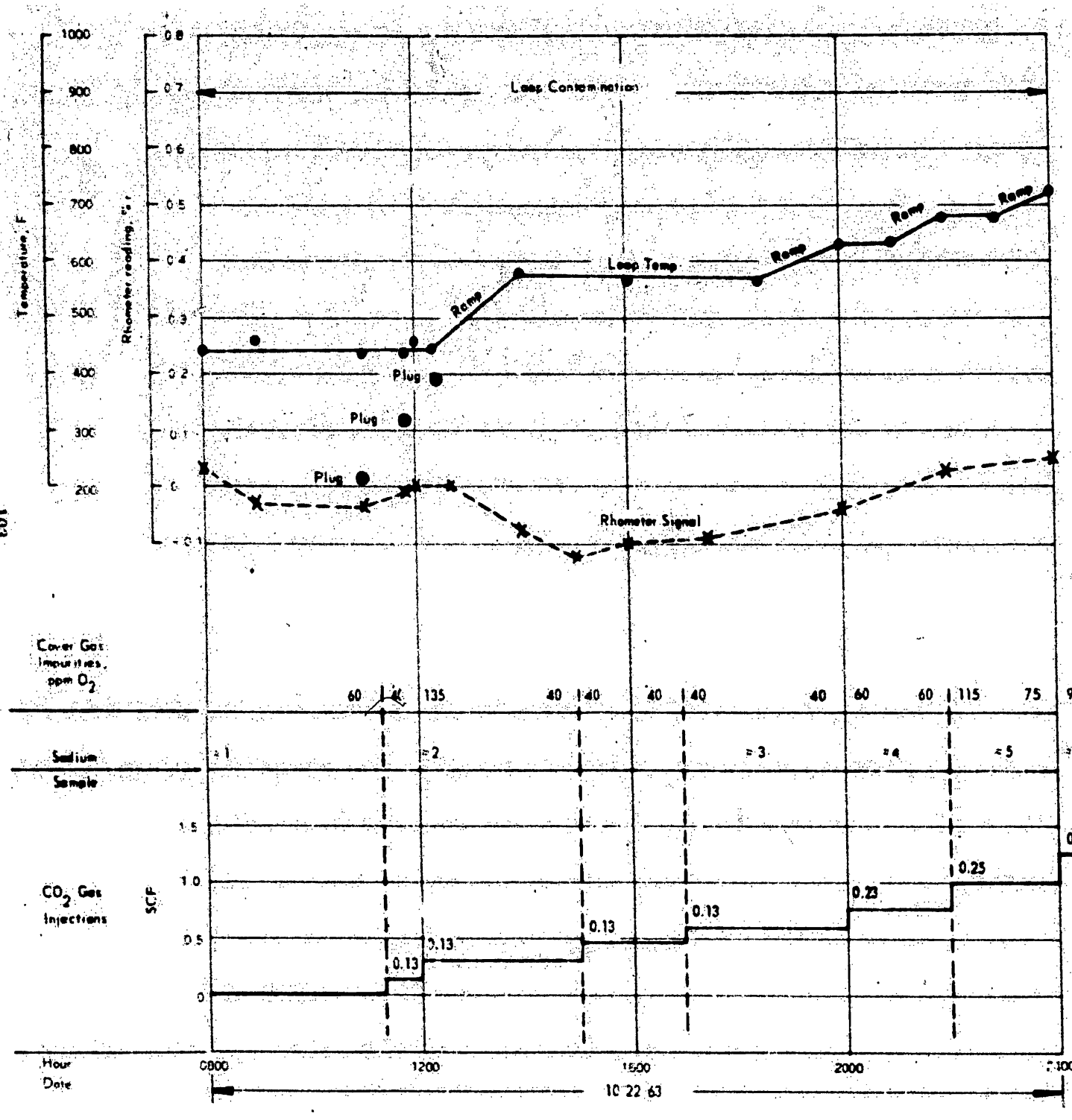
$$\Delta F = -216\ K\ cal/mol\ (calculated)$$

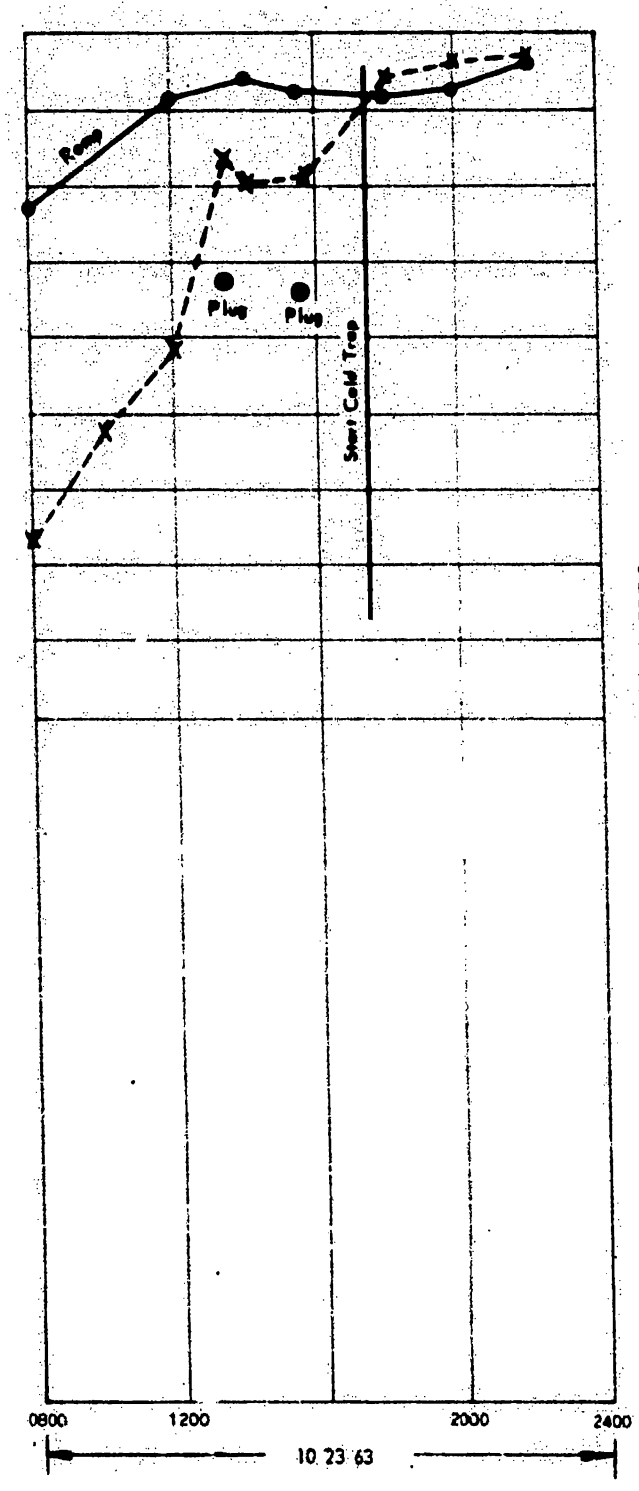
The first two gas injections were 1/8-cubic foot. Charges were then increased to 1/4-cubic foot, since no contamination carry over was observed in the cover gas.

To clear the probe port of residual gases each carbon dioxide injection was preceded and followed by a 2-to 3-minute purge with clean argon at approximately 400 cc per minute (Figure 22). Loop cover gas was also monitored at within 5-to 10-minute intervals before and after each injection.

As loop contamination proceeded, an attempt was made to detect any critical temperature relative to the thermal stability of the carbonate reaction product by ramping the operating temperature in 50 F and 100 F increments. This progression was terminated at 770 F and at the metered impurity of 250 ppm sodium carbonate. No contamination loss to the cover gas was detected.

As in the case of sodium carbonate contamination by direct tea bag injection, plugging temperatures in the present run were not always well defined; however, those plugs which were identified conformed precisely to the solubility data in Figure 28. The erratic performance of the Rhometer, during the previous sodium carbonate injection run was repeated during the carbon dioxide injection. The Rhometer (1) demonstrated a small signal gain throughout the entire run, (2) reacted to cold trap cut-in and plugging meter release, and (3) exhibited a weak irrational response to cumulative contamination levels. Throughout the injection procedures the Rhometer recorder strip showed the characteristic pattern of "blips" identified with particulate entrainment.





CONT'D ON SHEET 2

FIG 40 LOOP LOG OF CO_2 GAS INJECTION AND LOOP CLEAN-UP

CONT'D FROM SHEET 1

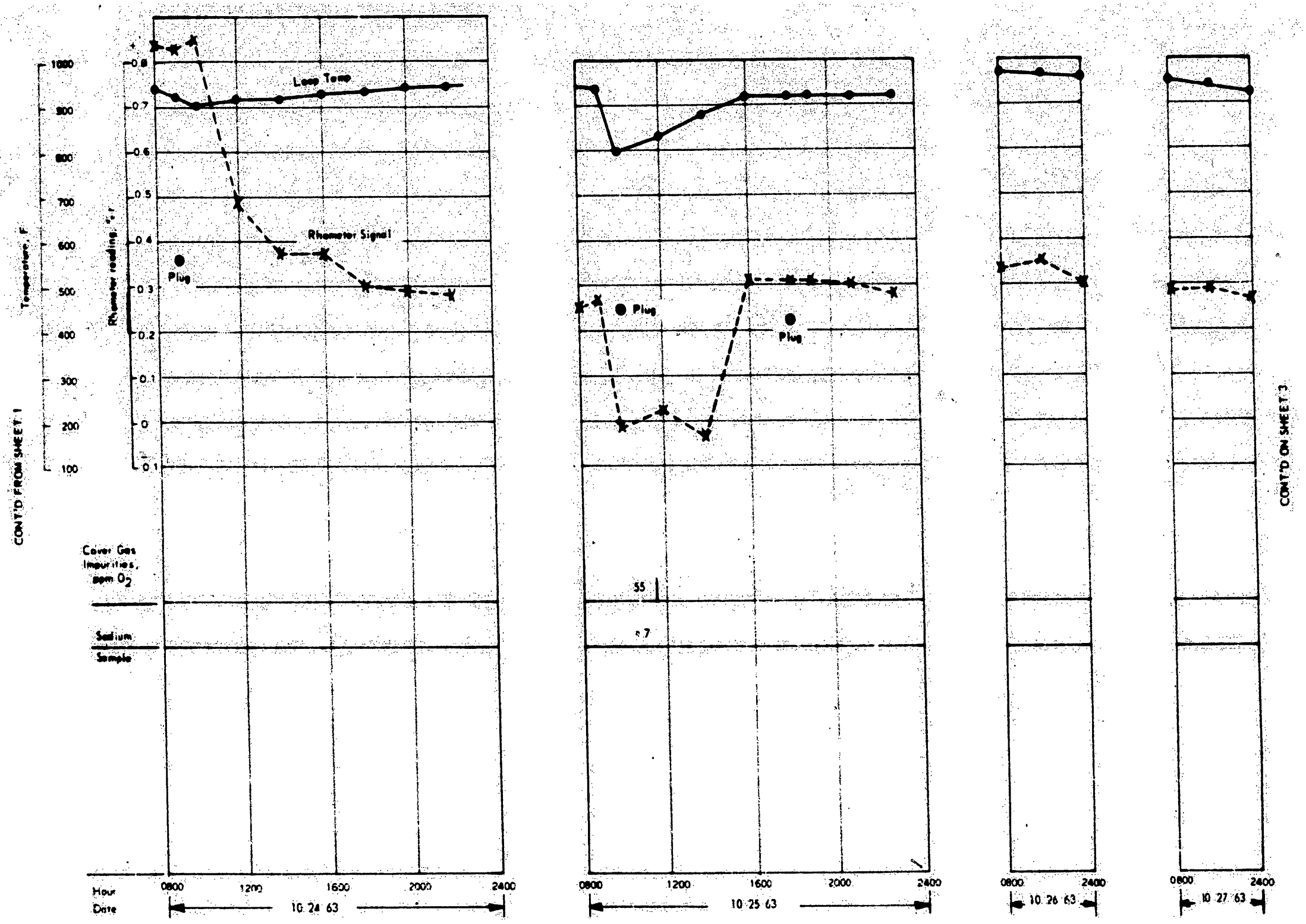


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FIG. 40 LOOP LOG OF CO_2 GAS INJECTION AND LOOP CLEAN-UP

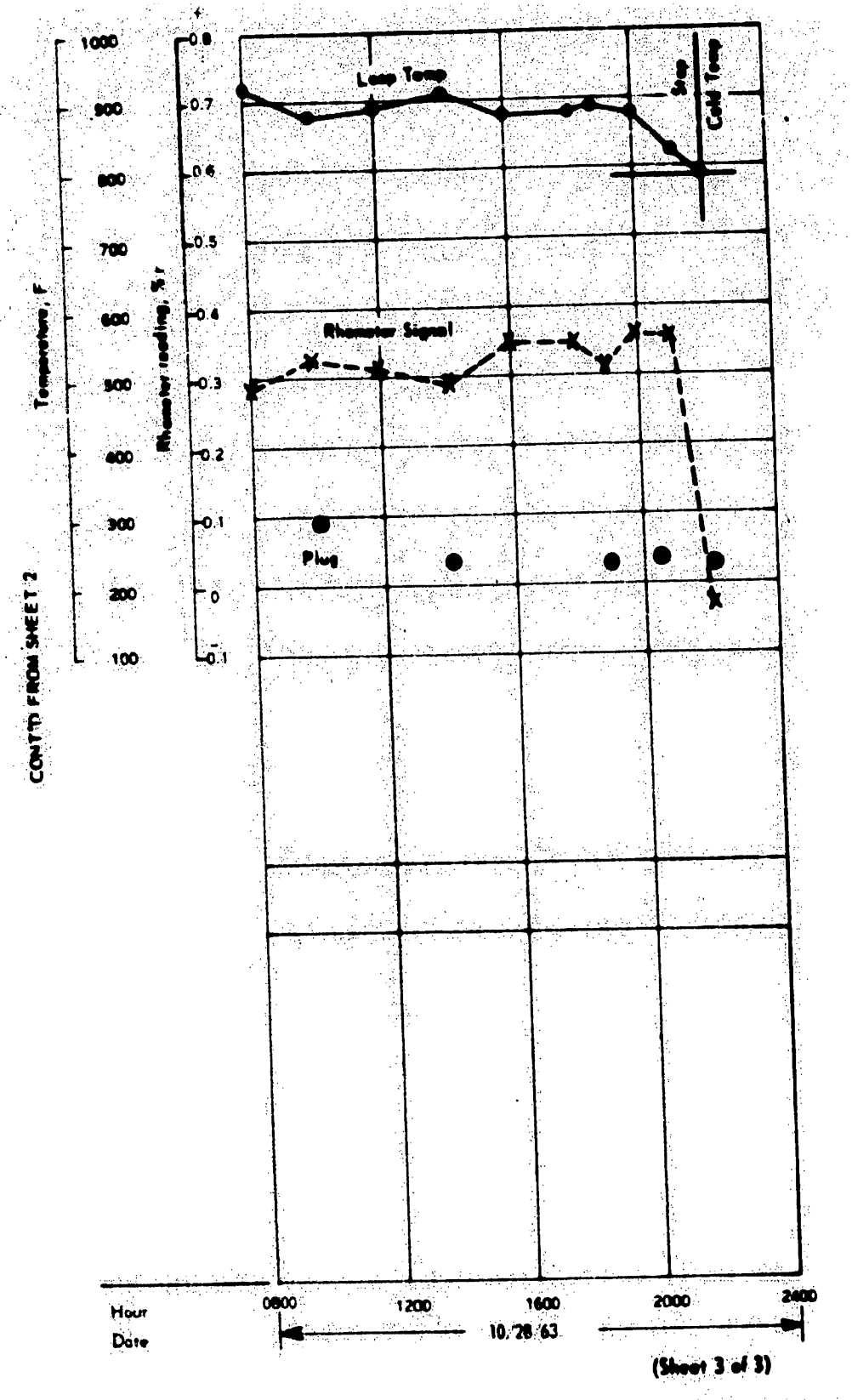

FIG. 40 LOOP LOG OF CO_2 GAS INJECTION AND LOOP CLEAN-UP

As loop temperature was increased to 925 F for cleanup, the Rhometer signal changed abruptly, the particulate pattern disappeared, and there was a vigorous signal gain from 0.14 to 0.87 % r. Plugging temperatures also became more sharply defined, and continued to be well defined to the end of the cleanup operation. Plugging temperatures fell from 685 F to 213 F in an orderly, chronological progression. During this 5-day period of cold trapping, the Rhometer signal was again irrational with reference to the plugging temperatures obtained, and continued to react to cold trap cut-in and plugging meter release.

DISCUSSION OF RESULTS

The calibration run for Rhometer and plugging meter response to carbon dioxide gas injections, Figure 41, was undertaken to supplement the earlier experiment with direct sodium carbonate injections. The metered carbon dioxide injections served to confirm the assumed reaction $4\ Na + 3\ CO_2 \longrightarrow 2\ Na_2CO_3 + C$, since predicted plugging temperatures based on this equation and experienced plugging temperatures were in precise agreement. No loss of sodium carbonate by dissociation was evident during the run, and it appeared that the carbon dioxide-sodium reaction went to completion at all operating temperatures.

The performance of the plugging meter was not entirely satisfactory during this injection period. Out of twelve meter runs only three of four plugs could be identified. Failure of the plugging meter to accomplish the usual "plating" action during the -5F/minute temperature ramp could be taken as an indication that sodium carbonate is held in some form of complex, at least within the doubtful 600 F to 900 F temperature range, in which neither the Rhometer nor the plugging meter functioned properly.

Sodium carbonate solution in the accepted sense was evident above 770 F from the immediate signal gain by the Rhometer, and from the sharper definition of plugging temperatures that followed. The weak and irrational signal of the Rhometer at 720 F and below paralleled the past performance of this instrument in responding to direct injections of sodium carbonate (Figure 39), except that no particulate pattern was reported in the previous sodium carbonate run. If it is assumed from this that the particulate pattern indicated entrained gas rather than entrained solids, it must also be assumed that there was some loss of carbon dioxide to the cover gas; however, such was not the case.

In summation, it is difficult to define the sodium carbonate-sodium system below 770 F at this time. It is believed that some complex of

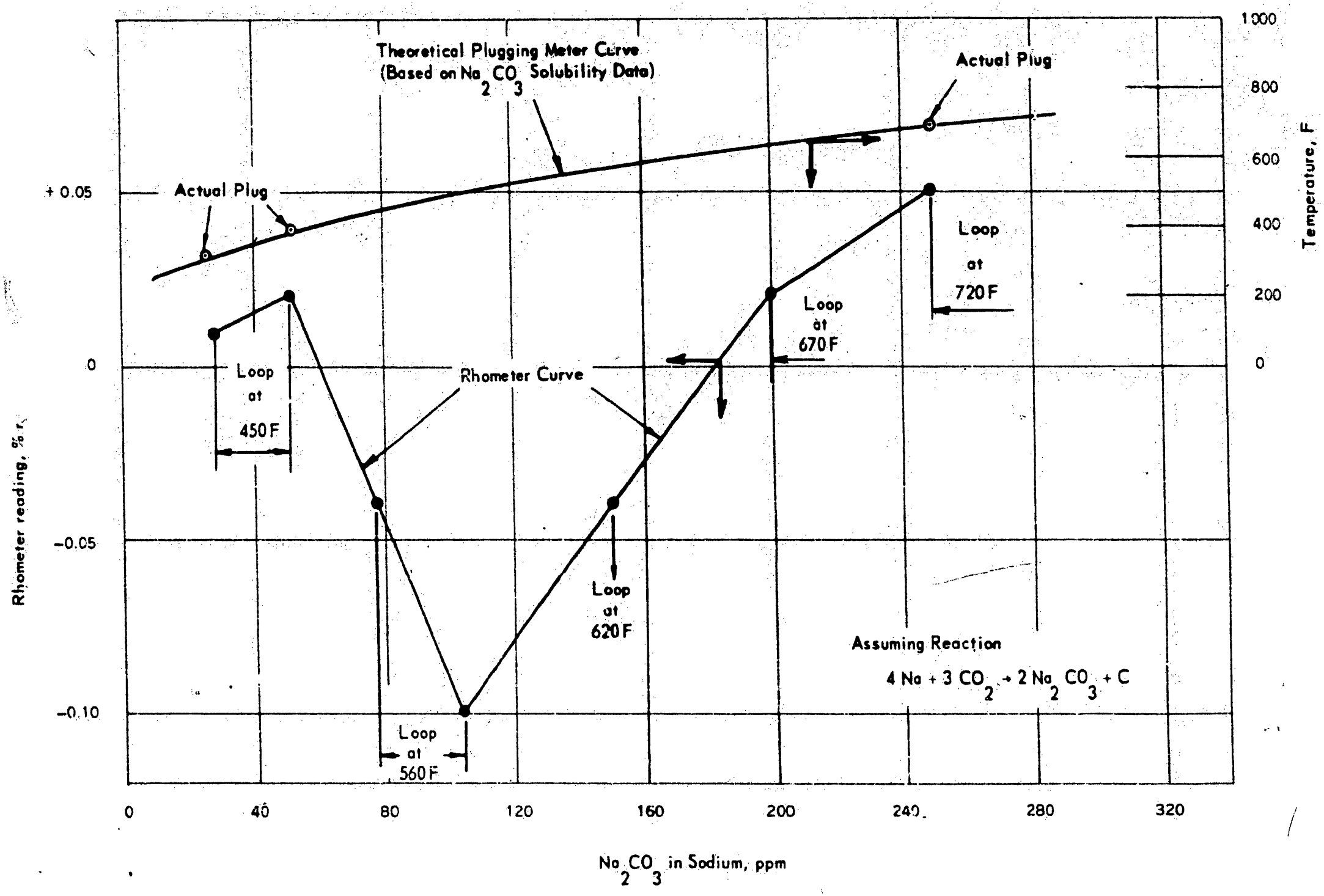

FIG. 41 CALIBRATION CURVES OF THE RHOMETER AND PLUGGING METER FOR CONTAMINATION BY CO_2 GAS INJECTION

carbonate is formed which obscured the definitive action of the plugging meter and defeated the sensory mechanism of the Rhometer. The sodium carbonate-sodium system appeared to be thermally stable within the temperature range of this experiment, and was responsive to cold trapping for system cleanup.

The presence of elemental carbon, in solution or particulate form, may be responsible for some of the irregularities noted in the carbonate runs. The solution of carbon could account for the vigorous signal gain reported in the 770 F to 925 F ramp.

CARBON MONOXIDE GAS INJECTION

PROCEDURE

Injection of carbon monoxide gas was expected to follow the same pattern as an earlier run with carbon dioxide (Figure 40), although reaction energies were lower.

$$2\ Na + 3\ CO \longrightarrow Na_2CO_3 + 2\ C$$

$$\Delta H = -190\ K\ cal/mol\ (calculated)$$

$$\Delta F = -151\ K\ cal/mol\ (calculated)$$

As in the carbon dioxide run, initial injections were made at 450 F in 1/4-cubic foot increments. After injection of 1/2-cubic foot at 450 F and 1/2-cubic foot at 560 F, no response was evident from the Rhometer or the plugging meter. Inspection of the cover gas at each interval revealed contamination levels that would account for all of the carbon monoxide gas introduced.

Cleanup was accomplished by purging out the cover gas and cold trapping the loop. As in other experiments with this loop, the Rhometer reacted to the initial cut-in of the cold trap and the plugging meter. Three days of cold trapping returned these meters to their original zero values.

DISCUSSION OF RESULTS

It was concluded from the foregoing experiments that carbon monoxide is not reactive in sodium within the temperature range of the experiment.

METHANE GAS INJECTION

PROCEDURE

Prognosis on the methane gas injection reaction was negative because of the high thermal stability of this gas in commercial cracking operations.

$$4\ Na + CH_4 \longrightarrow 4\ NaH + 4\ C$$

$$\Delta H = -38.1\ K\ cal/mol\ (calculated)$$

The initial injection of methane gas was made at 620 F. After injection of 1.5 cubic feet of gas, the Rhometer and plugging meter failed to indicate any contamination. Analysis indicated 100 per cent loss of methane to the cover gas. The experiment was then terminated and the loop cold trapped in preparation for a general overhaul of loop hardware.

DISCUSSION OF RESULTS

The energy available for methane-sodium reaction was calculated from the energy of formation of methane and sodium hydride. The reaction velocity for cracking methane is found in Reference 3.

APPENDIX I

THEORY OF RHOMETER DESIGN

The circuit of the Blake Rhometer is shown in Figure 7. Figures 43 and 44 show the Rhometer front panel and Rhometer toroid box. A general description of the operational principles of the device is given on pages 24 to 39.

A better understanding of the underlying operational theory can be obtained by consideration of the simplified circuit illustrated in Figure 42. The primary circuit current, I_p, is accurately defined as being

$$I_p = I_s \quad \frac{S}{N} \ , \tag{1}$$

where I_s is the current in the toroid, which comprises a single-turn secondary winding, and N is the primary winding turns. Since the toroid constitutes a single-turn secondary making S unity,

$$I_p = \frac{I_s}{N} \tag{2}$$

By Ohm's Law, the toroid current is defined as

$$I_s = \frac{E_s}{R_s} \ , \tag{3}$$

where E_s is the effective voltage induced in the toroid by the primary winding N, and R_s is the loop resistance of the toroid filled with the liquid metal. By substitution of (3) into (2),

$$I_p = \frac{E_s}{NR_s} \tag{4}$$

The induced voltage, E_s, is measured by means of the probe winding, n. Since the voltages of the windings in an electrical transformer are

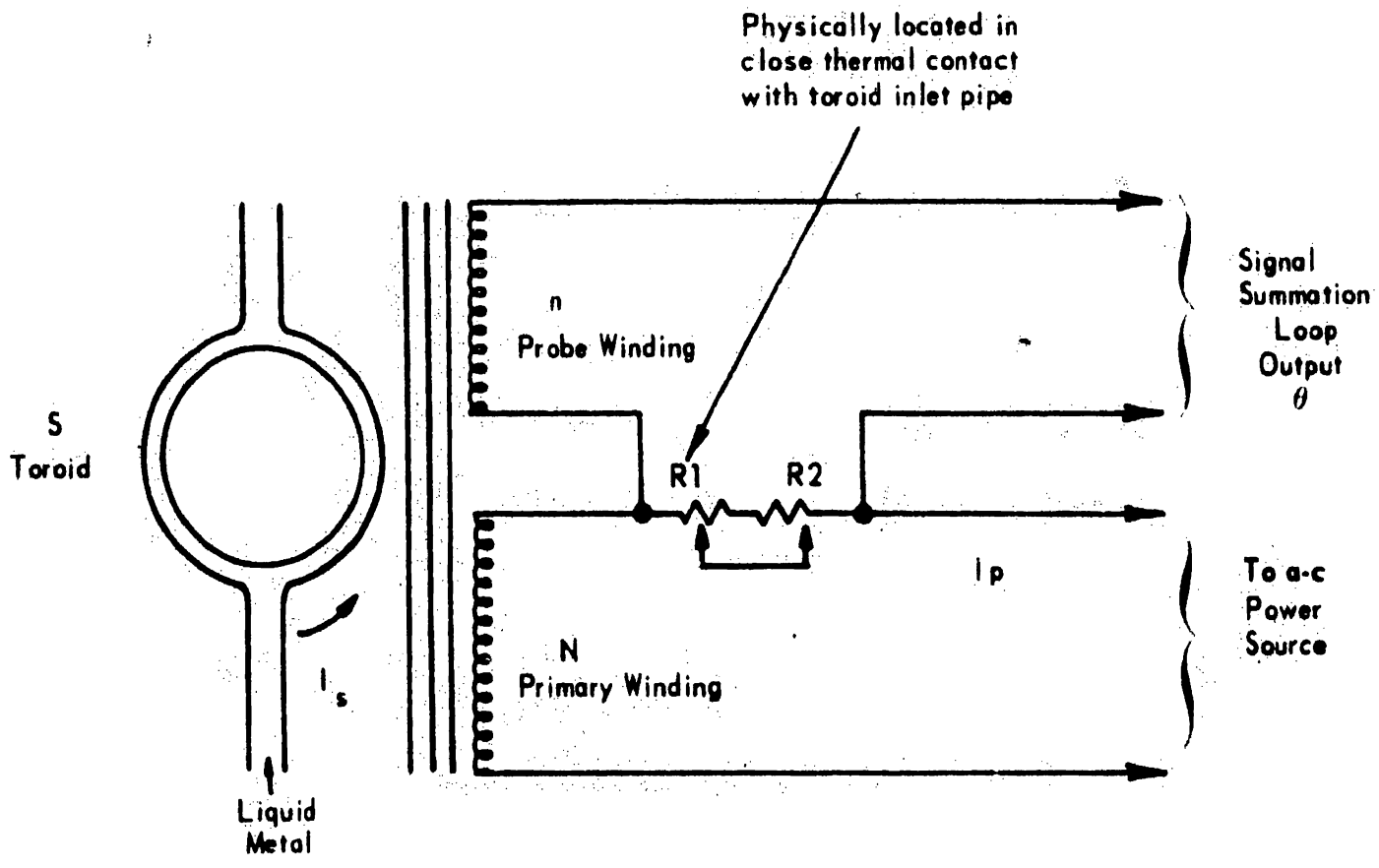

FIG. 42 BASIC CIRCUITS OF THE RHOMETER

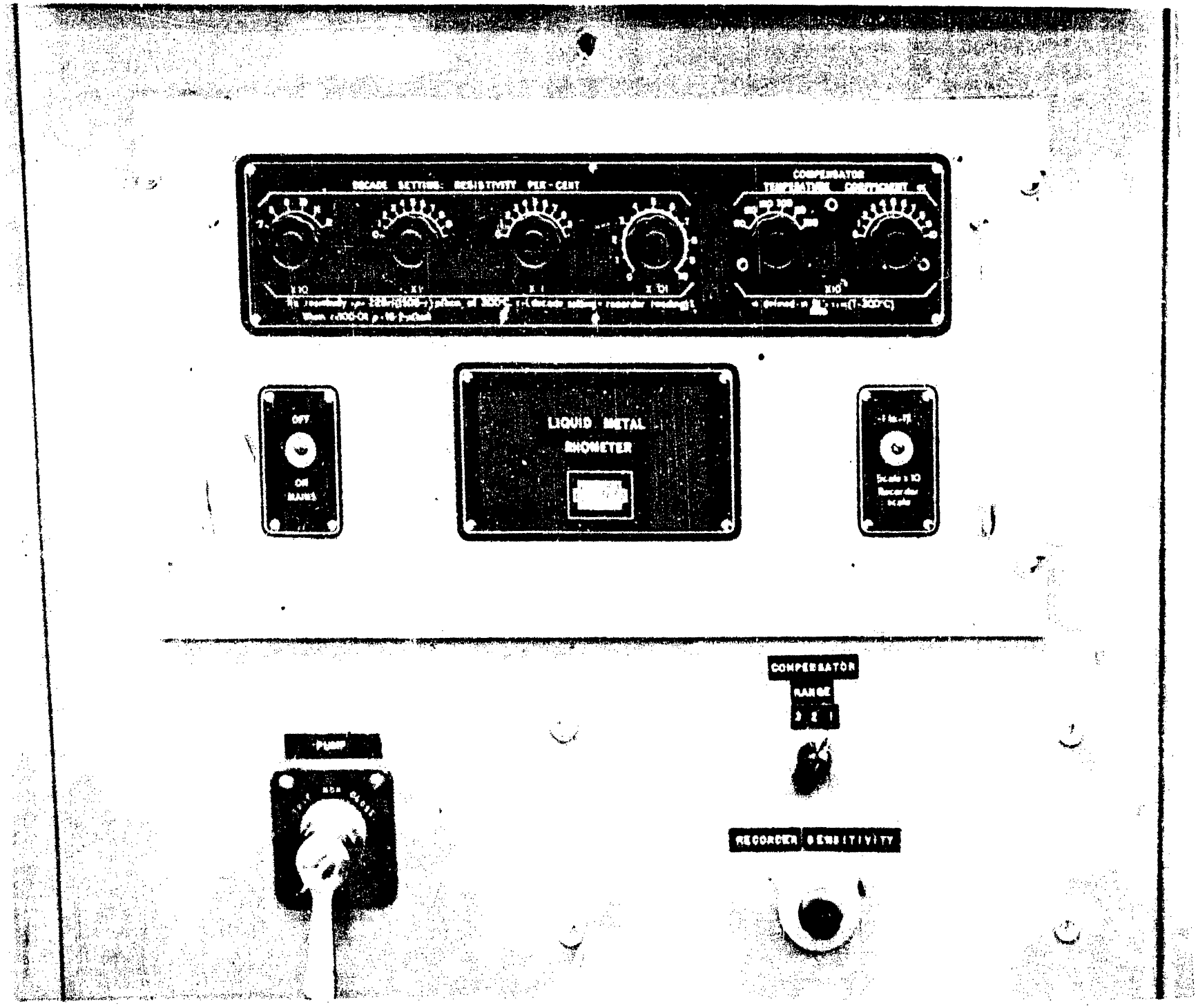

FIG. 43 RHOMETER FRONT PANEL

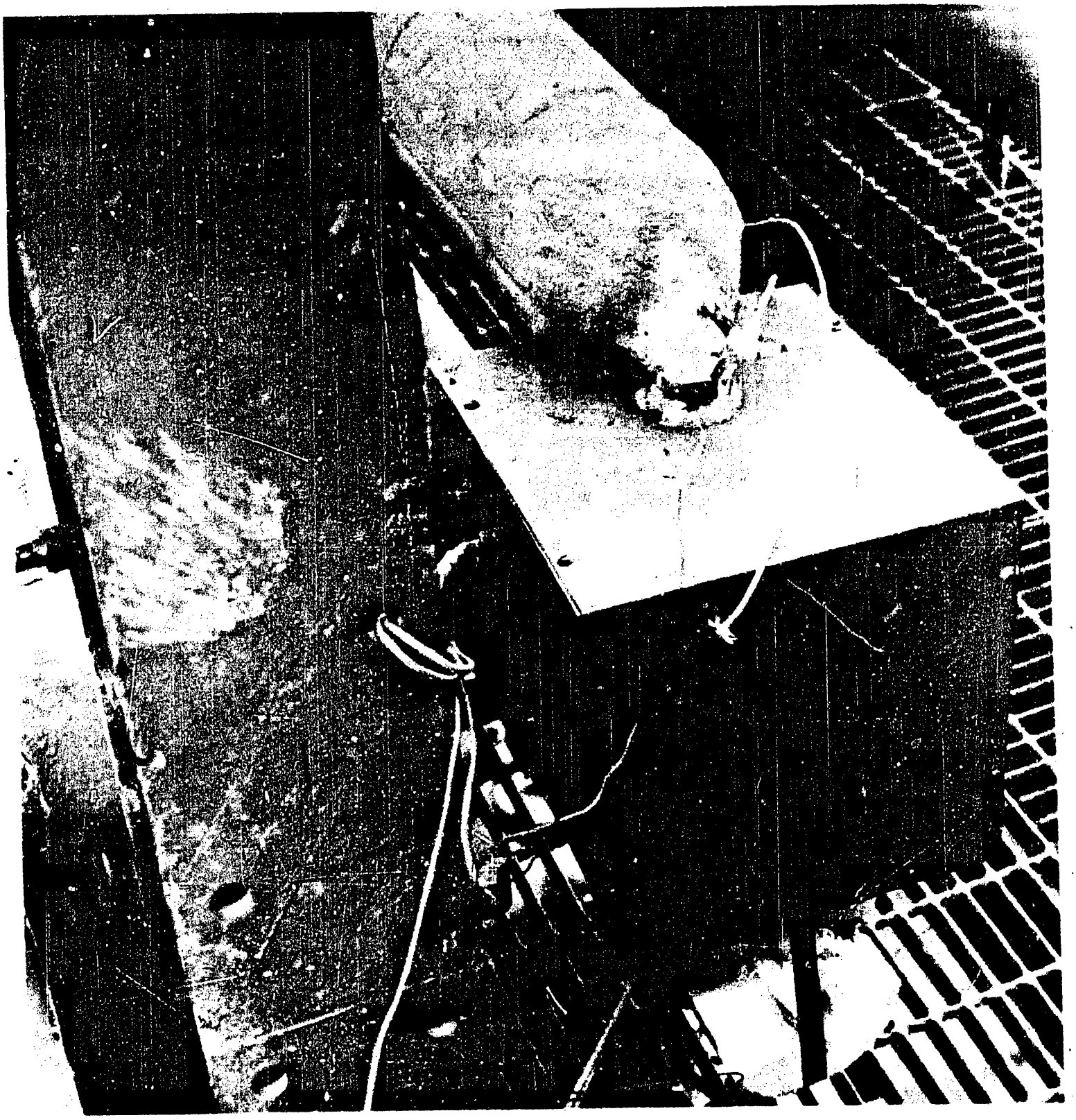

FIG. 44 RHOMETER TOROID BOX

proportional to their turns ratios, the probe coil voltage, E_n, is

$$E_n = nE_s, \tag{5}$$

where n is the probe winding turns; hence,

$$E_s = \frac{E_n}{n}, \tag{6}$$

and by substitution of (6) into (4),

$$I_p = \frac{E_n}{nNR_s}. \tag{7}$$

Determining I_p by the voltage drop, E_p, across resistance R, where

$$R = R_1 + R_2, \tag{8}$$

by Ohm's Law the primary current is

$$I_p = \frac{E_R}{R}. \tag{9}$$

Accordingly, substituting (9) into (7) and solving for the toroid circuit resistance,

$$R_s = \frac{RE_n}{nNE_R}. \tag{10}$$

It is noteworthy that the toroid circuit resistance is expressed by (10) in terms of known parameters of winding turns and directly measurable voltages.

The toroid circuit resistance, R_s, is the effective parallel resistance of the liquid metal and the toroidal pipe. Since their volumes and cross sectional areas are known, along with their temperature coefficients and the resistivity of the pipe material, the specific resistivity of the liquid metal is determinable from R_s. The Rhometer is implemented with tapped

transformers and switches to enable proportional adjustment, and subsequent summation of E_n and E_R to obtain a null balance. In the summation

$$E_R - \frac{E_n}{K} = \theta \tag{11}$$

and

$$\frac{RE_n}{nNE_R} - \frac{E_n}{K} = \theta , \tag{12}$$

where K is a scale factor implemented by a tapped transformer for adjustment of E_n, and θ is the summation loop error voltage. In the nulled condition, where $\theta = 0$

$$\frac{RE_n}{nNR_s} - \frac{E_n}{K} = 0, \tag{13}$$

and

$$R_s = \frac{RK}{nN} . \tag{14}$$

It is apparent that adjustment of K to maintain balance allows read-out of resistivity changes, i.e., under steady-state conditions, in terms of dial settings directly. Under transient conditions, resistivity read-out is provided by a recorder.

Sodium has a temperature coefficient of resistivity which is both large and linear (i.e., of first order). Under the conditions of high order of sensitivity required for the detection of resistivity effects of small contamination levels, even small sodium temperature variations can introduce large read-out errors. To obtain read-out stability, thermal compensation is required in the signal summation loop of the meter circuit.

Because of the large and linear temperature coefficient of sodium, close temperature compensation is a critical requirement in a high resolution resistivity monitoring instrument. The compensator used in the

Mark I unit is a platinum noninductive resistance which is wound on the toroid inlet pipe. A layer of 0.002-inch mica sheet is used to insulate the winding from the pipe. The temperature band of continuous compensation afforded by this form of compensator* has inherent practical limitations. The limitations are imposed by the rigid nonlinear resistivity characteristic of the platinum coil and the complex characteristic of the sodium in conjunction with the stainless steel toroid.

The resistivity of the sodium, R_{na}, after a temperature change of T is expressed by the familiar general formula

$$R_{na} = R_{nao} (1 + \alpha_1 T), \tag{15}$$

in which R_{nao} is the sodium resistivity at some base temperature from which T is determined, and α_1 is the temperature coefficient for sodium. The resistivity of the toroidal pipe, R_t, for temperature change T is expressed by a formula containing first and second order coefficients, thereby,

$$R_t = R_{to} (1 + \alpha_2 T - \beta_1 T^2), \tag{16}$$

where R_{to} is the toroid resistivity at the base temperature, and α_2 and β_1 are the first and second order temperature coefficients, respectively. The total resistivity of the sodium and toroidal pipe, R_s, is defined by the parallel resistance formula, namely,

$$R_2 = \frac{R_{na} \cdot R_t}{R_{na} + R_t} \tag{17}$$

To avoid a laborious expansion of (17) by substitution of (15) and (16), it should be sufficient to state that coefficients up to the third order are produced by the parallel combination. It is evident that the required temperature compensator must match the complex function of R_{na} and R_t. The platinum compensator used in the Mark I has the resistivity characteristic

$$R_{pt} = R_{pt_1} (1 + \alpha_3 T - \beta_2 T^2), \tag{18}$$

* Functionally based upon a match of the resistivity coefficients of sodium and some thermometric material such as platinum.

where R_{pt_1} is the platinum resistivity at the base temperature, and α_3 and β_2 are the first and second order temperature coefficients. Close and continuous match of the platinum compensator to the resistivity gradient of the sodium/toroidal pipe combination is obtained only over a limited temperature range, of the order of $\pm$ 10 F for a maximum resistivity error of 0.01 per cent.

APPENDIX II

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