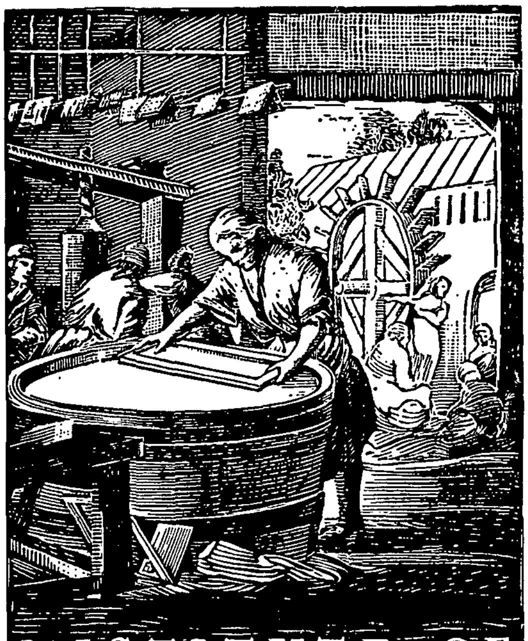
Proj 3025 #1



INSTITUTE OF
PAPER CHEMISTRY
Appleton · Wisconsin

INSTRUMENTATION STUDY–
BLACK LIQUOR SOLIDS CONTENT

Project 3025

Report One
A Summary Report
to
MEMBERS OF GROUP PROJECT 3025

February 23, 1972

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

INSTRUMENTATION STUDY - BLACK LIQUOR SOLIDS CONTENT

Project 3025

Report One

A Summary Report

to

MEMBERS OF GROUP PROJECT 3025

February 23, 1972

MEMBERS OF GROUP PROJECT 3025

- American Can Company
- Bowaters Southern Paper Corporation
- Container Corporation of America
- Continental Can Company, Inc.
- Crown Zellerbach Corporation
- W. R. Grace & Co.
- Green Bay Packaging Inc.
- Hammermill Paper Company
- Hoerner Waldorf Corporation
- Inland Container Corporation
- International Paper Company
- Kimberly-Clark Corporation
- Longview Fibre Company
- MacMillan Bloedel Limited
- The Mead Corporation
- St. Regis Paper Company
- Scott Paper Company
- Weyerhaeuser Company

TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

INSTRUMENTATION STUDY - BLACK LIQUOR SOLIDS CONTENT

SUMMARY

A comparative evaluation of two commercial instruments for measuring black liquor solids content (an Electron-Machine Corporation refractometer and an NUS Corporation sonic velocimeter) was carried out. The study showed that both instruments have the capability of measuring black liquor solids. The sonic velocimeter is quite sensitive to air bubbles and would probably be limited to use before the direct contact evaporator unless special provisions for deaerating the liquor were made. Both instruments are sensitive to changes in chemical composition of the black liquor and would require frequent recalibration. Procedures and limitations of on-line calibration are discussed in the report. The response of the velocimeter increases as the inorganic-to-organic ratio in the liquor increases. The response of the refractometer to such changes is less distinct, but tends to be in the opposite direction. This leads to the possibility that use of the two instruments in tandem could provide a means for detecting changes in liquor solids content and in chemical composition simultaneously.

INTRODUCTION

Reliable, continuous measurement of black liquor solids content is a subject of considerable importance to the pulp industry. The solids content of liquor introduced into a recovery furnace can have a pronounced influence on firing behavior. Current trends toward better control of the recovery furnace for reasons of safety and reduced air emissions require a greater degree of control over incoming solids content and appropriate adjustment of operating conditions to handle variations in solids content. This, in turn, requires a reliable method for continuously monitoring solids content. An important factor influencing the need for on-line measurement of solids content is the recommendation by BLRBAC (Black Liquor Recovery Boiler Advisory Committee) that a minimum solids content of 55% be maintained on firing to avoid smelt-water explosion hazards. The need for solids measurement is not restricted to high-solids liquors connected with furnace operation. There is also a need for solids measurement on weak liquors to permit control of evaporator and solids concentration entering the furnace envelope.

A number of devices are available for on-line measurement of black liquor solids content. These include instruments based on refractive index, nuclear attenuation, specific gravity, sonic velocity, and vibration amplitude. In addition, the ammeter reading of the cascade evaporator motor drive is often used as an indication of liquor solids content. In the proposal for this project, it was indicated that a general review of the state of the art of black liquor solids measurement would be carried out. This was to include a review of measurement methods, instrument manufacturers, and the extent of application in the industry. An extensive survey of the use of black liquor solids monitoring devices in the kraft industry has been recently carried out by the Instrumentation Subcommittee of BLRBAC (1). The following conclusions were reached:

1. Instruments are available for successfully measuring black liquor solids concentration continuously. These instruments have sufficient dependability, accuracy, and reliability to permit their use in promoting safe operation of recovery boilers.

2. Refractive index-type instruments are more widely accepted and far more successful with less maintenance requirements than other types of instruments presently or previously used for this service.

3. Refractometer installations have proven sufficiently reliable and accurate to be used for automatic alarming on low black liquor solids concentration.

4. There remains a considerable need for improvement of instruments presently available and for the development of new techniques and/or instruments for monitoring and control of black liquor solids concentration.

In view of the fact that a survey such as we had contemplated would duplicate the work done by BLRBAC and the fact that most sponsors of this project are members of BLRBAC, it was decided not to carry out a survey. Specific details of the mill survey are on file with the BLRBAC subcommittee and are available to any member of BLRBAC upon request. We are not free to divulge the findings of that study.

All of the methods for continuous measurement of black liquor solids are indirect methods in that they measure some property of the black liquor which is dependent on solids content. Thus, they must ultimately be calibrated in terms of some method for the direct determination of solids content. The accuracy of the continuous methods is thus ultimately dependent on the accuracy of the direct measurement and the calibration procedure employed. Direct measurement of black liquor solids content is not completely straightforward. Black liquor is a complex mixture of organic and inorganic compounds, and at the present time there exists no laboratory method for determination of black liquor solids content which is acceptable to all segments of the kraft pulping industry. Parker et al. (2) have carried out a comprehensive review of methods for off-line measurement of solids content and have discussed the problems involved. The problems of accuracy in methods for direct determination of black liquor solids are fundamental to the general problem of measurement of this quantity and will be discussed later in this report.

The major emphasis of this project was directed toward a comparative evaluation of two commercial instruments for black liquor solids measurement. The two instruments which were chosen were as follows:

1. An Electron-Machine Corporation Model BL-168 Black Liquor Analyzer which is based on measurement of the refractive index of black liquor.
2. An NUS Corporation Model 6161-139 Sonic Solution Monitor which employs a measurement of sonic velocity of the liquor.

The evaluation was directed mainly toward the applicability of these instruments in on-line measurement of black liquor solids, and investigation of potential sources of errors in their use. A major objective was a study of the effect of liquor composition on instrument response.

APPARATUS AND PROCEDURES

FLOW LOOP

The two instruments were installed in a flow loop which was constructed to permit simulation of on-line operation. A schematic diagram of the flow loop is shown in Fig. 1. The instruments were mounted in a vertical leg of the flow loop with the sonic velocimeter located immediately below the refractometer. The sonic velocimeter was mounted in a standard 4-in. tee. The refractometer was mounted on a special Electron-Machine elbow adapter which was furnished with the instrument. The adapter was sized for a standard flanged connection to a 1-in. process line.

The flow loop consisted of a circulating pump, a heat exchanger, the instruments, a pressurized accumulator, and the necessary piping. A steam-jacketed vessel with an integral stirrer was used for making up liquors prior to their introduction into the flow loop. This vessel could be sealed and evacuated to permit deaeration of the liquors before feeding them into the main loop. A Moyno pump was used to pump the liquor from this storage vessel into the test loop.

In the initial configuration of the flow loop, a La Boor centrifugal pump was used as the only circulating pump, with the Moyno pump used solely for feeding liquor to the system. In order to avoid the possibility of introducing air into the system at the centrifugal pump, the piping was changed to permit using the Moyno pump as a circulating pump as well as a feed pump. In the final configuration, either the centrifugal pump or the Moyno pump could be used as a circulating pump.

The accumulator, located at the high point in the loop, was simply a cylindrical pressure vessel 10 in. i.d. and 30 in. long, with a side arm attached halfway up for incoming black liquor. A sight gage was installed to permit

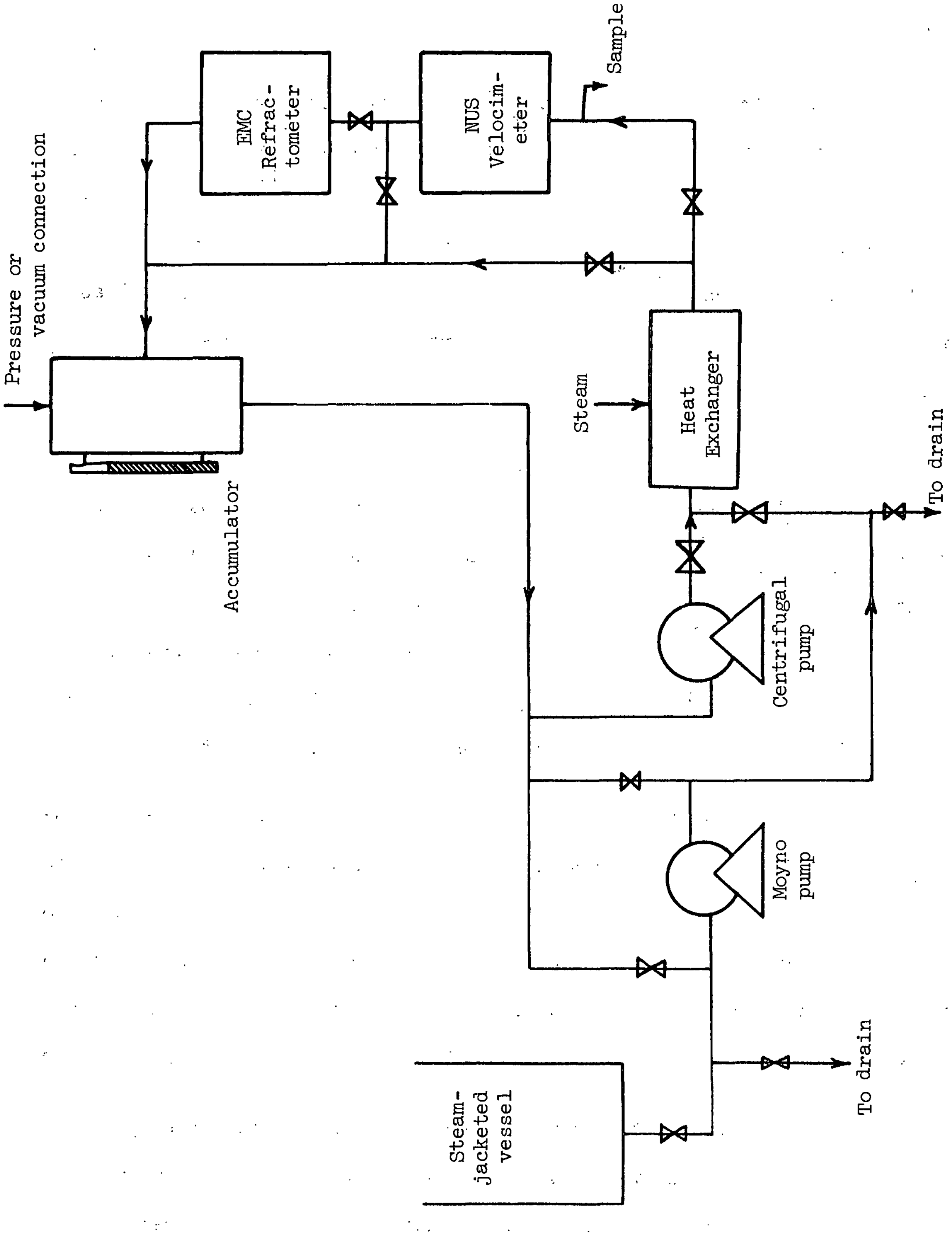


Figure 1. Schematic Diagram of Test Loop

observation of the liquor level. At the top of the accumulator, provisions were made for pressurizing the loop with nitrogen and for evacuating the loop. The return leg to the circulating pump was taken from the bottom of the accumulator.

A bypass line ran directly from the heat exchanger to the accumulator to permit control of flow through the instrument test zone. With the Moyno pump, an additional mode of flow control was available through adjustment of the pump speed with a Reeve's drive. A separate bypass line around the refractometer was installed to permit reducing the velocity through the smaller refractometer adapter if desired. With the exception of the piping in the immediate vicinity of the instruments, all piping in the main loop containing the centrifugal pump was 2-in. diameter pipe. The feed lines from the storage vessel and the piping around the Moyno pump were of 1-in. diameter pipe.

The capacity of the flow loop was about 15 gallons. The rated capacity of the centrifugal pump was 100 g.p.m., while the maximum capacity of the Moyno pump was about 10 g.p.m. The heat exchanger was rated at 20,000 B.t.u./hr. and provided the capability to control temperature over the range from 60 to 140°C. The loop was capable of being pressurized up to 140 p.s.i.g. A thermocouple was installed in the tee which held the velocimeter. Once it was established that the temperature measurement in the NUS instrument was reliable, the NUS temperature measurement was used for the bulk of the work. A sample tap was provided immediately ahead of the velocimeter tee. This was used for taking samples for off-line measurement of solids content.

PROCEDURES

The normal operating procedure was to start with high-solids liquors as obtained from the mills. The semisolid liquor was scooped into the steam-jacketed storage vessel and heated to boiling while stirring. When this point was reached, all valves in the flow loop were opened, the accumulator vent was opened to the atmosphere, and the liquor was then pumped slowly into the flow loop until the desired level in the accumulator was reached. The storage vessel was then valved off, the system pressurized with nitrogen to the desired level, bypass valves adjusted, and circulation of liquor begun. With black liquor, the Moyno pump was used almost exclusively as the circulatory pump. A run would then be carried out varying temperature, velocity, and pressure as desired and observing the instrument response. Liquor samples were taken for off-line solids measurement. At the completion of a run, the liquor would be forced back to the storage vessel by the pressurization of the loop. Water would be added at that point to reduce solids concentration, the liquor heated to boiling, and the procedure repeated.

The flow loop was used for a series of runs with industrial black liquors and some introductory runs with sucrose solutions. Much of the work on the effect of composition on measurement response was made external to the flow loop. The main reason for doing this was to cover a wider range of compositional variables than was possible in the flow loop. The difficulty with using the flow loop itself for studies of compositional effects was the relatively large volume of liquor required (about 15 gallons) and the time needed to make up a sample, feed it into the loop and carry out a run. To measure sonic velocity, the NUS probe was simply inserted into a beaker containing the sample, with a water bath used for temperature control. The EMC refractometer was not used in "out of loop" studies because the geometry of the adapter section was not suitable for this mode of testing. Instead, a laboratory refractometer was used to determine the effect of changes in composition on the refractive index. The laboratory instrument was a Bausch and Lomb Type 334558 refractometer.

SOLIDS MEASUREMENT

Direct measurement of solids content of liquor samples was used as a reference in interpreting instrument response. Several methods were used for these determinations including different ovendry procedures and a distillation method. The most successful procedure was that taken from a final draft of a proposed revision of TAPPI Standard T 625 ts-64, "Solids Content of Black Liquor," as submitted to the Standards Editor of TAPPI in June, 1969. In this procedure, which follows many of the recommendations of Parker et al. (2), liquor samples are dried at 105°C. for a minimum of six hours. An inert surface extender and a controlled flow of dried air are used to increase drying rate and eliminate moisture entrapment. Strong black liquors are diluted to allow volumetric handling and to reduce scum formation.

Measurement of the solids content by the distillation method tended to give slightly lower values of solids content than the ovendry method. In order to keep a single base for evaluating the instruments, all of the data reported herein related to the NUS velocimeter or the EMC refractometer are based on ovendry solids values.

In the runs with black liquor in the flow loop, liquors were progressively diluted to vary solids content. The amounts of dilution water used were recorded and used to minimize uncertainty in measured solids values. The method of doing this is described below. It was assumed that the accuracy of the solids determination improved as the liquor became more dilute, and so the most dilute liquor was used as a base. The working equation for the solids smoothing was:

$$Y_i = \frac{x}{W + x - \Delta_i} \qquad (1)$$

where

Y_i = solids content of ith sample,

x = total solids in loop at end, lb.,

W = total water in loop at end, lb., and

Δ_i = dilution water added from ith sample to end, lb.

Inverting Equation (1) gives:

$$\frac{1}{Y_i} = \frac{W}{x} + 1 - \frac{\Delta_i}{x} \qquad (2)$$

or

$$\frac{1}{Y_i} - 1 = \frac{W}{x} - \frac{\Delta_i}{x} \qquad (3) .$$

Equation (3) was used to minimize the uncertainty in the solids data. The solids content (Y_i) and the amount of dilution (Δ_i) were measured quantities. A plot of $(1/Y_i) - 1$ *vs.* Δ_i was then made. The best straight line consistent with a reasonable estimate of the initial solids (x , which relates to the slope) and the greater reliability of low-solids samples was used to determine the set of values of solids content in the runs. An example of this method of handling the solids data is shown in Fig. 2. These particular data show an excellent agreement between measured solids content and amounts of dilution water. The agreement was generally poorer with higher solids content liquors.

LIQUOR ANALYSIS

Three different commercial liquors were used in the tests. Two liquors (labeled A and B) were obtained from a southern kraft mill pulping southern pine to high yield and mixtures of pine and hardwoods to low yields. Liquor B was obtained

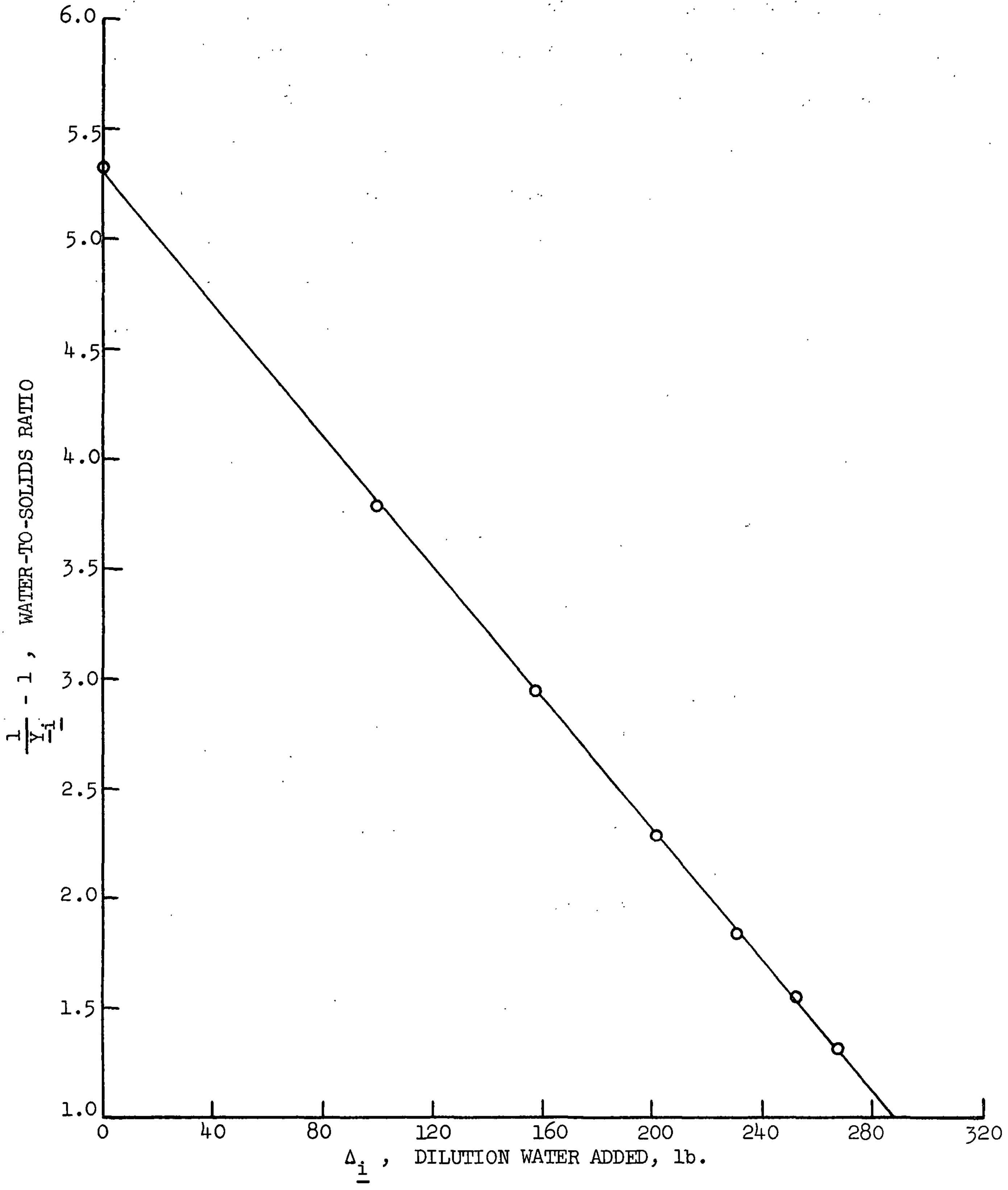


Figure 2. Interrelation Between Measured Solids Content and Dilution Water

from the same mill five weeks after Liquor A. A third liquor (Liquor C) was obtained from a northern kraft mill pulping softwoods to conventional kraft yield levels. The results of chemical analyses of these liquors are shown in Table I. It should be noted that although Liquors A and B were obtained from the same mill and have similar inorganic contents, there is a difference in the degree of oxidation of the sulfur compounds. Liquor C contains significantly more sulfur and also has a distinctly higher inorganic content. In all cases, the liquors were obtained at high solids concentration and were shipped to the Institute in sealed drums.

TABLE I

CHEMICAL COMPOSITION OF BLACK LIQUORS

All results are expressed as weight percent on black liquor solids,
and are based on TAPPI Procedure T 625

	A	B	C
Sulfated ash, %	34.0	32.6	36.5
Organic, %	66.0	67.4	63.5
Total sodium, %	19.4	19.3	21.9
Total sulfur, %	3.4	3.4	5.0
Na_2S, %	1.03	0.29	4.14
$Na_2S_2O_3$, %	3.93	3.16	4.10
Na_2SO_4, %	5.43	7.05	5.14
Inorganic sulfur, %	3.24	2.99	4.53

EMC REFRACTOMETER

DESCRIPTION OF INSTRUMENT

The EMC refractometer, model BL-168, uses the principle of critical angle refractometry by which dissolved solids content is related to the refractive index of the solution. The basic unit consists of a sensing head and control console, Fig. 3. The sensing head is mounted on the adapter installed in the process line and the process solution is viewed through a transparent window. The surface of the solution which is in contact with the window is optically scanned by a motor-driven octagonal prism. The refractive index is determined by a beam of light from the prism which repeatedly sweeps at a varying angle at the surface of the solution. At a point in the cycle, as the angle between the incident light beam and the surface decreases, the light beam instead of refracting into the solution is reflected back into the optical system. The point of change from refraction to reflection depends on the refractive index of the solution and is known as the critical angle. The prism scans the beam of light through the critical angle at the rate of 480 Hz. A photodetector measures the alternating light and dark periods and its electrical output is used to provide a readout of refractive index in the required units (R. I., % concentration, degrees Brix., etc.). A principal advantage of this method is that it measures the index of refraction at the surface of the process solution. Since the light beam does not penetrate into the solution, the instrument can be used for opaque as well as transparent materials.

The optical system is shown in Fig. 4. The light from the tungsten lamp source passes through a collimating lens and an aperture to give a narrow beam. The octagonal prism rotated at 60 r.p.s. causes the beam to oscillate as each face of the prism traverses the beam; the light exiting from the prism is displaced by an amount equal to the width of the faces. The cycle is repeated for each face

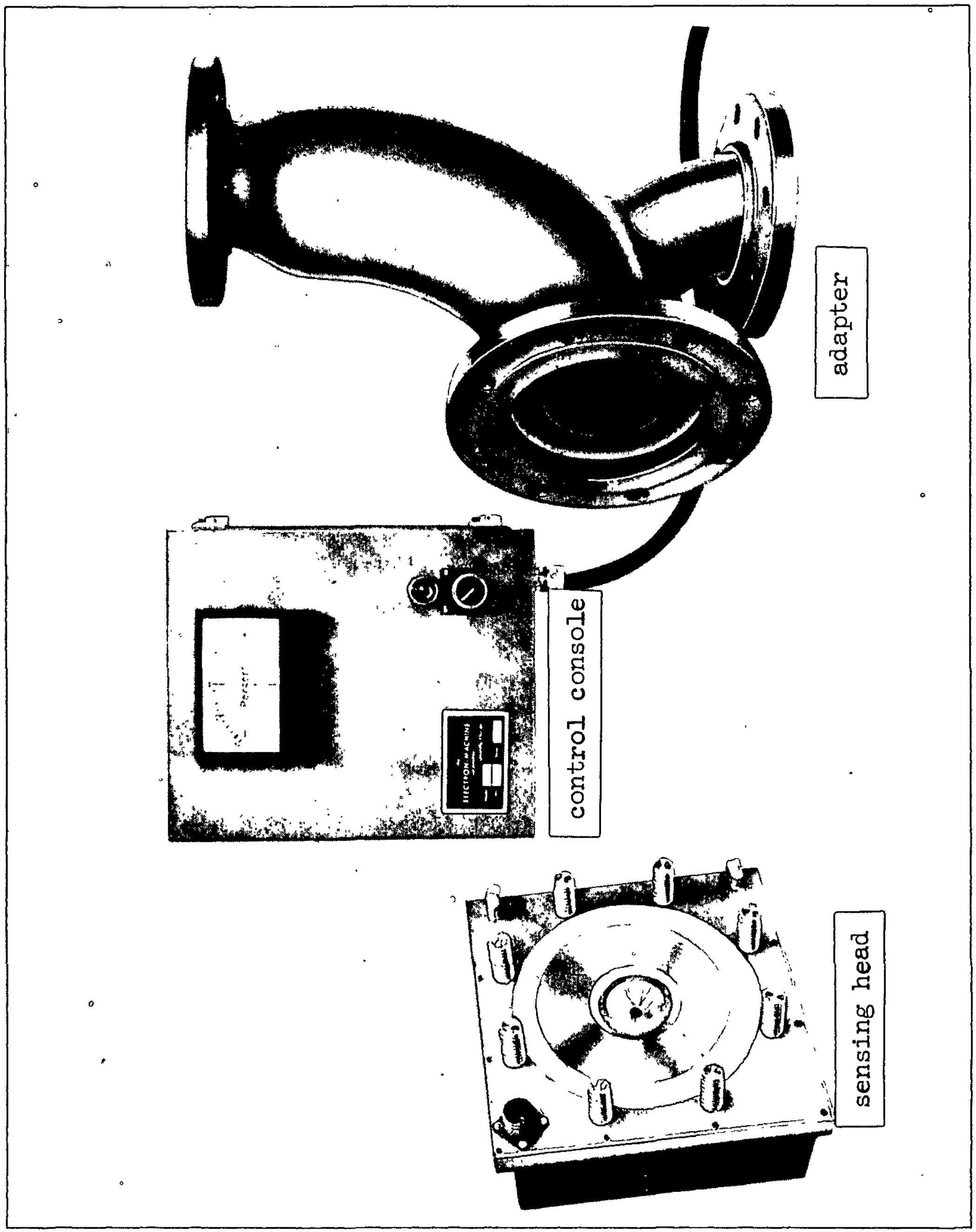


Figure 3. Photograph of EMC Refractometer

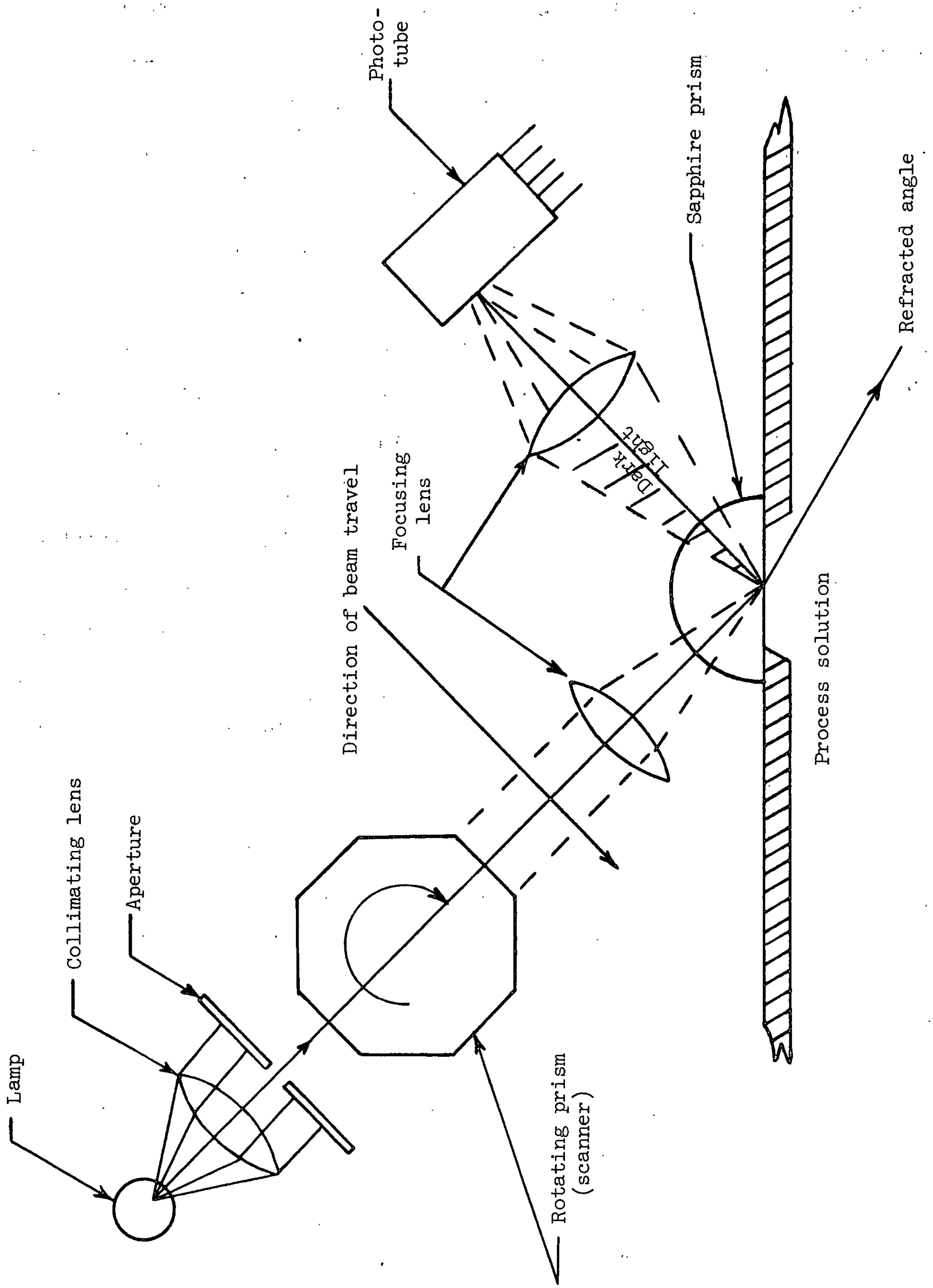


Figure 4. Schematic of Optical System of Refractometer

so that the frequency of oscillation is 8 x 60 = 480 c.p.s. This beam is focused at the interface of the sapphire prism and the process solution. The effect of focusing is to cause the light to enter the process solution at an angle which varies as the light beam oscillates. At the higher angles, the light is refracted into the solution. At the shallower angles, the light is reflected through the sapphire, through a lens assembly, to the photodetector. The ratio of refracted to reflected light varies with the refractive index of the solutions being measured. The light and dark periods on the photodetector produce a 480-Hz a.c. output from the device which is transmitted to the control console. The function of the electronics in the console is to condition the signal so that the light and dark periods can be compared. The resulting signal which is proportional to refractive index is used to drive the front panel meter which reads directly in percent solids. The signal passes through a preamplifier; the output of the preamplifier is squared; the positive and negative portions averaged and compared by a differential amplifier, the output of which drives the meter. The signal conditioning provides an output which is dependent on light and dark periods (reflection and refraction periods), and hence the output is not sensitive to changes in the light intensity.

Temperature compensation is applied at the input of the differential amplifier. This compensation is necessary because the refractive index of the solution changes with temperature. The temperature is sensed by a thermistor located close to the sapphire prism on the sensing head.

An Electron-Machine elbow adapter (Fig. 3), supplied with the refractometer, was used to mount the sensing head on the process line. The adapter not only provides for physical attachment of the sensing head but also serves to direct the black liquor flow against the window. Thus, fresh liquor is continuously brought into intimate contact with the window. This is important because the index of refraction of the liquor is measured at the solution-window interface, and misleading readings could be obtained with a relatively stagnant film of liquor next to the window. The turbulence associated with the jet of liquor impinging on the window also helps to minimize the build-up of deposits.

It is necessary to provide cooling water for the scanning prism motor. There is also provision in the head for a steam purge nozzle for cleaning deposits from the window. In this evaluation, no use was made of any prism cleaning apparatus, and the purge tap was simply plugged. There was never any indication of deposits during the test period, and the window was found to be clean whenever the head was removed from the loop.

The unit is factory calibrated for each specific application and the manufacturer states that it normally requires no adjustment when installed. The unit which we evaluated was factory calibrated to read percent solids over the range of 45 to 75%, and the temperature compensation was set for a particular liquor. Manufacturer's specifications for the instrument are:

Range:	1.2 to 1.7 R.I. converted to indicate percent soluble solids within this range.
Accuracy:	± 1% meter span – standard meter spans 5% soluble solids 10% soluble solids 20% soluble solids 40% soluble solids.
Response time:	1.0 second.
Solution temperature range:	0 to 400°F.
Temperature compensation:	Continuous over full range, adjusted to compensate within ± 0.1% over ± 20°F. range specified by customer.

Although the instrument is factory calibrated, there are several adjustments provided in the control console. These are a ZERO and SPAN to calibrate the lower and upper ends of the meter scale, TEMP to provide the proper temperature compensation for the solution being measured, and AGC (automatic gain control) which insures that the circuit is operating in the proper range. The operating and service manual which is provided with the instrument provides simple instructions for making these adjustments. If a major change in the range is desired, the manufacturer recommends that the instrument be returned to the factory for recalibration since this requires a mechanical adjustment in the optical system.

No information is available as to the life expectancy of the various components in the instrument. However, the manufacturer recommends that the following spare parts be kept on hand: exciter lamp, lamp transformer, phototube, prism motor, encapsulated preamp module, fuses, and replacement printed circuit cards.

INSTRUMENT CHECKS

At the start of the program, several tests were made on the effect of environmental conditions on the refractometer. These included checks on the effects of line voltage variations, stray magnetic fields, and vibration. A twenty-four-hour stability check was also run. All of these tests were run with the loop filled with a sucrose solution but with no circulation.

In the test of the effect of line voltage on instrument response, the instrument was plugged into a 15-amp. powerstat. The output of the powerstat was monitored with a GE type P-3 voltmeter. The loop was filled with a sucrose solution, and the refractometer was adjusted to read about 53% solids with the temperature compensation disconnected. The solution was at a temperature of 35°C.

The line voltage was adjusted from 95 volts to 125 volts. The results of this test are shown in Table II.

TABLE II

EFFECT OF LINE VOLTAGE ON REFRACTOMETER OUTPUT

Line Voltage, volts	Refractometer Output Temp. Compensation On, % solids	Temp. Compensation Off, % solids
115	53.1	56.8
105	53.1	56.8
95	53.1	56.8
125	53.1	56.8
115	53.1	56.8

It can be seen that variation in the line voltage between 95 and 125 volts had no effect on the meter reading.

In order to check the effect of stray magnetic fields, a coil of wire connected to a 60-cycle line was used to generate the field, and this was moved to various locations around the probe and console. The only location of the field that affected the instrument output was at the top and side of the probe (sensing head). In this case, the reading was increased from 53.1 to 53.6%. Placing the field to the front of the sensing head (away from the flow loop) did not affect the reading. Locating the field near the console unit and the interconnecting cable did not affect the reading.

The vibration test was run by clamping a "Lightnin'" model F motor with an off-centered shaft to a flange on the refractometer adapter in the loop. Sufficient vibration was produced to be felt at both the refractometer sensing head and at the NUS probe mounted below. The vibration did not affect the refractometer reading.

The twenty-four-hour stability check was run by allowing the system to stabilize for two hours and then taking readings periodically. The temperature compensation on the refractometer was disconnected for this test. The reason for this was that the temperature compensation pot was adjusted for a black liquor while a sucrose solution was used for the test. The results are shown in Table III.

TABLE III

STABILITY CHECK ON REFRACTOMETER

Time, hr.:min.	Refractometer Output, % solids	Temperature, °C.
16:30	53.4	32.1
19:40	53.55	29.5
22:40	53.6+	27.8
8:05	53.7	27.0
9:00	53.7	27.0
10:15	53.7	27.2
12:00	53.7	27.6
13:00	53.7	28.2
15:00	53.7	28.7

In general, the stability of the output over a twenty-four-hour period is quite good. The slight increase in reading corresponds with a decrease in temperature as the sucrose solution responded to changes in ambient temperature. A decrease in temperature of the sucrose solution would increase its index of refraction and thus cause a higher output reading. Allowing for the changing temperature, it appears that the output did not change by more than 0.1% solids over the twenty-four-hour period.

INSTRUMENT CALIBRATION

The major part of the program regarding the EMC refractometer was devoted to an evaluation of the ability of this instrument to measure solids content of black liquor, and to study those factors which could affect its usefulness under industrial conditions. Since the instrument actually measures refractive index, it must be calibrated to give liquor solids content as an output. Any variable affecting the index of refraction (such as temperature or chemical composition) would affect the response of the unit. For this reason, the calibration procedures employed are important in interpreting the results of this study.

The output of the EMC refractometer is a reading on a meter having a linear scale ranging from 45 to 75% solids. This is because this instrument is intended for use in measuring high solids content black liquors and was factory adjusted to the refractive index range of such liquors. There are three adjustable potentiometers which are used to calibrate the instrument to read directly in percent solids; these are ZERO, SPAN, and TEMP. The ZERO pot serves to set a base line for the output meter. The SPAN pot adjusts the proportionality between the output reading and refractive index. The TEMP pot determines the amount of temperature compensation employed. These pots are twenty-five turn trim pots and are not susceptible to ready determination of pot settings. Thus, if a given pot is adjusted to a new value, it cannot be easily returned to its original setting.

In commercial operation, it is, of course, highly desirable to adjust the instrument so that the output (meter reading) corresponds to the true solids content of the liquor. In order to do this, a two-point calibration is used to set ZERO and SPAN. This should be carried out at a fixed temperature in the midrange of expected temperature variations. A known value sample in the low solids range is put in and the ZERO pot adjusted until the meter reading corresponds to the known value of the sample. Next, a known sample from the high end of the range is put in and the SPAN pot adjusted until the meter reading corresponds to the known value. Since adjustment of the SPAN can affect the offset, the procedure may have to be repeated. Note that this calibration procedure assumes an essentially linear relationship between the measurement (refractive index) and the percent solids. The TEMP pot is adjusted to hold the meter reading constant as the liquor is heated or cooled. Adjustment of the TEMP pot normally requires a readjustment of the ZERO also.

In this evaluation study, it was decided that more useful information could be obtained by minimizing pot adjustments than would be obtained by setting up the instrument to read solids directly for each liquor tested. The emphasis is then on instrument response to a wide range of variables (including solids content) rather than on deviations between meter reading and solids content. In particular, attention was focused on the items listed below.

1. A determination of whether or not, for a given liquor at a given temperature, a linear relationship exists between the meter output and the solids content of the liquor. If a linear relationship does exist, proper adjustment of the ZERO and SPAN pots would put the meter reading into a one-to-one correspondence with the liquor solids content.

2. A determination of the ability of the temperature compensation circuitry to handle the effect of temperature changes on the refractive index. For temperature compensation to be useful, it should not be necessary to adjust the TEMP pot at different solids levels.

3. A determination of the effect of liquor flow rate, system pressure, degree of liquor aeration, and the presence of undissolved solids on instrument response.

4. Examination of the relationship between chemical composition of the liquor and the refractometer response. In order to cover a wider range of variables than was possible in the flow loop, data from a laboratory refractometer were used to complement data from the EMC instrument regarding these effects.

The instrument, as obtained, was factory adjusted for a particular high-solids black liquor. The instrument checks discussed previously were made with the loop filled with a sucrose solution. The ZERO was adjusted at that time to obtain an on-scale reading. Initial runs were carried out with sucrose-Na_2CO_3 solutions of various proportions, and with temperature compensation connected and disconnected. At the start of these series of runs, the ZERO and SPAN pots were adjusted to keep the meter on scale over the temperature range employed. The SPAN pot adjustment was relatively small. At the completion of the sucrose-Na_2CO_3 runs, actual black liquor was used in the loop. Liquor C was the first liquor tested. The ZERO pot was adjusted to give a meter reading corresponding to a preliminary estimate of solids content. The TEMP pot was given one turn counterclockwise. The SPAN pot was not adjusted. These pot settings were then held constant for all remaining tests. The TEMP pot was given one turn clockwise at the completion of the program to restore its original setting.

BASIC INSTRUMENT RESPONSE

The initial runs were carried out with specific mixtures of sucrose and sodium carbonate. These were done to obtain some idea of the basic response of the instrument with simple one- and two-component solutions of organics and inorganics. The tests were carried out at several solids levels and over a wide range of temperatures. Both uncompensated and temperature-compensated outputs were obtained. The results for tests on sucrose solutions, solutions containing 3 parts of sucrose to 1 part of Na_2CO_3, and solutions containing equal parts of sucrose and Na_2CO_3 are shown in Fig. 5, 6, and 7.

There are several interesting features of these data. The offset due to temperature compensation is clearly shown. This is the reason a change in the TEMP pot would normally require a readjustment of ZERO. It also shows why the temperature compensation should be connected and the temperature held at the midpoint of the operating range when setting ZERO and SPAN. It is also clear that the instrument is overcompensating for the effects of temperature in these runs. This is not surprising since the TEMP pot was not set to provide the correct amount of compensation for these solutions. The uncompensated responses are nearly linear functions of temperature over the range tested. There is, however, a tendency for the output to drop more steeply at the high temperature end. The only exception to this behavior is the set at 40% solids of the equal parts sucrose-Na_2CO_3 solution. The reason for this anomalous behavior is not known. The degree of curvature of the uncompensated curves is not very extreme and a linear approximation over a 30°C. range would certainly appear adequate. In all cases, the compensated response has an S-shaped characteristic. The output rises more steeply over the midrange of temperatures than it does at either end. The reasons for this behavior are not known, but it should be noted that this occurs over a much wider temperature range than the 40°F. compensation range stated in the instrument specifications. The basic response of the instrument (general form of the curves) was not significantly affected by changes in organic-inorganic ratio.

The data in Fig. 5, 6, and 7 may be cross-plotted to show output <u>versus</u> solids content at fixed temperature levels. These results are shown in Fig. 8, 9, and 10. It can be seen that a linear relationship between output and percent solids does exist for all cases shown. In addition, the lines for a given liquor

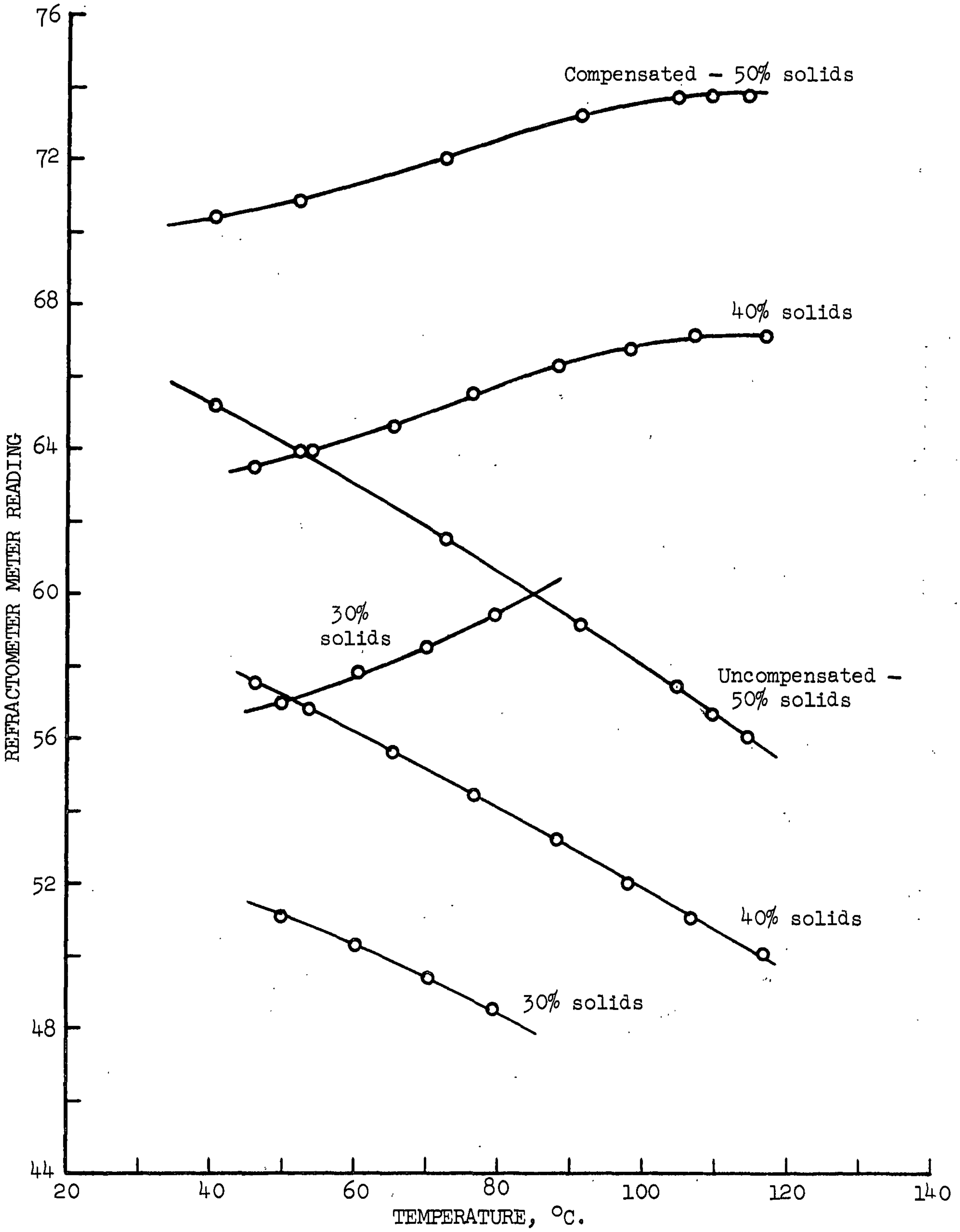


Figure 5. Refractometer Output on Sucrose Solution

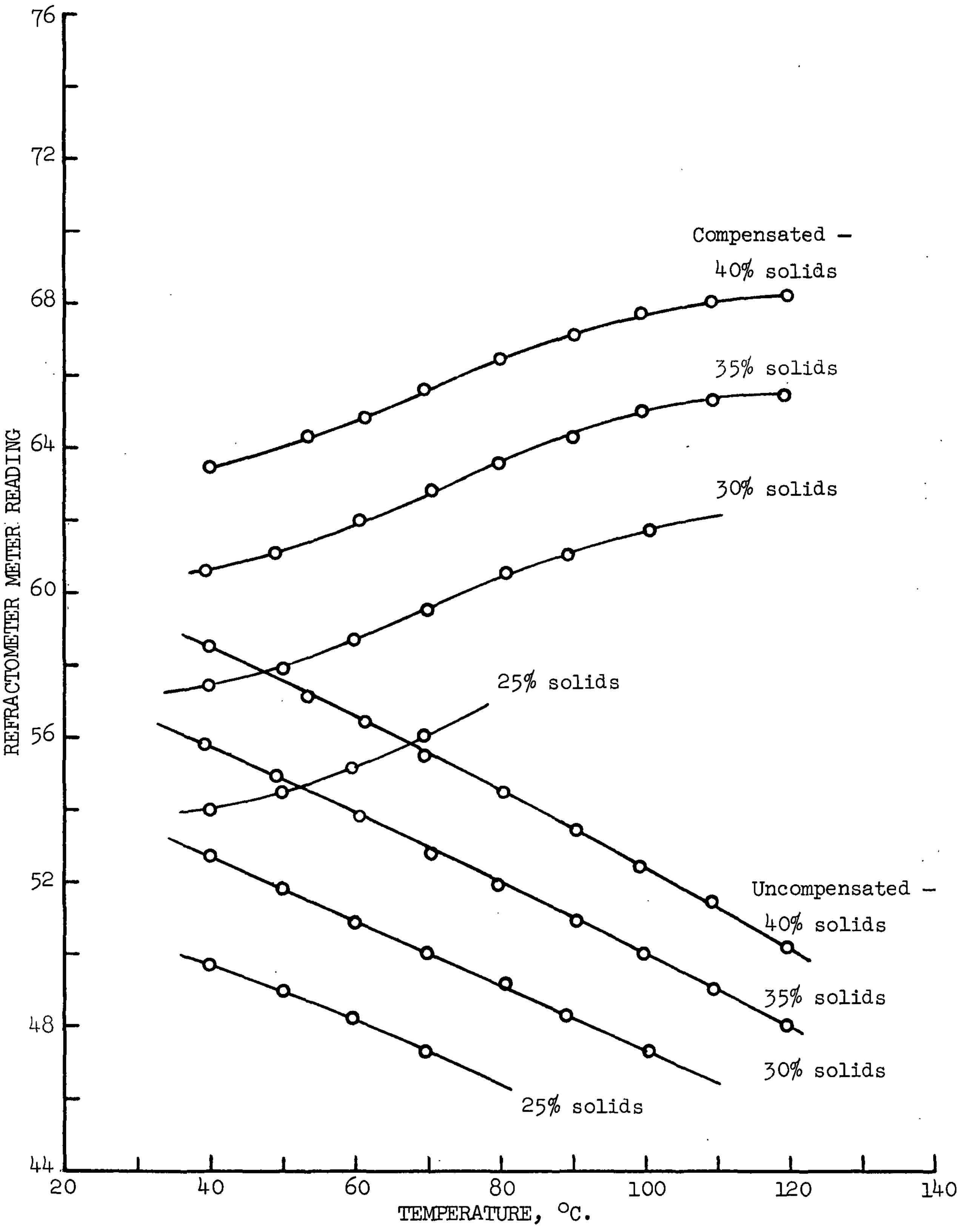


Figure 6. Refractometer Output on a 3:1 Sucrose-Na_2CO_3 Solution

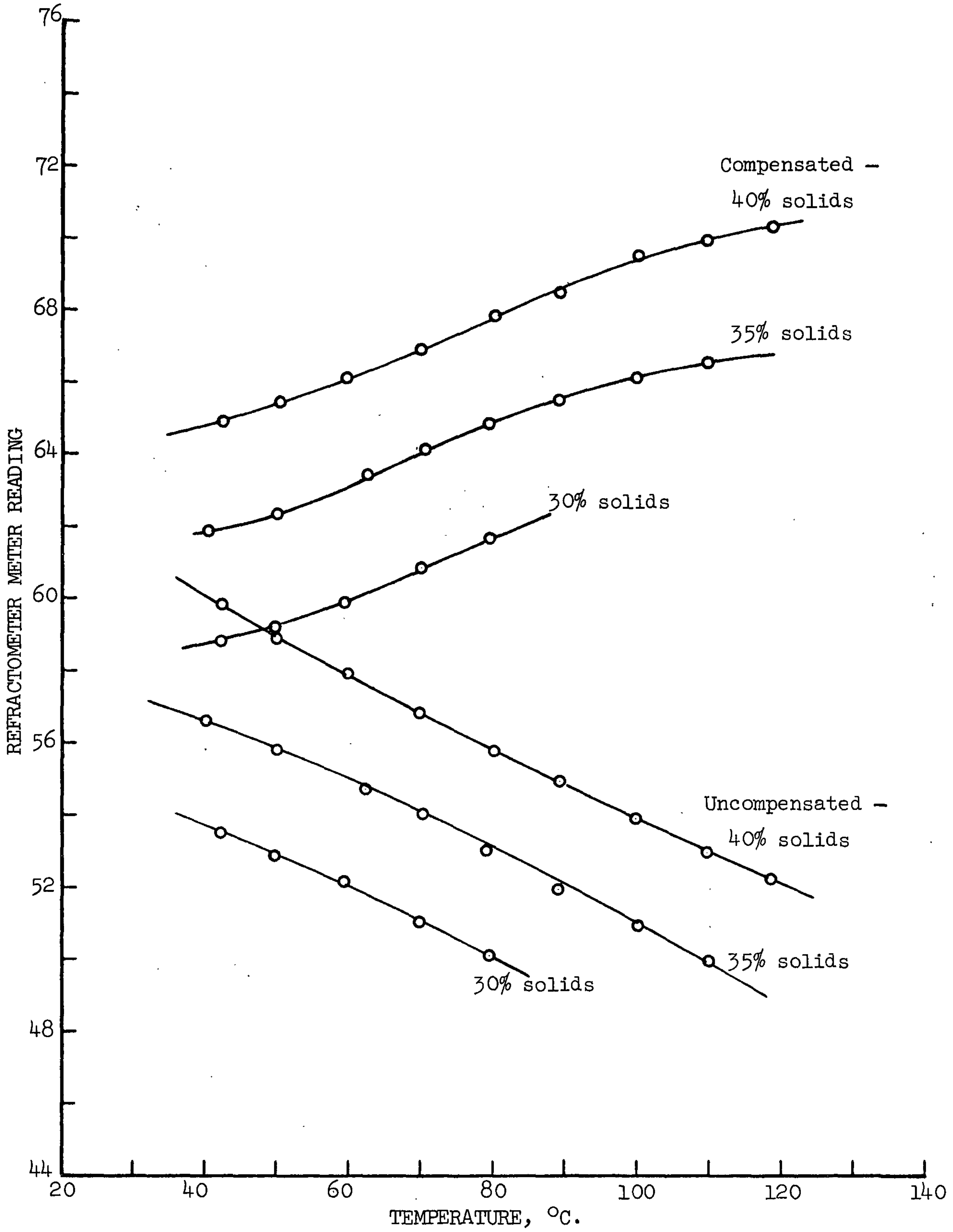


Figure 7. Refractometer Output for a 1:1 Sucrose-Na_2CO_3 Solution

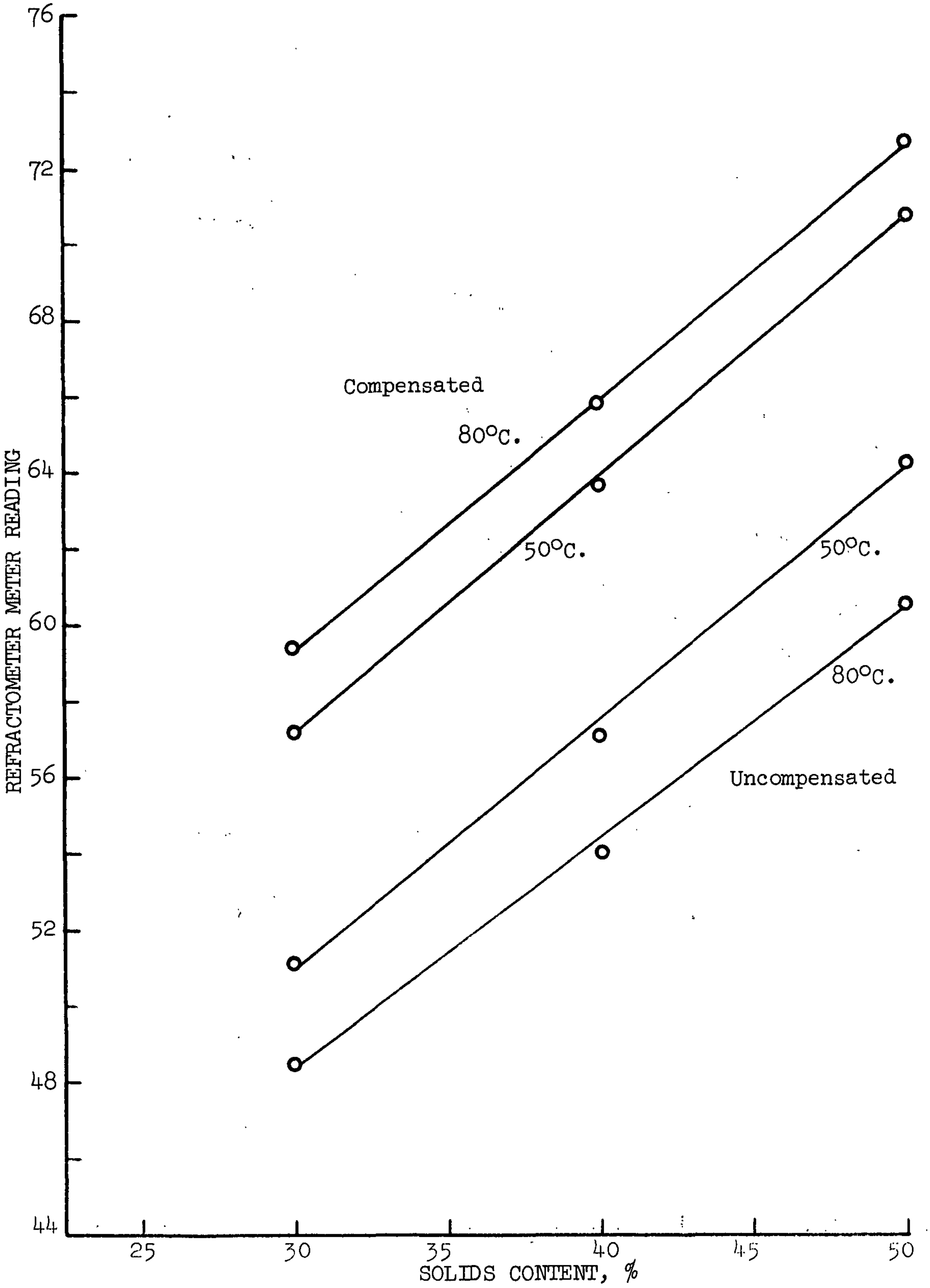


Figure 8. Refractometer Output vs. Solids Content – Sucrose Solution

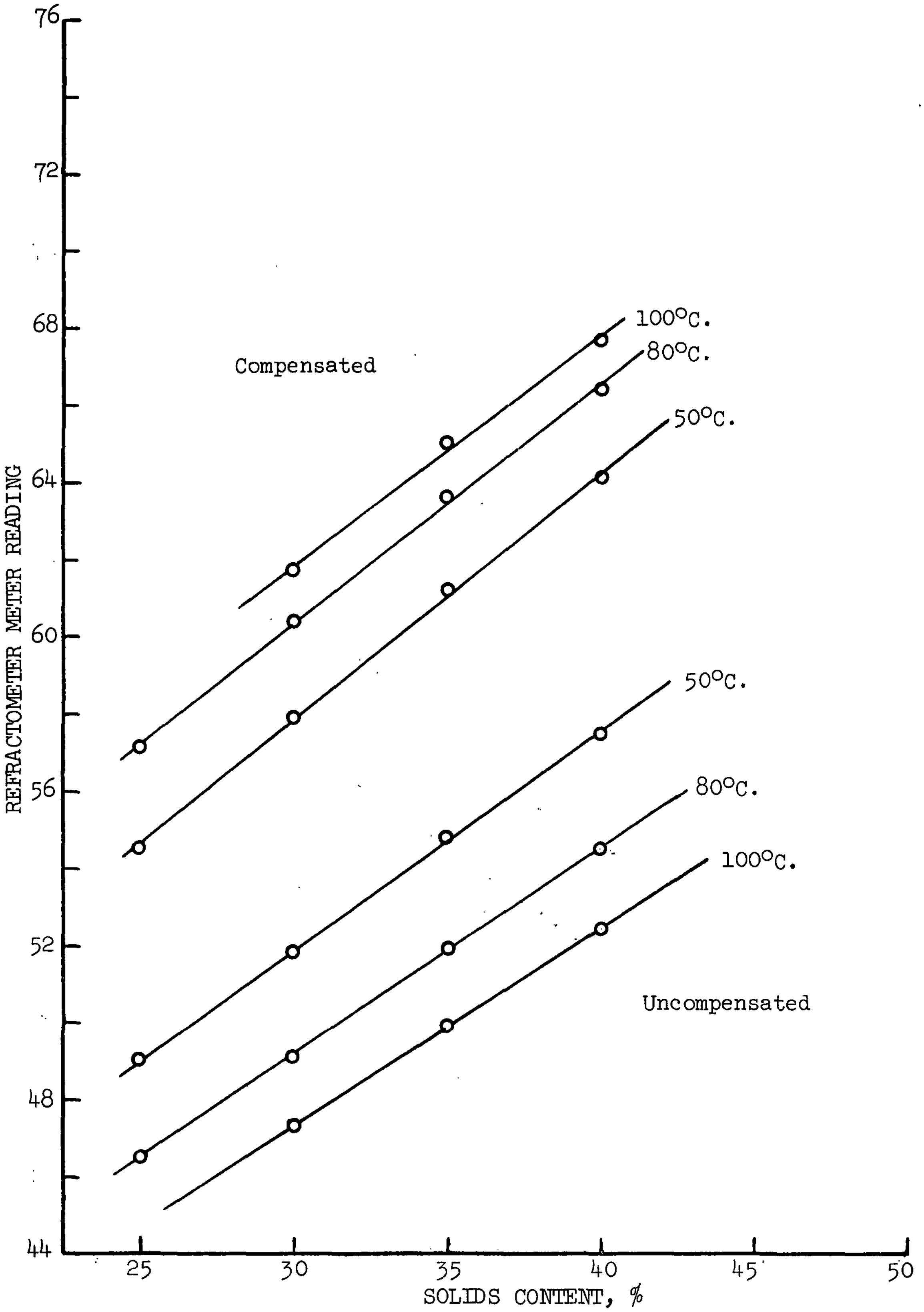


Figure 9. Refractometer Output vs. Solids Content – 3:1 Sucrose-Na_2CO_3 Solution

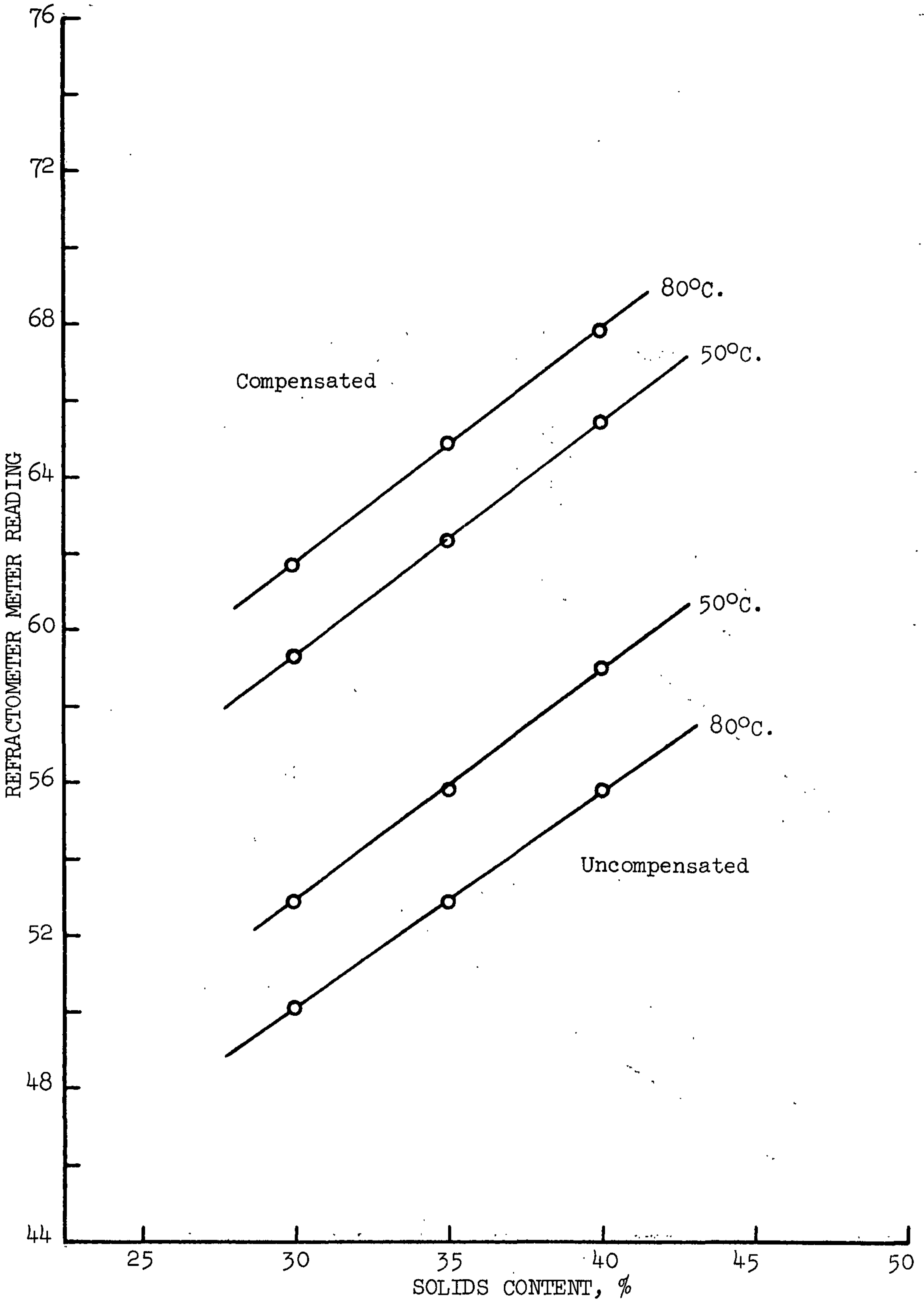


Figure 10. Refractometer Output vs. Solids Content – 1:1 Sucrose-Na_2CO_3 Solution

composition are all nearly parallel, regardless of temperature and whether the compensated or uncompensated response is used. Establishing linearity of response to output solids variation is basic to use of adjustable ZERO and SPAN pots for direct readout of percent solids. The parallel nature of the curves shows that the temperature effects can be separated out and handled by temperature compensation circuitry. It also shows that the temperature compensation circuitry does not introduce any nonlinearity into the response. In essence, these data confirm the adequacy of the controls provided (ZERO, SPAN, and TEMP) for calibrating the instrument to give a direct readout of solids content.

SPENT LIQUORS

Runs were carried out with the three different black liquors discussed previously. The temperature compensation circuitry was connected for all of these runs. The runs were carried out in the order Liquor C, then Liquor A, and finally Liquor B. The run with Liquor C was initiated immediately after the completion of the work with sucrose and Na_2CO_3 solutions. The ZERO pot was adjusted so that the meter reading corresponded to an initial estimate of the solids content in the loop. The SPAN pot was not adjusted. The TEMP pot was given one turn counterclockwise. No known changes were made in the pot settings during the remainder of the test program. Since the pots on the refractometer did not bear markings which would indicate what the settings were, it was not possible to verify that no changes were made.

A plot of the refractometer output (meter reading) versus liquor solids content is shown in Fig. 11 for Liquors A, B, and C. The line of direct correspondence between the meter reading and the percent solids is also shown. The indicated output is an average of the temperature-compensated output over the temperature range covered at each point. It is evident that a reasonably linear

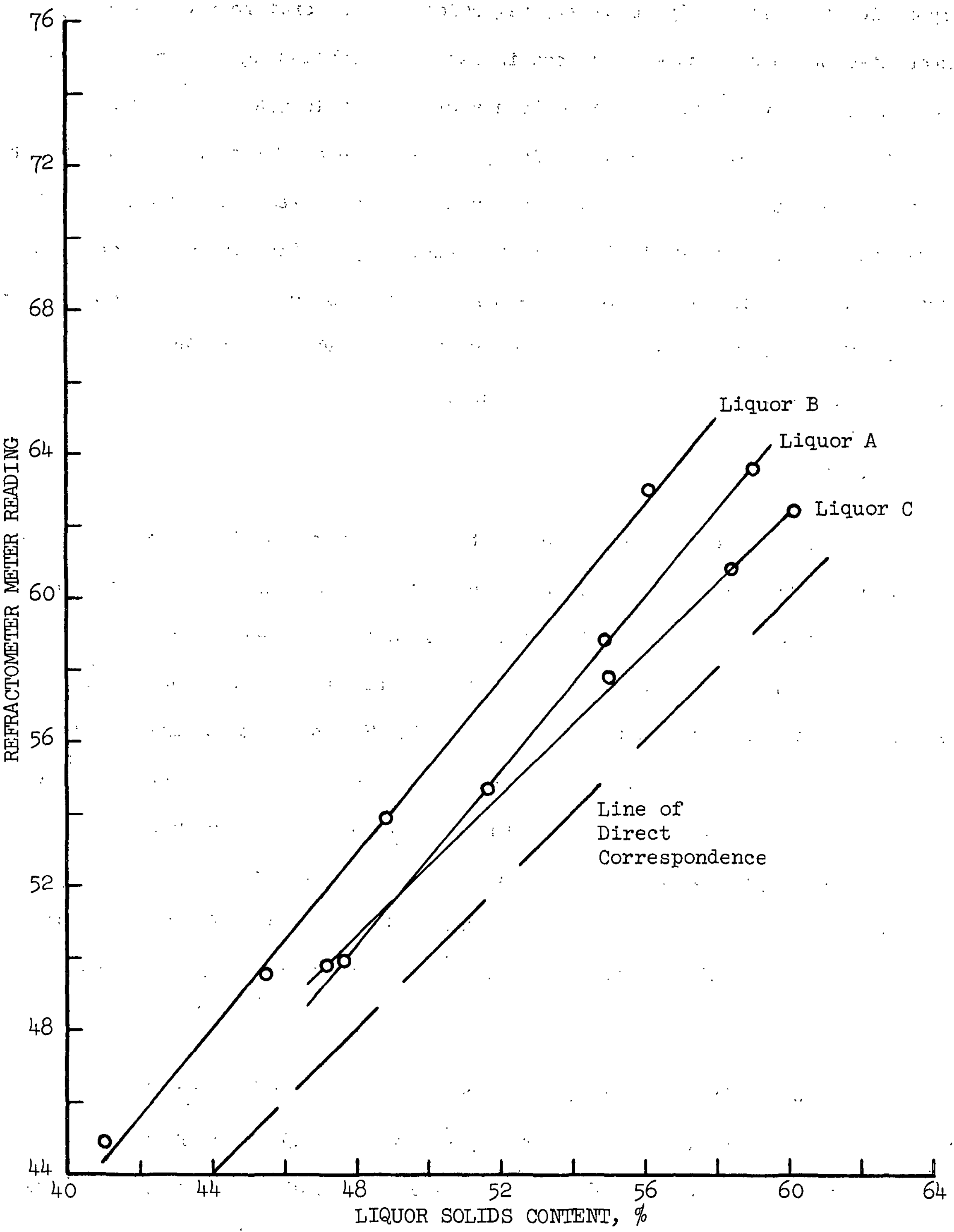


Figure 11. Refractometer Output vs. Solids Content for Black Liquors

relationship between refractometer output and solids content exists for all three liquors. This would indicate that proper adjustment of the ZERO and SPAN pots could shift any of these response curves into direct correspondence. It must be emphasized that the fact that no response curve is in direct correspondence is to be expected since the necessary calibration procedure to bring this about was not employed.

The fact that the response curves are not identical is primarily an indication of the effects of liquor composition, although some of the difference might be due to long-term drifts in the instrument, since the runs were carried out over a period of several weeks. A detailed discussion of composition effects will be given later; however, some features of these curves are of interest. The lines for Liquor A and Liquor B are nearly parallel. This is interesting because Liquors A and B were obtained from the same mill, and according to the data in Table I have similar chemical compositions. The differences between Liquors A and B could be taken care of simply by adjustment of the ZERO. Liquor C, which has a significantly inorganic content and much more sulfur, shows a different slope as well as an offset. The fact that the line for Liquor C nearly parallels the line of direct correspondence must be considered coincidental.

TEMPERATURE COMPENSATION

The ability of the instrument to provide temperature compensation was examined in some detail. At each solids content, the temperature of the liquor was varied over a range of about 40°C. and the compensated output recorded. The results of these tests are shown in Fig. 12 for Liquor C and in Fig. 13 for Liquor A. The small initial adjustment of the TEMP pot was made for Liquor C and it is clear that excellent compensation was obtained. There was no observable change in the meter reading over the temperature range from 80 to 110°C. for each of four

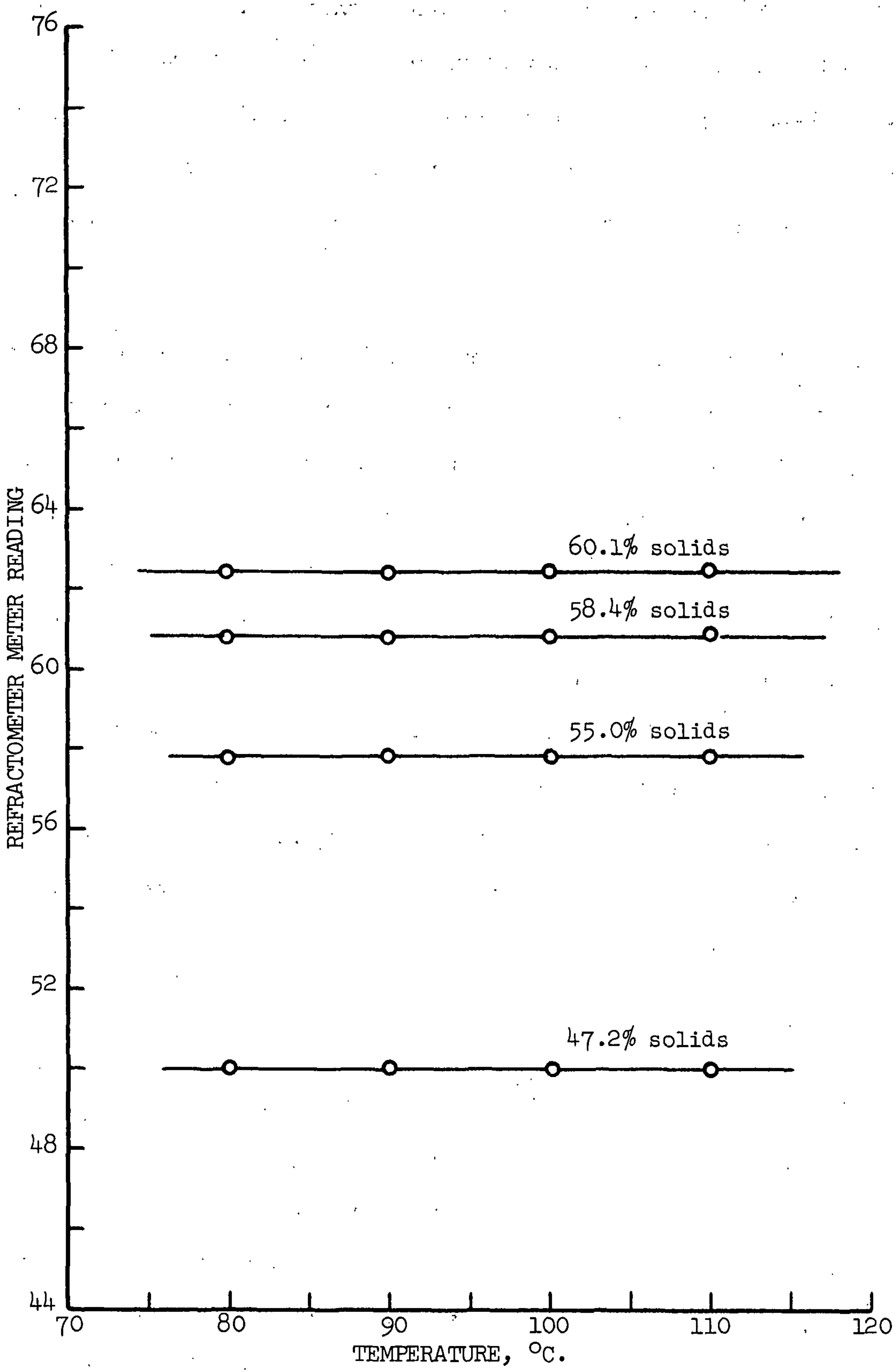


Figure 12. Temperature-Compensated Response for Liquor C

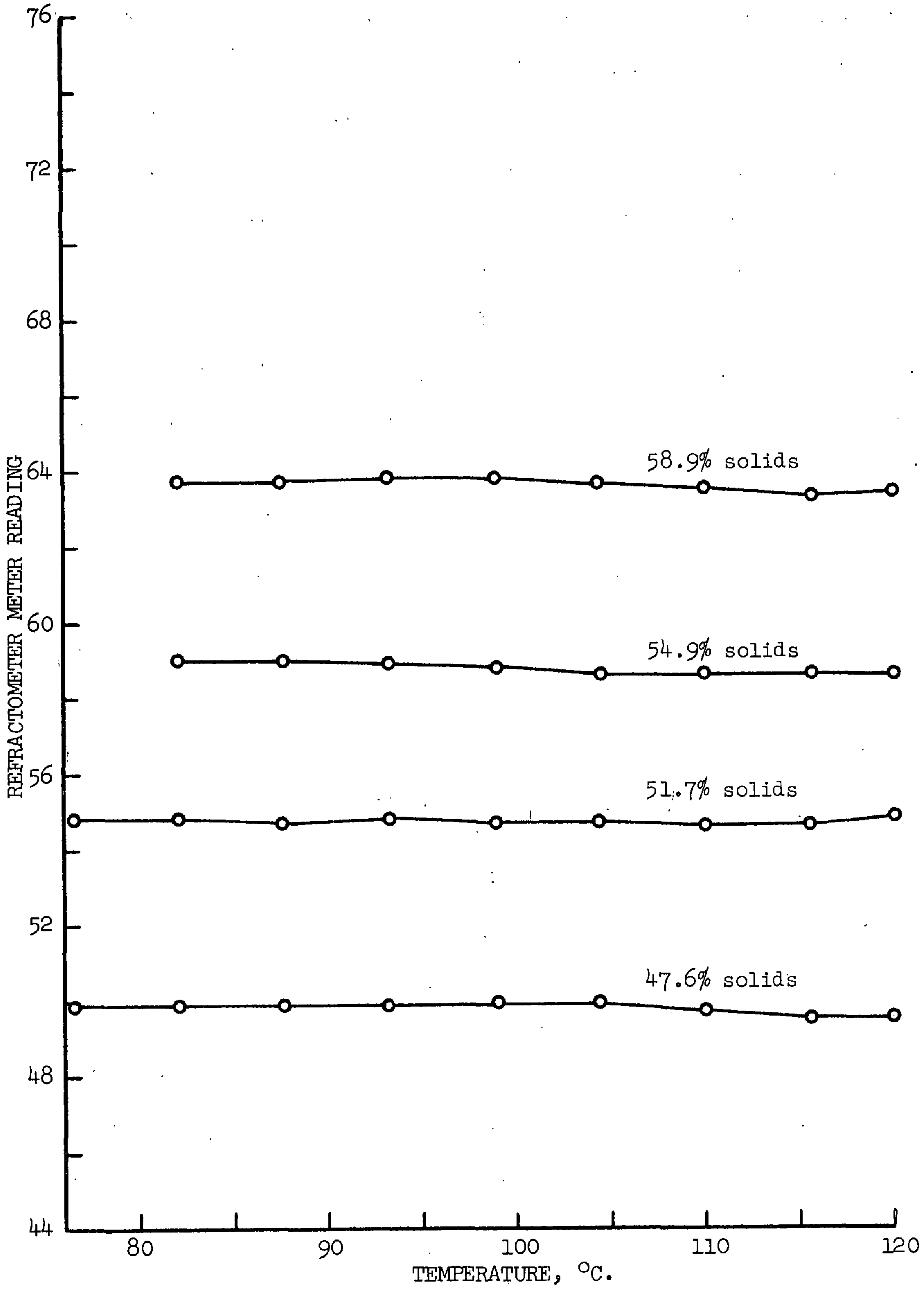


Figure 13. Temperature-Compensated Response for Liquor A

different solids levels. This would indicate that the amount of compensation needed is not a strong function of solids content. The data in Fig. 13 for Liquor A also show excellent temperature compensation. The largest difference in output at any solids level is 0.4 of a unit on the meter over a 40°C. temperature range. There is a slight tendency toward a drop in indicated output at the high temperature end. It should be noted that the TEMP pot was not adjusted for this particular liquor. This would indicate that the effect of temperature on refractive index of spent liquors is not a strong function of composition. This could be important from the standpoint of industrial use of the instrument, because a simple setting of the TEMP pot based on laboratory tests could be adequate. One final point should be noted in connection with the slight deviation present in Fig. 13. The temperature range over which the tests were carried out (40°C.) is nearly twice as great as the 40°F. range for which temperature compensation is claimed in the instrument specifications.

SYSTEM VARIABLES

The effect of several other variables on refractometer response was also examined. Flow rate through the refractometer adapter had no observable effect over the range from dead stop to 50 gal./min. The pressure in the system was varied from atmospheric to 60 p.s.i.g. with no observable effect on the reading. The refractometer also did not appear to be affected by the presence of air bubbles in the liquor. This was most apparent in initial runs with Liquor C when the centrifugal pump was used. In these cases, liquor aeration was severe enough to prevent sonic velocity readings, yet refractometer response was unaffected. Stopping flow, which would permit bubbles to rise, also did not affect the response. An attempt was made to see how the refractometer response was affected by undissolved solids. This was not successful. The main problem was finding a method for characterizing the amount of undissolved solids in a circulating loop. A second problem was a tendency for undissolved solids to plug the pump.

COMPOSITION EFFECTS

One of the main purposes of this investigation was to gain some insight into the effects of liquor composition on refractometer response. It is clearly shown in Fig. 11 that liquor composition can have a significant effect. At the same actual solids content, Liquor B gives a reading which is 2.6 units higher than Liquor A. This is of particular interest since both A and B were obtained from the same mill, only five weeks apart, and the data in Table I indicate only minor differences in composition. Based on the sulfated ash determination, the organic content of Liquor B is 67.4%, while that of Liquor A is 66.0%. In addition, there is a slightly higher degree of oxidation of the sulfur compounds in Liquor B. The response line for Liquor C is generally below the other two curves and has a smaller slope. Liquor C is from a different mill, has a smaller organic content and a higher sulfur content than A and B. Thus, it is not too surprising that its response curve has a different slope.

In order to gain greater insight into this behavior, the refractive index was measured as a function of solids content for several solutions including single components and mixtures. These data were taken on the laboratory refractometer described previously at a constant temperature of 28°C. Refractive index data were obtained for Liquor C and for solutions of Na_2CO_3, sucrose, a 50-50 mixture of Na_2CO_3 and sucrose, NaCl, Na_2SO_4, oxalic acid, and phenol. These data are shown in Fig. 14. It can be seen that Liquor C has the highest values of all the substances tested. Refractive index values fall off in the order Na_2CO_3, NaCl, sucrose, Na_2SO_4, and oxalic acid. Phenol has a high value for the solids content at which the measurement was made. Examining these data, there is no obvious ranking of

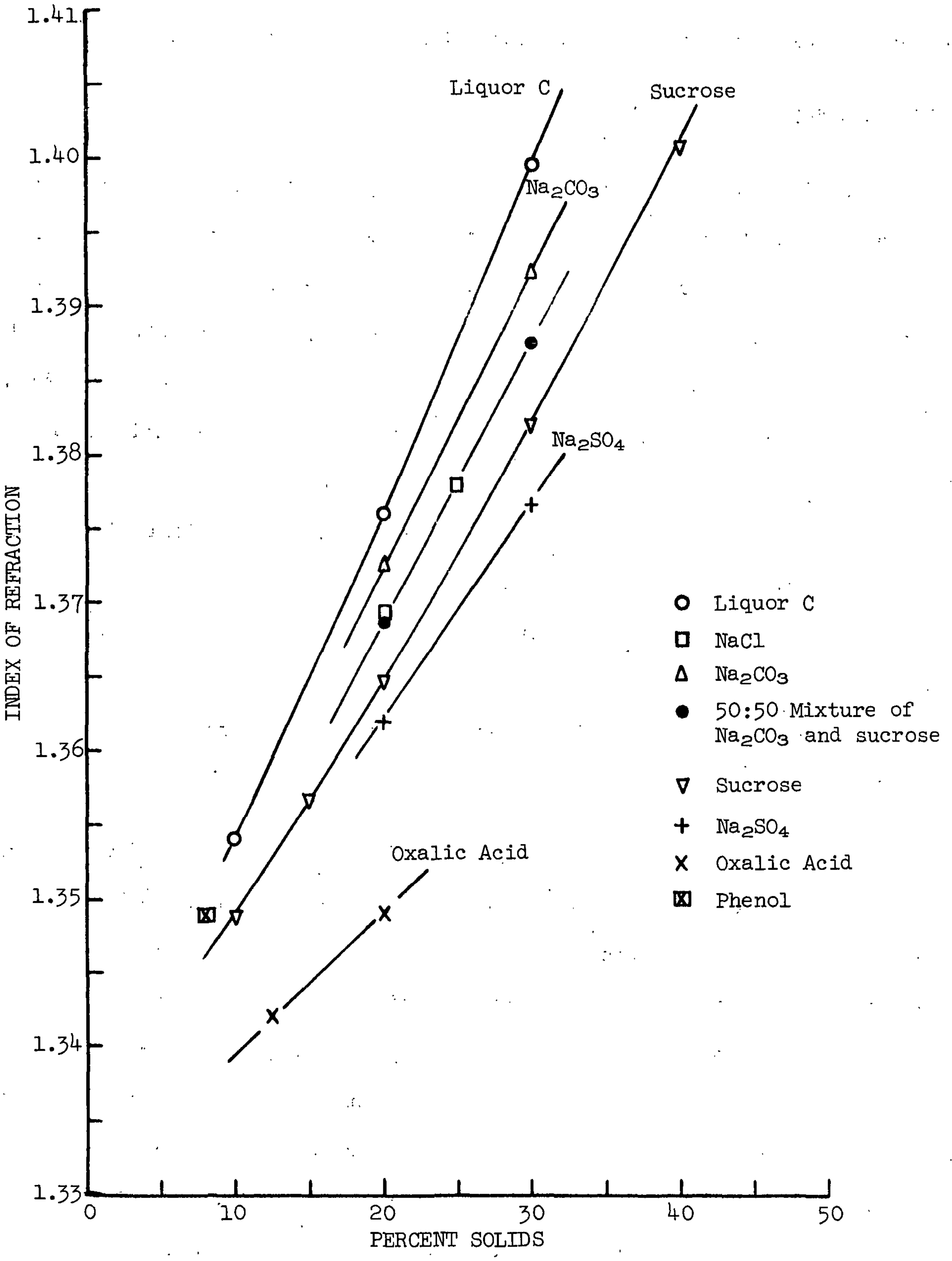


Figure 14. Refractive Indices of Various Solutions

organic and inorganic substances. Liquor C, which is mostly organic, has the highest refractive indices, sucrose is significantly lower, while oxalic acid is very low. Phenol, on the other hand, seems to have high values. The inorganic compounds also vary considerably. Na_2CO_3 is nearly as high as the black liquor, while Na_2SO_4 is much lower.

Further insight into composition effects can be gained by examining the behavior of mixtures. This is most easily done with solutions of two pure components, but it is also enlightening to look at the addition of various amounts of a pure material to black liquor. Both approaches were used in this study. Refractive index data for various mixtures of sucrose and Na_2CO_3 at both 20 and 30% solids are given in Fig. 15. It is seen that refractive indices of the mixtures lie between those of the pure substances. However, the curves are not linear. This would mean that a simple linear combination rule based on the addition of the fraction of the refractive index of each pure substance would not predict the refractive index of mixtures. Refractive index data for mixtures of black liquor with sucrose and sodium chloride are given in Fig. 16. The data for liquor-sucrose mixtures are at 60% solids. For solubility reasons, the data for liquor and salt are at 25% solids. In both cases, the refractive index increases as the proportion of liquor increases. This is not surprising since the data in Fig. 14 showed that both sucrose and NaCl solutions had lower refractive indices than Liquor C at the same solids content. With liquor and NaCl, a linear relationship is observed, while a curved relation exists with liquor and sucrose. In general, it appears that the refractive index of mixtures lies between the indices of the pure compounds, but a linear combination of each component is the exception rather than the rule. The tendency toward nonlinear combinations (indices of each component not additive) seems to increase as the solids content increases.

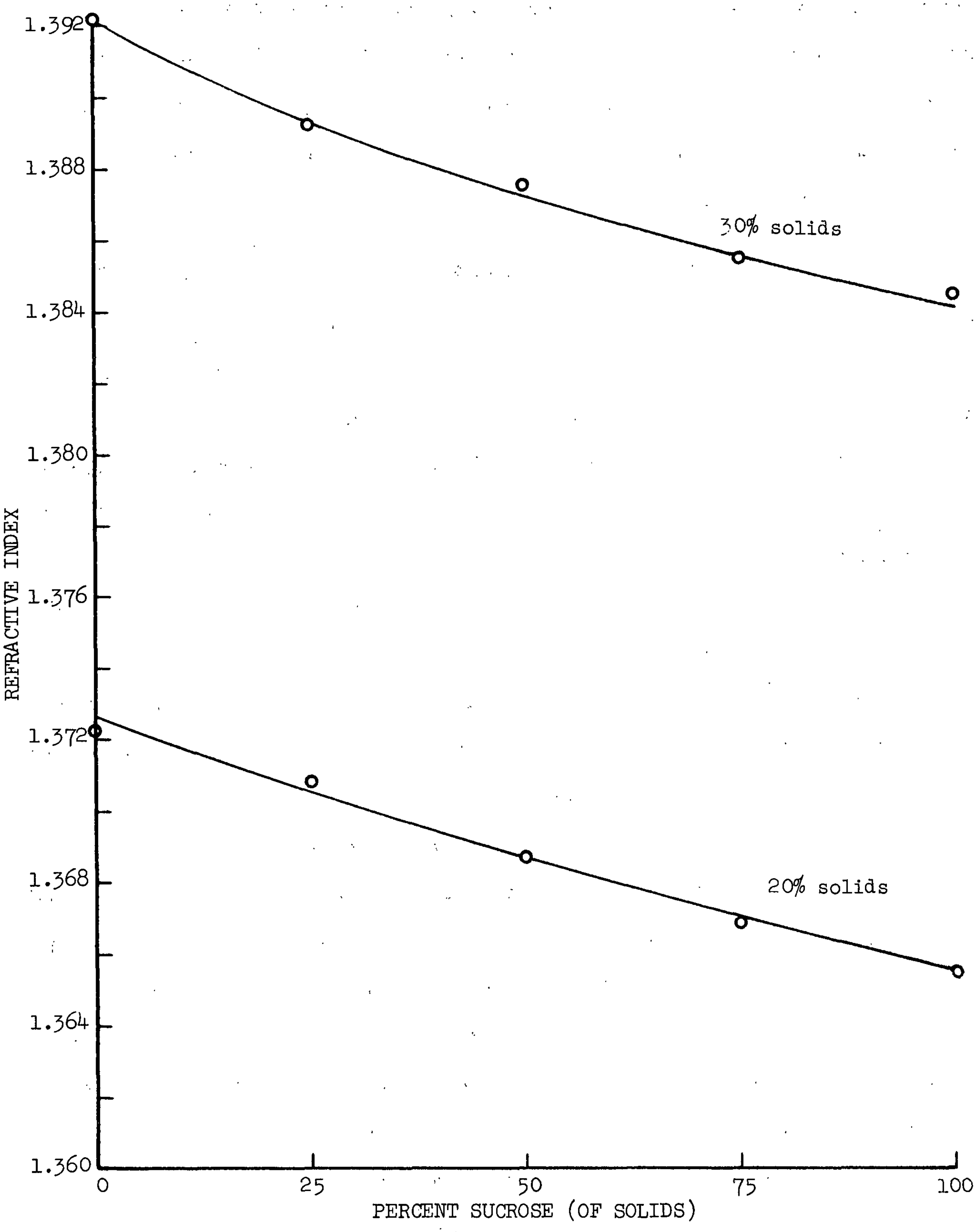


Figure 15. Refractive Indices of Sucrose-Na_2CO_3 Solutions

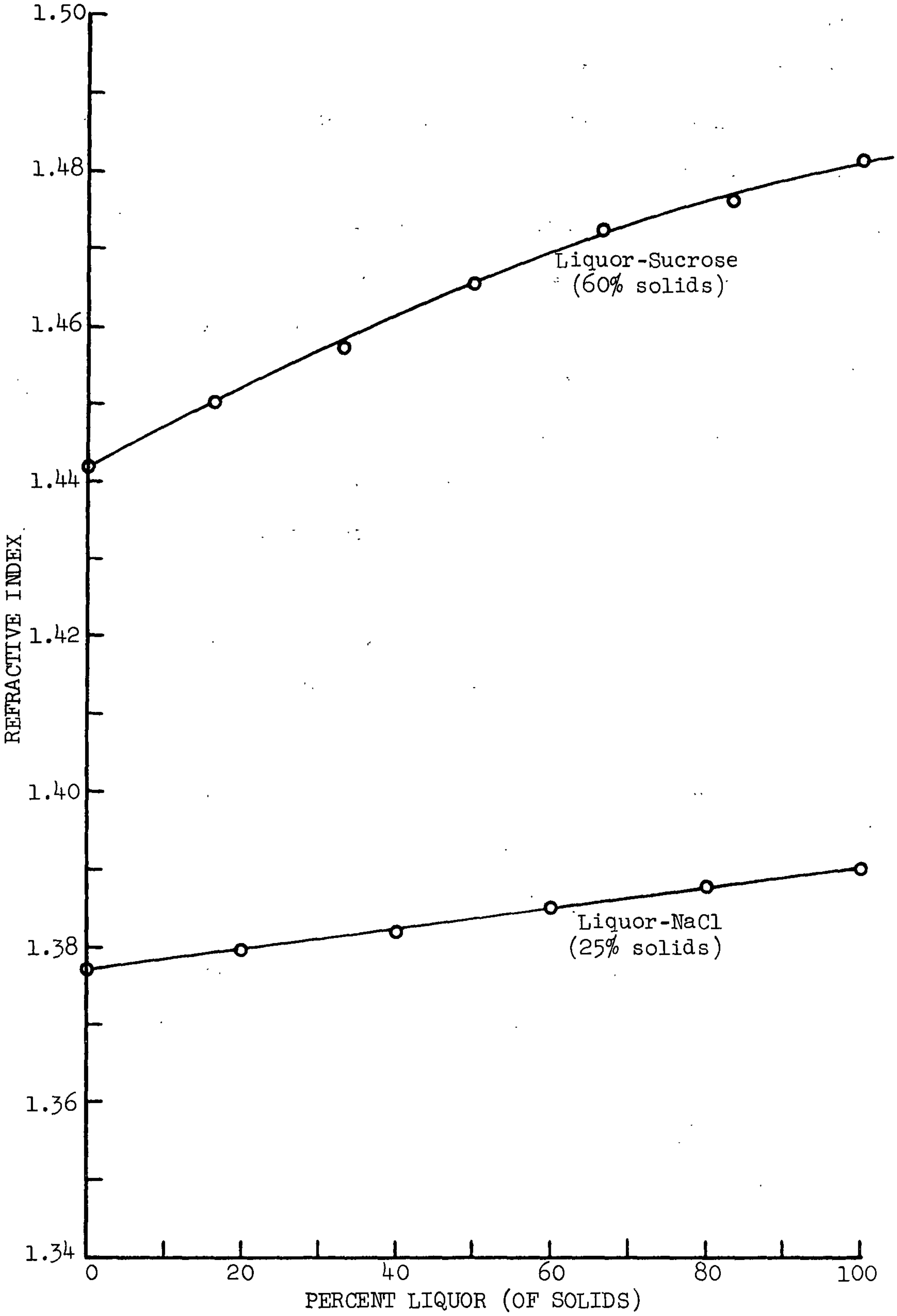


Figure 16. Refractive Indices of Mixtures of Black Liquor and Other Substances

It is impossible to make any quantitative predictions about the effect of liquor composition on refractive index. Black liquor is simply too complex to permit this. The organic material originates from lignin and carbohydrates in the wood and is at least partially substituted with sodium and sulfur. In addition, there will remain a certain amount of cooking chemicals. Thus, the composition (and refractive index) of the black liquor would depend on wood species as well as cooking conditions. The most simplistic treatment of liquor would have to consider it made up of a ligneous fraction (aromatics), a carbohydrate fraction (sugars), and the inorganics (NaOH, Na_2CO_3, Na_2S, etc.). If it is assumed that black liquor can be described in this manner, then the data in Fig. 14, 15, and 16 would seem to indicate that the high refractive indices of black liquor originate mainly with the ligneous material. The inorganics tested and sugar (sucrose) all lie below the black liquor line. Phenol, on the other hand, an aromatic compound, lies almost on the black liquor curve. A means of correlating refractive index data for organic compounds by means of an $\underline{R}$ factor is described in Table IV. Higher $\underline{R}$ values give higher refractive indices. It should be noted that the presence of double or triple bonds, aromatic structures, and rings tends to increase $\underline{R}$ values. It is especially interesting to note the high $\underline{R}$ values associated with sulfur bonds.

The following generalizations, although by no means proved, are consistent with all of the data examined. An increase in the inorganic content of a black liquor will tend to lower the refractive index at a given solids content. An increase in organically attached sulfur will tend to increase the refractive index. The main contributor to the refractive index of black liquor is of ligneous origin.

TABLE IV

REFRACTIVE INDEX OF ORGANIC COMPOUNDS[a]

The following equation can be used to correlate refractive indices of organic compounds.

$$R = \frac{(n^2 - 1)}{(n^2 + 2)} \frac{M}{d}$$

where:

$\underline{n}$ = index of refraction,
$\underline{M}$ = molecular weight, and
$\underline{d}$ = density, g./cc.

$\underline{R}$, in units of cc./mole, is additive for bonds which are present. A partial tabulation follows:

C	2.591	C_6H_5	25.463	ethylenic bond	1.575
H	1.028	$C_{10}H_7$	43.00	acetylenic bond	1.977
=O	2.122	>S	7.729	4-member ring	0.317
>O	1.643	=S	7.921	3-member ring	0.614
OH	2.553				

---

[a] Taken from "Handbook of Chemistry and Physics," 4th ed., C. D. Hodgman, ed., Cleveland, O., Chemical Rubber Publishing Co., 1958.

Composition effects would certainly be an important factor in the reliability of refractometers in the field since changes in composition could be read as changes in solids content. It appears very likely that a change in organic/inorganic ratio would change the refractometer response. Wood species and pulp yield would also play an important role. The effects of chemical composition re-emphasize the need for proper calibration during use.

REFRACTIVE INDEX MEASUREMENT

An interesting observation was made during the refractive index measurement with the laboratory refractometer. There are two methods for determining refractive index with such a refractometer. In the first method, an incident beam of light shines through a thin film of the solution, and the beam of light emerging on the other side is observed through a lens system. This lens system is rotated until the critical angle appears at a set of cross hairs in the eyepiece. What the observer sees is a circle with the cross hairs at the center, and when set properly, the lower half of the circle is dark and the upper half is light. The only difference in the second method is that the incident beam of light is on the same side of the solution as the observation lens system. This permits the observation of opaque solutions, and this is the same type of arrangement as is used in the EMC refractometer. In observing the critical angle of black liquor by the second method, it becomes immediately obvious that the line of separation between dark and light is much less distinct than it is with transparent solutions using the first method. In fact, when viewing through the eyepiece, it is sometimes difficult to see the separation unless one sweeps back and forth through the critical angle. It is difficult to quantitatively determine what effect this has on the EMC refractometer precision; however, it does imply that the refractive index might not be determined as precisely as is possible with transparent solutions.

ON-LINE CALIBRATION

The basic response of the unit, showing a linear relationship between refractometer output and solids content along with the demonstrated capability to provide temperature compensation, indicates the potential of the refractometer for reliable measurement of black liquor solids content in industrial use. The basic requirement affecting reliability is the ability to maintain the proper calibration of the instrument in the industrial environment. Accordingly, it is necessary to consider the question of calibration in some detail.

There would appear to be three major factors which could cause significant deviations between indicated output and actual solids content for an instrument which is initially properly calibrated:

1. Build-up of deposits on the window,
2. Long-term drifts in the instrument, and
3. Changes in the chemical composition of the liquor.

Any solids which deposit on the window will interfere with proper measurement because the optics will tend to see the deposits rather than the liquor. The proper action to take in this case is to clean the window and not adjust the instrument calibration to compensate. Changing the calibration could cause erroneous results. In the extreme case, solids deposits could completely isolate the liquor from the optics. If solids deposits are found to cause trouble, a prism cleaner should be installed and operated on a regular schedule. Provisions should also be made for isolating the instrument from the flow line for inspection as needed.

Any long-term drifts in instrument response due to changes within the instrument should be corrected by changing the calibration pot settings. No direct evidence for such drifts was obtained in these tests. The instrument is stable for at least 24 hr., but stability tests over a period of weeks were not run. If the drift is only in the zero, adjustment of the ZERO pot will correct for the drift. This would require only a single determination of solids content. The problem is more severe if there is drift in range or span, since a two-point calibration is required to set ZERO and SPAN pots. If instrument drift is a more serious problem than liquor composition variability (which is unlikely), it may be simplest to periodically recalibrate the refractometer off-line with known solutions.

Changes in chemical composition of the liquor are probably the major reason for refractometers getting out of calibration. The degree to which composition changes cause difficulty depends on the detailed effect of composition on response. It is possible to distinguish three cases:

1. A composition change that affects the actual value of refractive index at a given solids level (hence the meter zero) but has little or no effect on the change in refractive index per unit change in solids (slope of index _vs._ solids curve or span) or the effect of temperature.

2. A composition change that affects the slope and intercept of the refractive index-solids curve (hence zero and span) but which does not affect the temperature coefficient.

3. A composition change that affects the entire refractive index _vs._ solids curve and the temperature coefficient (hence zero, span, and temperature compensation).

The first case can be handled by a simple adjustment of the ZERO pot. The second involves adjustment of both ZERO and SPAN pots and hence a two-point calibration. The third requires simultaneous adjustment of ZERO, SPAN, and TEMP.

The first case is readily adapted to on-line calibration since it involves single-point calibration. It is necessary only to take a sample of liquor while recording the output reading, run an analysis of the liquor solids content, and then adjust the ZERO pot to make up the difference between the indicated output and the analytical solids content. If the effect of composition change is mainly to cause a zero shift, this procedure would be adequate.

The second case is more complicated because adjustment of the ZERO and SPAN pots requires a two-point calibration, and thus liquor analyses should be run at both the low and high ends of the concentration range. This is not a very suitable procedure for on-line calibration since it requires a significant change in liquor solids content and freedom to vary liquor solids does not usually exist in a mill situation. The time lag in analyzing solids content in liquor samples also would cause problems in a two-point on-line calibration. There are two alternatives which can be used here: Either the instrument would be calibrated off-line, adjusting ZERO and SPAN, or it would be calibrated on-line, adjusting only the ZERO. In the first case, two batches of liquor of known solids content would be used in the normal calibration procedure. The second approach could be used if the change in response-curve slope was small, or if the solids content did not change much. Under these conditions, only small errors result if the ZERO is kept in adjustment. There is a hazard in this second approach. Over a period of time, the SPAN setting may differ appreciably from the proper value, and large errors could occur if there were large changes in solids content. For example, if a liquor is being monitored at a normal solids content of 65%, and the calibration is maintained by ZERO adjustment only, there could be considerable error at solids contents on either side of 65% (such as at 55% solids for automatic alarming purposes). If ZERO adjustment calibration is used, the instrument should be taken off-line occasionally for ZERO and SPAN adjustment.

In the third case, where composition affects the temperature coefficient also, the instrument must almost certainly be taken off-line for recalibration. The interaction between ZERO and TEMP settings and the need to cycle temperature practically requires off-line operation. Fortunately, the indications of this test program were that composition changes had a relatively small effect on the amount of temperature compensation needed. It would appear that the TEMP setting should be checked occasionally when the instrument is pulled off-line for two-point ZERO and SPAN adjustment.

The following summary statements regarding calibration of the refractometer can be made.

1. The absolute accuracy of the refractometer in reading percent solids is determined primarily by the accuracy of the analytical procedure for solids measurement employed in calibrating the refractometer.

2. The only suitable method for on-line calibration is adjustment of the ZERO pot based on single-point analysis of solids content.

3. The instrument should periodically be removed from the line for two-point ZERO and SPAN adjustment and to check on the ability to compensate for temperature variations.

4. The calibration should not be changed to handle the effect of solids deposits on the window. The window (prism) should be cleaned instead.

NUS VELOCIMETER

PRINCIPLE OF OPERATION

The NUS velocimeter provides an indirect determination of black liquor solids content through measurement of the velocity of sound in the liquor. The instrument operates on the "sing-around" principle for measuring sonic velocity. A sound velocity transducer transmits a sound pulse through the solution under test to a reflector which is separated from the transducer by a fixed distance. The pulse is then reflected back to the transducer which also serves to detect the pulse. After detection of the reflected pulse, a new pulse is transmitted and the sequence repeated. The result is a train of pulses at a frequency ("sing-around" frequency) which is dependent on the sonic velocity of the solution.

The "sing-around" period (time from the start of one pulse to the start of the next) is determined by the sum of the pulse transit time (path length divided by sonic velocity) and the electronic delay time (time between detection of one pulse and transmission of the next). This results in the following equation relating the sonic velocity to the sing-around frequency.

$$c = \frac{Af(1 + \alpha t)}{7 - Bf \times 10^{-6}} \qquad (4)$$

where

$\underline{c}$ = sonic velocity in meters per second,

$\underline{A}$ = sonic path length in meters,

$\underline{B}$ = electronic delay time in microseconds,

α = coefficient of thermal expansion of the velocimeter probe material, $^{\circ}C.^{-1}$,

$\underline{t}$ = temperature, °C., and

$\underline{f}$ = "sing-around" frequency, hertz.

The factor of 7 appears in the denominator because the actual frequency is electronically multiplied by 7 in the instrument.

SPECIFICATIONS

The manufacturer gives the following specifications on the Model 6161-139 Sonic Solution Monitor which was tested in this program.

Sound Velocity Range: 900 to 2250 meters/sec.

Operating Temperature Range:

Probe: 20 to 120°C.

Electronics: 0 to 50°C.

Output:

Sound velocity: 4-20 milliamperes and 0-10 volts.

Temperature: 4-20 milliamperes and 0-10 volts.

Repeatability:

Sound velocity: ± 0.025%.

Temperature: ± 0.05°C.

Temperature Compensation:

First-order correction of sound velocity for temperature variations to within 0.1°C. Compensation coefficient is continuously adjustable from 0 to ± 10.00 meters/second/°C.

Probe Material: 316 SS, platinum, and teflon.

DESCRIPTION OF INSTRUMENT

The instrument consists of a sensing probe (Fig. 17) which mounts on the process line and a control console (Fig. 18). The probe contains the sonic velocity transducer, while the control console contains the electronics and signal-conditioning equipment. The instrument also measures the temperature of the solution under test. This measurement can be fed to appropriate circuits to provide a sound velocity signal which is compensated for temperature over a given range.

Figure 19 is a simplified block diagram showing the basic operation of the instrument. The probe is inserted into the process solution and the transducer transmits and receives sonic pulses. In the control unit, the sound velocity electronics operate to produce the "sing-around" frequency. The S-V electronics also monitor the attenuation of the sound pulse in passing through the solution. The frequency and attenuation are examined and the information passed to the NORMAL and OUT OF RANGE lamps on the front panel. The outputs from the S-V electronics are the "sing-around" frequency and the attenuation signal (essentially amplitude ratio of detected and transmitted pulse). The attenuation signal is routed to the front panel meter where it can be read. The "sing-around" frequency then passes through the SOUND VELOCITY RANGE selector (apparently a frequency divider) to a scaling counter. In the scaling counter, the sound velocity signal is offset by the value set on the LOW END ADJUST switches. These latter are set up to operate off an octal code. The digital output of the scaling counter (essentially the digital overflow beyond the offset) is routed to a digital-to-analog converter. The resulting analog signal is sent to the meter where it can be read as sonic velocity deviation and is also routed to the compensation electronics.

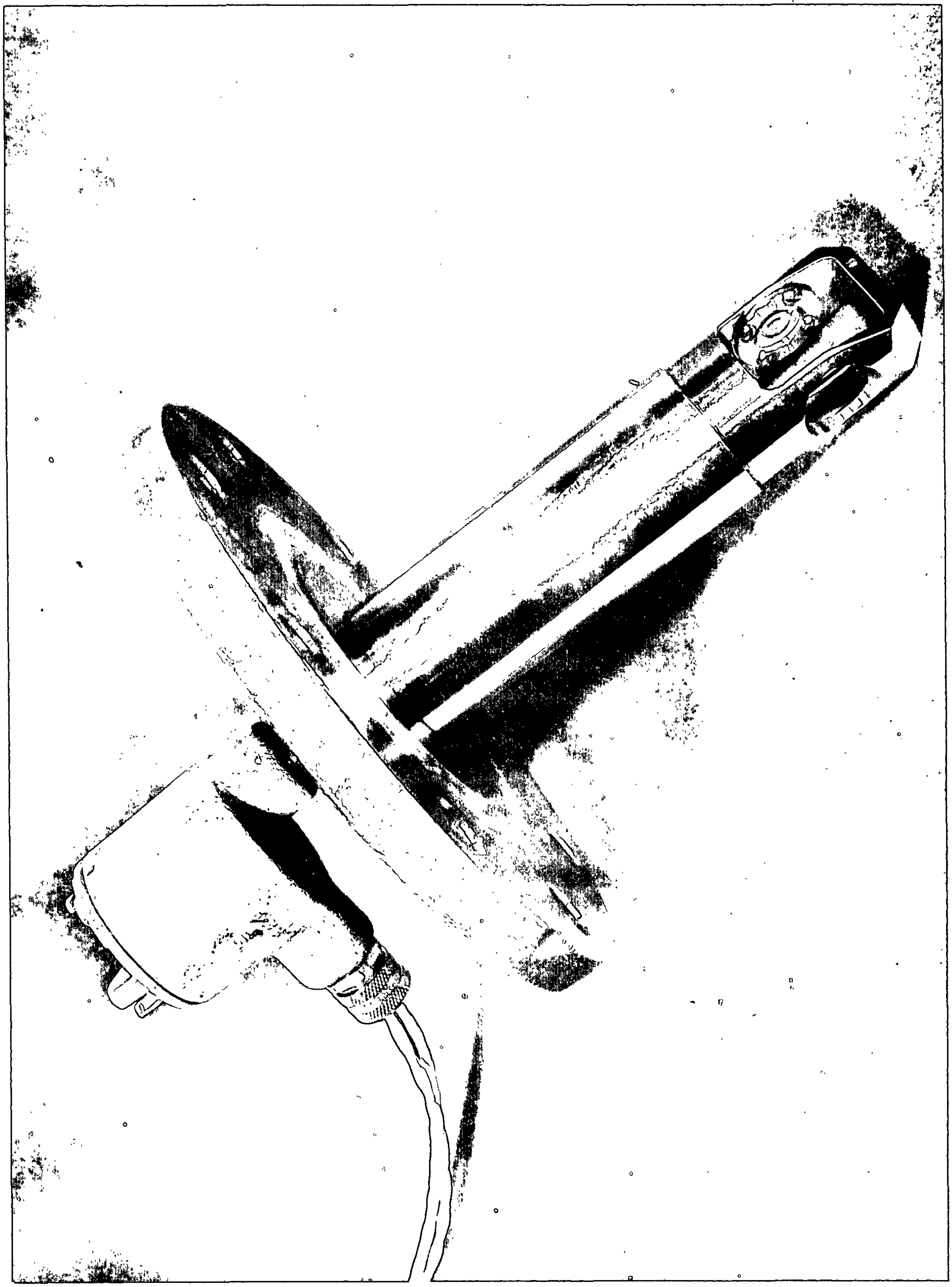


Figure 17. Photograph of NUS Sensing Probe

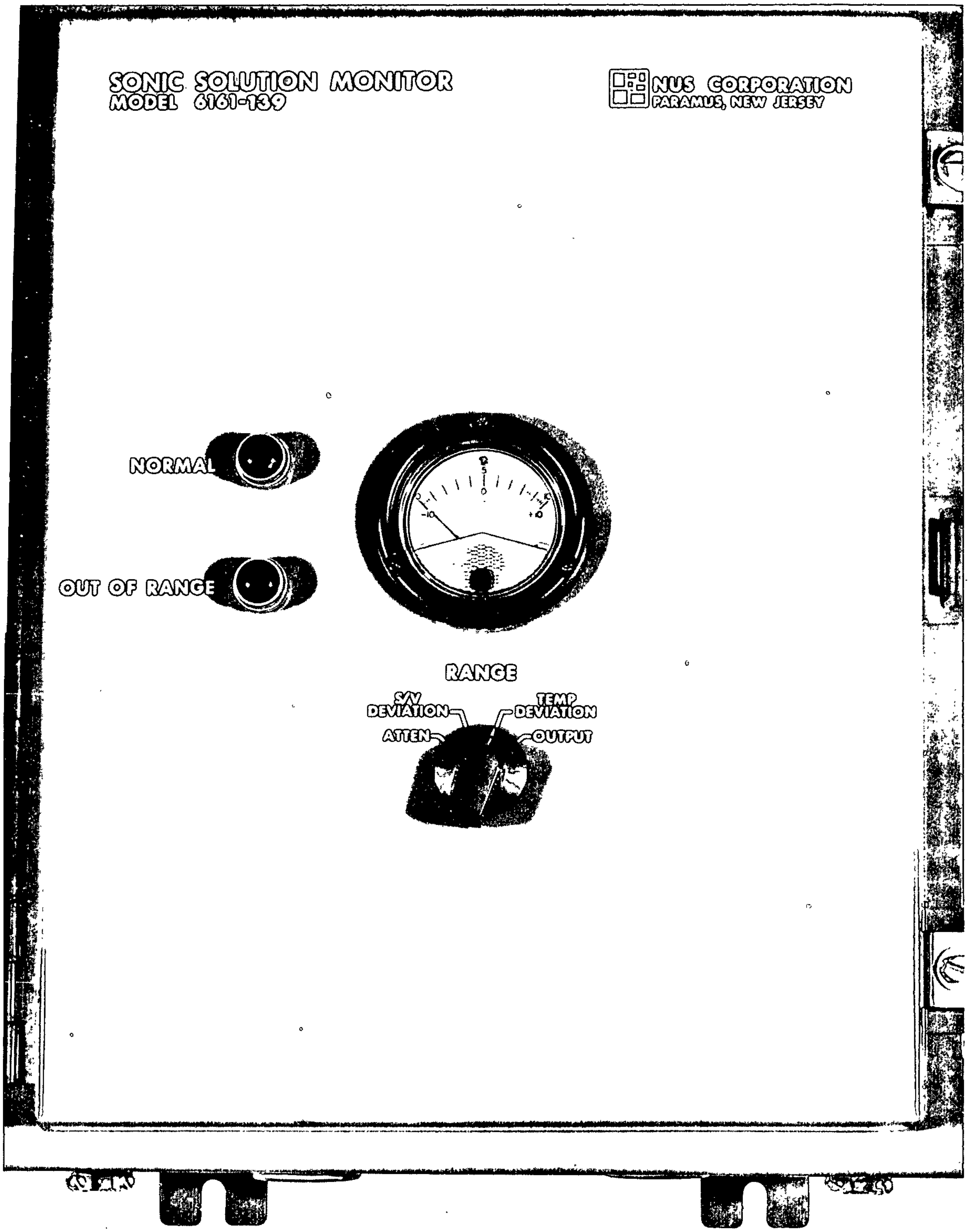
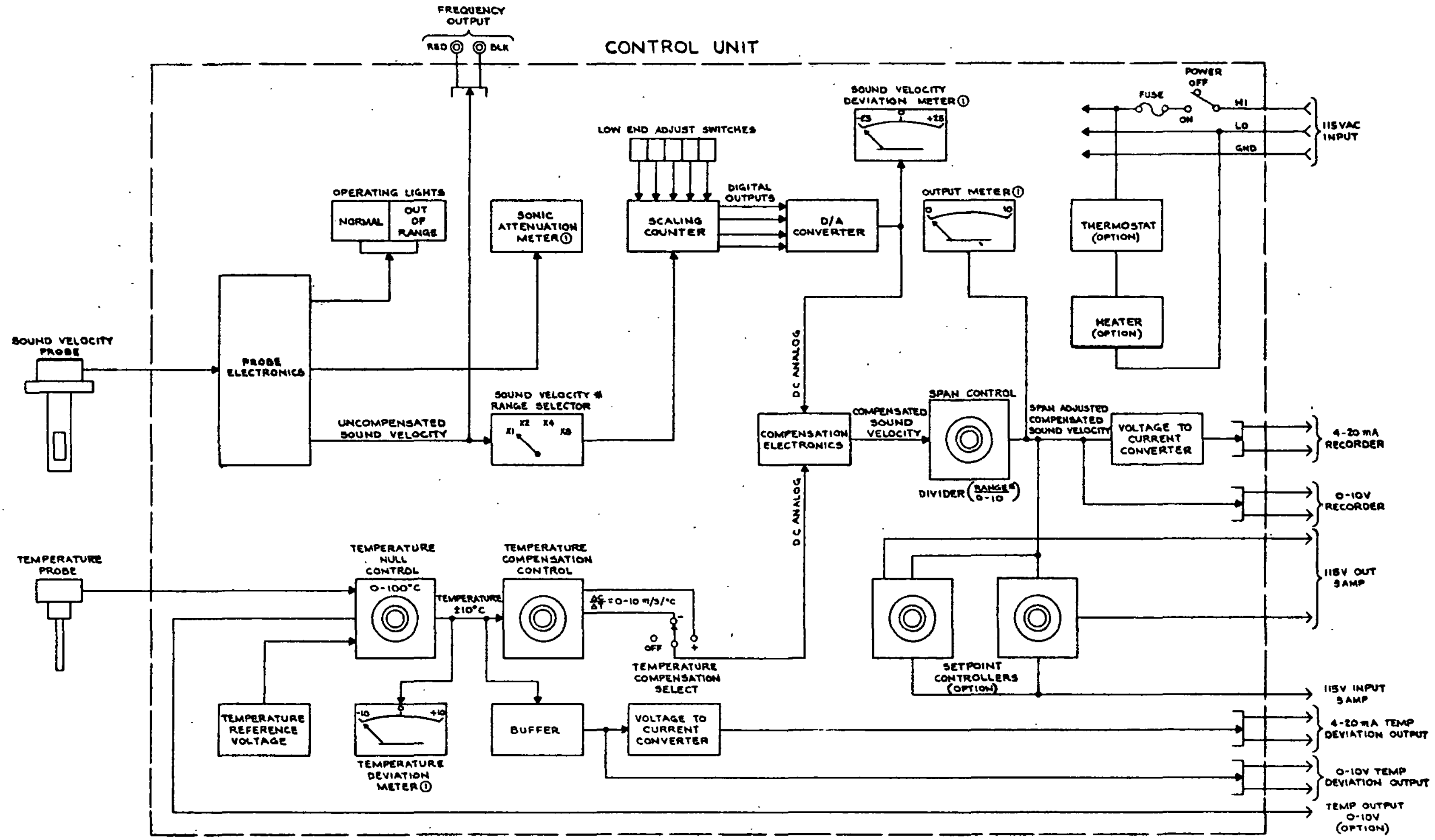


Figure 18. Photograph of NUS Control Console



* - SOUND VELOCITY RANGES
X1 = ± 25 m sec
X2 = ± 50 m sec
X4 = ± 100 m sec
X8 = ± 200 m sec

① STANDARD MODEL USES ONE MULTI-FUNCTIONAL METER WITH SELECTOR SWITCH.

Figure 19. Block Diagram for NUS Velocimeter

At the pipeline, the temperature-sensing element generates a d.c. signal which is proportional to temperature. A temperature reference is also provided. These signals are sent to the TEMPERATURE NULL control, which is used to null out the temperature signal. The NULL control is a vernier helipot calibrated in terms of degrees centigrade. The nonnulled portion of the signal is sent to the meter where it can be read as the temperature deviation. By reading the null setting and the temperature deviation, the temperature at the probe can be monitored. The temperature deviation signal, which is proportional to the difference between the actual temperature and the null setting, is also sent to the temperature COMPENSATION ADJUST. This varies the gain on the temperature deviation signal to generate the desired sonic-velocity-related signal for compensation. The adjusted signal is then sent to compensation electronics where it is effectively added to the sonic velocity signal coming from the digital-to-analog converter. A switch is provided to allow compensation upward or downward as needed as well as to shut off the compensation. The signal from the compensation electronics is sent through SPAN ADJUST, another variable gain, and then to the output position on the meter. This last gain adjustment allows the operator to increase readout resolution or to set up the reading for a particular set of units (such as percent solids).

The output meter has a dial indicator with two ranges on the dial (-10 to +10 and 0 to +10). The signal which is being displayed on the meter is controlled by a METER SELECTOR switch. The four functions which can be monitored are as follows:

1. S/V DEVIATION. This reading, in conjunction with the SOUND VELOCITY RANGE selector measures the deviation in the sound velocity from the value set in the LOW END ADJUST switches. The value on the meter (± 10 full scale) should be multiplied by the setting on the SOUND VELOCITY RANGE selector for a true sound velocity deviation.

2. ATTEN. This displays the attenuation of the sonic pulse in the solution in percent of full scale. If attenuation exceeds 90%, measurements should not be performed.

3. TEMP DEVIATION. This displays the deviation in temperature (up to ± 10°C.) of the solution from that set on the TEMPERATURE NULL control.

4. OUTPUT. This displays the sonic velocity deviation signal after temperature compensation (if selected) and after SPAN ADJUST. This would enable the operator to monitor the concentration of the solution after the instrument has been adjusted.

The controls which are available to the operator include the following:

1. SOUND VELOCITY RANGE Selector. This brings the Control Unit into the mode most compatible with the sound velocity range of the solution under test. This control works directly with the S/V DEVIATION display.

2. LOW END ADJUST Switches. These enable the operator to select the operating range of the instrument by offsetting the sound velocity span which is below the low range of the solution being monitored. The numbers on the switches (which are in octal) may be used, together with the S/V DEVIATION reading, to determine an actual sound velocity value.

3. TEMPERATURE NULL Control. This enables the operator to select the average temperature to which readings are corrected. This control, in conjunction with the TEMP DEVIATION reading, permits determination of the process temperature.

4. TEMP COMP SELECT. This is a switch that connects or disconnects temperature compensation, and also the polarity of the compensation (+ for a positive temperature coefficient and - for a negative temperature coefficient).

5. COMPENSATION ADJUST. This enables the operator to set the correct amount of temperature compensation. After the setting has been made, the control scale will indicate the temperature coefficient of the solution.

6. SPAN ADJUST. This permits a change of gain on the output meter to either increase readout resolution or indicate solids content changes directly. The action is one of dividing the gross span by any number between 0 and 10.00. If no adjustment is to be made, this control is set at 1.00.

A convenient feature of this instrument is that all settings and adjustments are made on calibrated switches or dials. Once a calibration procedure has been performed, it can be precisely reset at a later date for exactly the same operating conditions. Even more significant is the fact that the numbers on the dials (and switches) have actual physical meaning. For example, the TEMPERATURE NULL dial markings are equivalent to degrees centigrade, COMPENSATION ADJUST markings are equivalent to m./sec./^{o}C., and SPAN ADJUST markings give the divider factor on gross span. The numbers on the LOW END ADJUST switches are an octal representation of a number which is proportional to "sing-around" frequency and can be used to compute the mean sonic velocity setting.

In summary, it is possible to read the following quantities with this instrument:

1. Sonic velocity of the solution in meters per second. This is obtained by reading the sonic velocity (S/V) deviation on the meter, multiplying by the setting on the S/V range switch, and adding the result algebraically to the value of sonic velocity corresponding to the setting of the low end adjust switches.

2. The percent attenuation of the sonic pulse sent through the solution. This is read directly on the meter when the meter selector switch is set on attenuation.

3. Temperature of the solution in degrees centigrade. This is obtained by reading the temperature deviation on the meter, adding it algebraically to the vernier reading on the temperature null control dial, and adding 20°C.

4. A temperature-compensated output proportional to some quantity which in turn is proportional to sonic velocity (such as percent solids). This would be read directly on the meter after proper calibration and adjustment of the S/V range switch, low end adjust switches, temperature compensation adjust, and the span adjust.

In addition to the outputs and controls normally provided with the instrument, a connection was made to tap the "sing-around" frequency signal and send it to a Hewlett Packard 5512-A digital counter. This provided additional information and a way to get sonic velocity data independent of the meters.

INSTRUMENT CHECKS

A series of checks on the effect of environmental conditions on the NUS velocimeter were carried out simultaneously with the checks on the refractometer described previously. These runs were made with sucrose solution in the loop and included tests on the effects of line voltage variations, stray magnetic fields, and mechanical vibrations. It was found that the sonic velocity deviation reading was unaffected by line voltage variations from 95 to 125 volts. The reading was also unaffected by the presence of a magnetic field near the probe, console, or connecting cable. Mechanical vibration had no noticeable effect on the meter reading. It was noticed, in a later test with the probe lying on a table, that the arcing from a motor running nearby caused the meter to go off scale. In this particular situation, the probe did not have the benefit of being shielded by the mounting flange and tee section.

An overnight (24-hour) stability check was run on the velocimeter concurrently with the test on the refractometer. The results of that test are given in Table V.

TABLE V

TWENTY-FOUR-HOUR STABILITY TEST ON NUS VELOCIMETER

Time of Day	S/V Deviation	Counter, Hz	NUS Temp., °C.
1630	0.0	134920	32.1
1940	-0.5	134750	29.5
2240	-0.7	134630	27.8
0805	-0.9	134540	27.0
0900	-0.9	134550	27.0
1015	-0.9	134570	27.2
1200	-0.8	134600	27.6
1300	-0.7	134630	28.2
1500	-0.6	134690	28.7

The performance of the instrument was monitored by observing the readings on the sonic velocity deviation meter as a function of time. Although the temperature compensation selector switch was turned off during this test, the sonic velocity deviation reading would not be affected by compensation anyway. The temperature of the sucrose solution in the loop cycled somewhat as the room cooled overnight and then reheated. All of the observed changes in the meter reading are essentially caused by the temperature changes. This is readily apparent in Fig. 20, in which the sonic velocity deviation meter readings and the counter readings are plotted versus the temperature of the solution. Since the counter reading is essentially the "sing-around" frequency, the change in the meter reading with temperature is reflecting actual changes in sonic velocity with temperature. Thus, the instrument appears to be stable over at least a twenty-four-hour period.

TEMPERATURE MEASUREMENT

A check on the NUS temperature-measuring system was carried out early in the program. An iron-constantan thermocouple (Conax) was installed in the flow loop immediately upstream of the velocimeter probe. An ice bath was used as the cold junction, and the thermocouple emf was read with a Cambridge Portable Potentiometer No. L-316688. The NUS temperature was determined by adjusting the temperature null control until the temperature deviation read zero, and then adding 20°C. to the vernier readings on the null control dial. This check on the temperature-measurement system was carried out with 50% sucrose solution circulating in the loop. The results of this test are presented in Table VI. It can be seen that the NUS instrument tended to read a slightly lower value over the whole range from 30 to 120°C. The deviation is largest at the extremes (about 1°C.) and is smaller in midrange (about 0.5°C.). It should be noted that the instrument specifications make no claim on accuracy of temperature measurement. What is specified

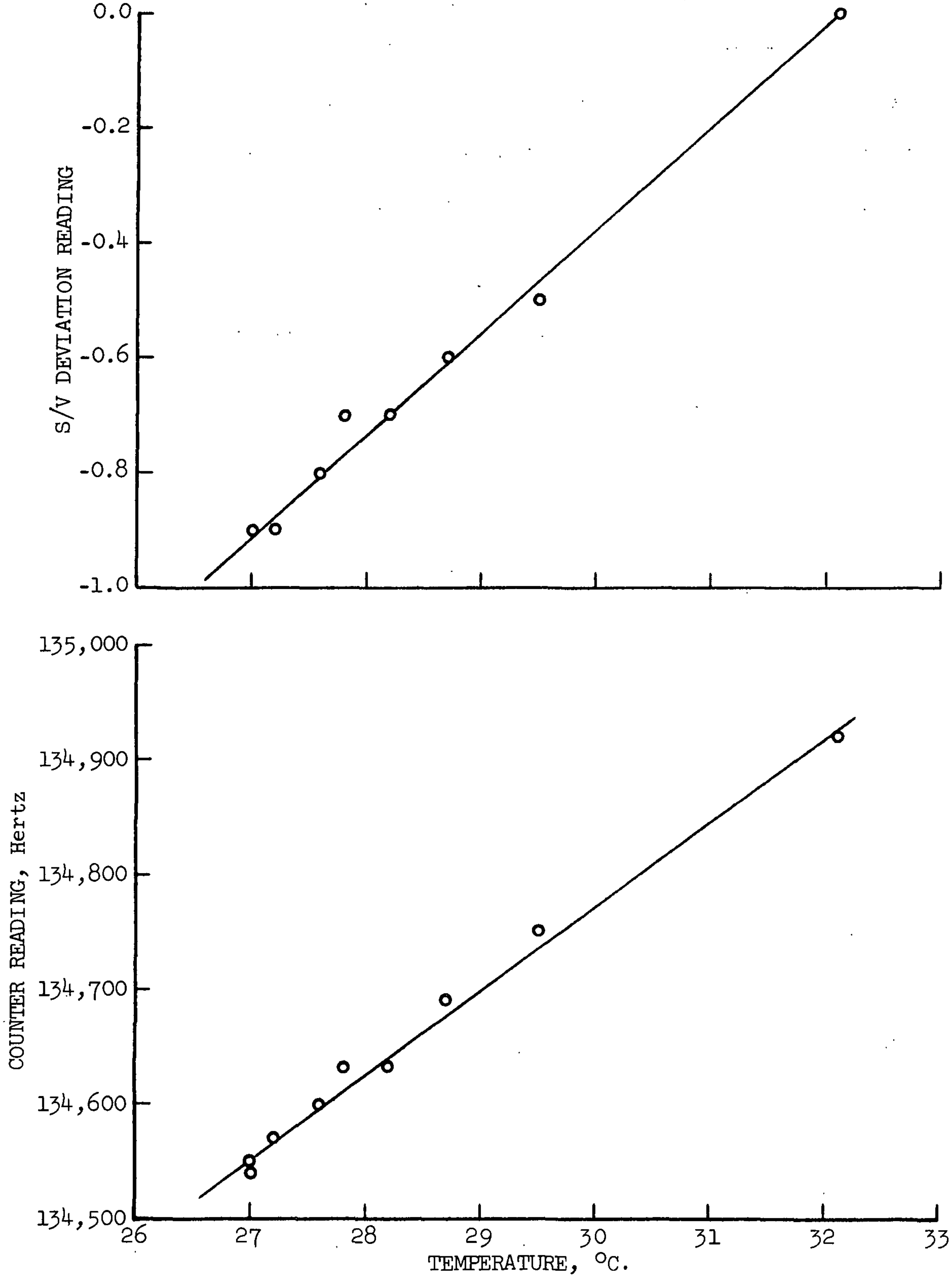


Figure 20. Data from Stability Test on NUS Velocimeter

is a repeatability of ± 0.05°C. and the ability to provide first-order correction of sound velocity for temperature variations to within 0.1°C. The instrument certainly appears capable of doing this. Because of the reasonable agreement between the NUS temperature measurement and the thermocouple and the convenience of the NUS method, the NUS instrument was used for all temperature measurement in the flow loop.

TABLE VI

ACCURACY OF NUS TEMPERATURE MEASUREMENT

Thermocouple emf, mv.	Thermocouple Temp., °C.	NUS Temp., °C.	NUS – T.C., °C.
1.75	34.2	33.3	-0.9
2.73	52.8	52.3	-0.5
3.75	71.8	71.4	-0.4
4.45	84.8	84.2	-0.6
5.27	100.0	99.1	-0.9
5.72	108.3	107.2	-1.1
6.42	121.2	119.9	-1.3

OPERATIONAL VARIABLES

The effects of several operational variables on instrument response were examined. These included the flow rate of liquor past the probe, system pressure, and the presence of entrained air in the liquor. It was found that the instrument was unaffected by variations in liquor velocity past the probe over the range from 0 to 5 ft. per second. A small effect due to system pressure changes was found. This was observed with Liquor A at 15% solids and a temperature of 27.9°C. Increasing the total pressure in the system from 0 to 60 p.s.i.g. caused an increase in the "sing-around" frequency measured by the counter from 131,770 Hz to 131,800 Hz, or an increase in sonic velocity of 0.023%. This would amount to a change in sonic velocity of about 0.0004% per p.s.i. This observed effect seems to be quite small and would not seriously affect the use of the instrument. If maximum measurement precision is desired, variations in total pressure should be avoided. It should be noted that a pressure effect was not unexpected since sonic velocity depends on the density and bulk modulus of the solution, and these could be pressure dependent.

Entrapped air seriously affected the operation of the velocimeter, particularly at high solids contents. Aeration of the liquor resulted in an attenuation of the sound pulse by more than 90%, thus causing the out-of-range light on the front panel to come on. In all cases when air bubbles were present, the instrument went out of range rather than simply giving an erroneous reading. Observation of the attenuation signal provided a ready means of detecting aeration problems. Under normal operating conditions, the attenuation of the sound pulse was low, on the order of 5% or less. When bubbles were present, the attenuation would rise to over 90%. Under some conditions, the attenuation reading might bounce from very high to very low values. Pressurizing the flow loop to 60 p.s.i.g. did not overcome the air bubble problem. It is not known if conditions could occur where aeration would cause significant changes in sonic velocity without also causing sufficient attenuation to trigger the out-of-range signal. In all of these tests, aeration did cause the out-of-range light to come on.

In this program, the problems associated with aerated liquors were overcome by preheating the liquor to a boiling condition in the steam-jacketed vessel (see Fig. 1) which allowed the air bubbles to rise to the top, and by eliminating the use of the centrifugal pump for recirculation. All of the liquors which were used in this program were aerated when received from the mills, most probably because of aeration during direct contact evaporation. The aerated nature of the liquor as received could be seen by observing the alternate expansions and contractions in volume of a liquor sample exposed to vacuum and atmospheric pressure. Thus, the problem with aeration in this program had to be solved by first deaerating the liquor and then preventing reaeration. The deaeration was carried out by heating to a boil while stirring in the steam-jacketed vessel. The loop was then filled from the bottom by pumping the liquor from the vessel with the Moyno pump. When the loop was filled, the valving was adjusted so that the Moyno pump served as the circulating pump also.

In nearly all cases where a high attenuation of the sonic pulse occurred, the problem could be ascribed to air bubbles. In the flow loop, there were no indications that black liquor itself became opaque to sound waves. No discernible trend of increased attenuation with increasing solids content was observed. The only evidence of liquor opacity was obtained in some beaker tests with Liquor C. At temperatures of 40°C. and solids contents above 50%, attenuation of the sound pulse became significant. This is apparently associated with the high viscosities of low-temperature, high-solids liquors. Otherwise, the cause of high attenuation was air in the liquor. Zacharias (3) has stated, "Bubbles and solid particles larger than 50 microns may cause erroneous readings. Also, emulsions containing large liquid droplets may be opaque to sound at high concentration levels, and slurries with large quantities of suspended particles may scatter the sound excessively." This could indicate that undissolved salt cake could also cause difficulties. The effects of the presence of undissolved salt cake were not tested for the reasons described earlier in the section on the refractometer.

BLACK LIQUOR MEASUREMENT

There are, at a minimum, two requirements which must be met for the sonic velocimeter to be useful for measuring solids content of black liquor. First, the instrument must be capable of measuring sonic velocity in black liquor, and second, there must be a reasonable functional relationship between the sonic velocity of the liquor and the solids content. The first question was alluded to in the previous section. As long as air bubbles are not present in the liquor, the instrument does measure sonic velocity and the black liquor is not opaque to the sound pulse. The second question is best examined by determining the sonic velocity response curves of black liquor as functions of solids content and temperature.

The most complete set of data on the sonic velocity response was obtained with Liquor A. Some additional data were obtained with Liquor B. When Liquor C was used in the flow loop, the problem of deaerating the liquor had not yet been solved. In these early runs, the velocimeter was out of range nearly all of the time and the only sonic velocity data on Liquor C were obtained in small beaker tests at 40°C. The sonic velocity data on Liquor A are shown as a function of temperature at different solids contents in Fig. 21. A cross plot of these data to show the dependence on solids content directly is presented in Fig. 22. Similar data for Liquor B are given in Fig. 23 and 24.

There are several features which are apparent in these data. The sonic velocity decreases with temperature over the full temperature and solids range. Curves of sonic velocity vs. temperature are steepest and essentially linear at the highest solids contents and become less steep and slightly curved at the low solids end. No maximum in the sonic velocity-temperature curve was observed over the range of variables tested. These data indicate that the temperature dependence of sonic velocity in black liquor is better behaved than might be expected. Zacharias (3) says that aqueous solutions or emulsions generally exhibit nonlinear characteristics in which velocity increases to some maximum value and then decreases. As concentration increases, the value of sound velocity would change so that the maximum would occur at lower temperatures. The data in Fig. 21 and 23 show that if a maximum exists at all, it exists outside the range of normal interest. The kind

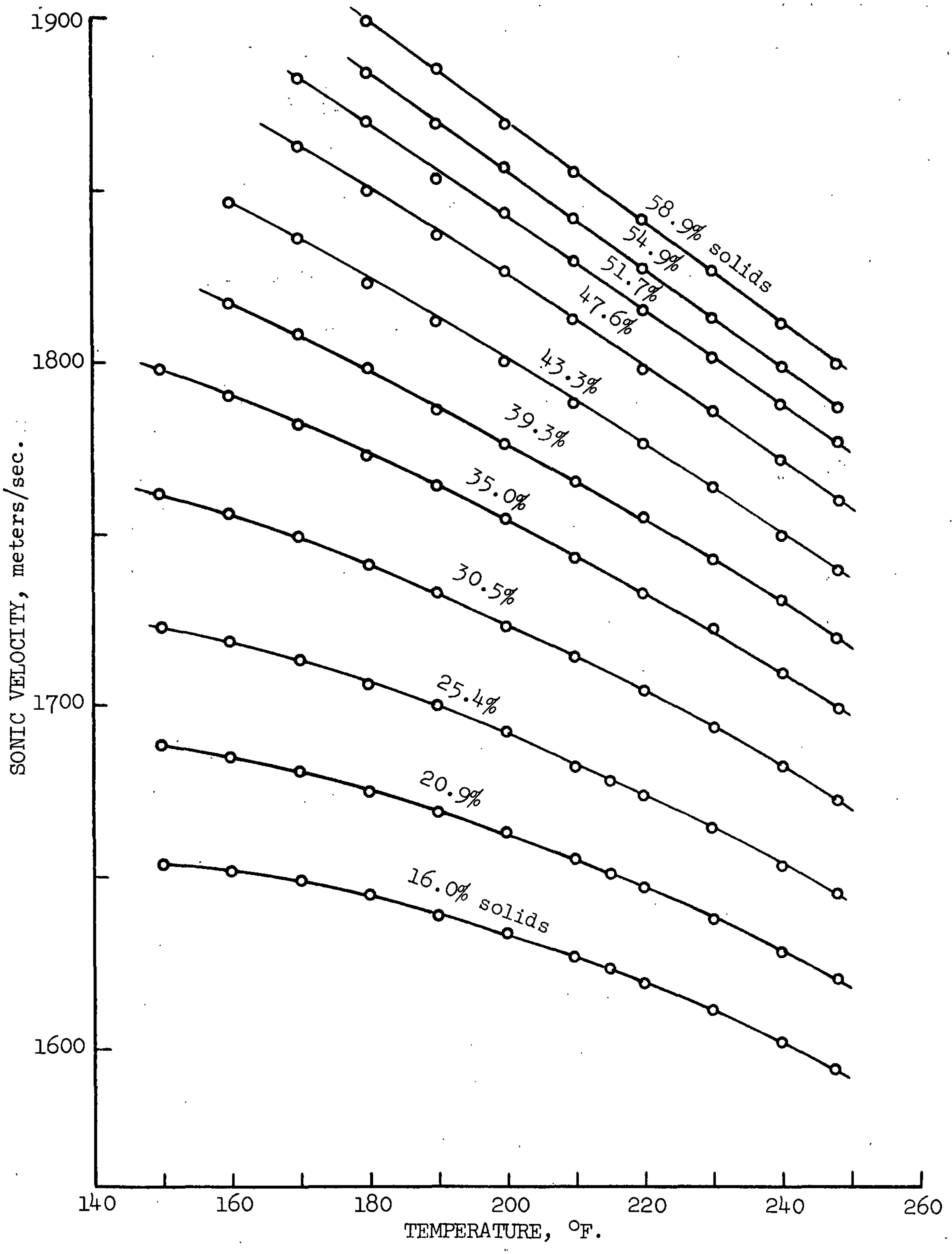


Figure 21. Sonic Velocity Data for Liquor A

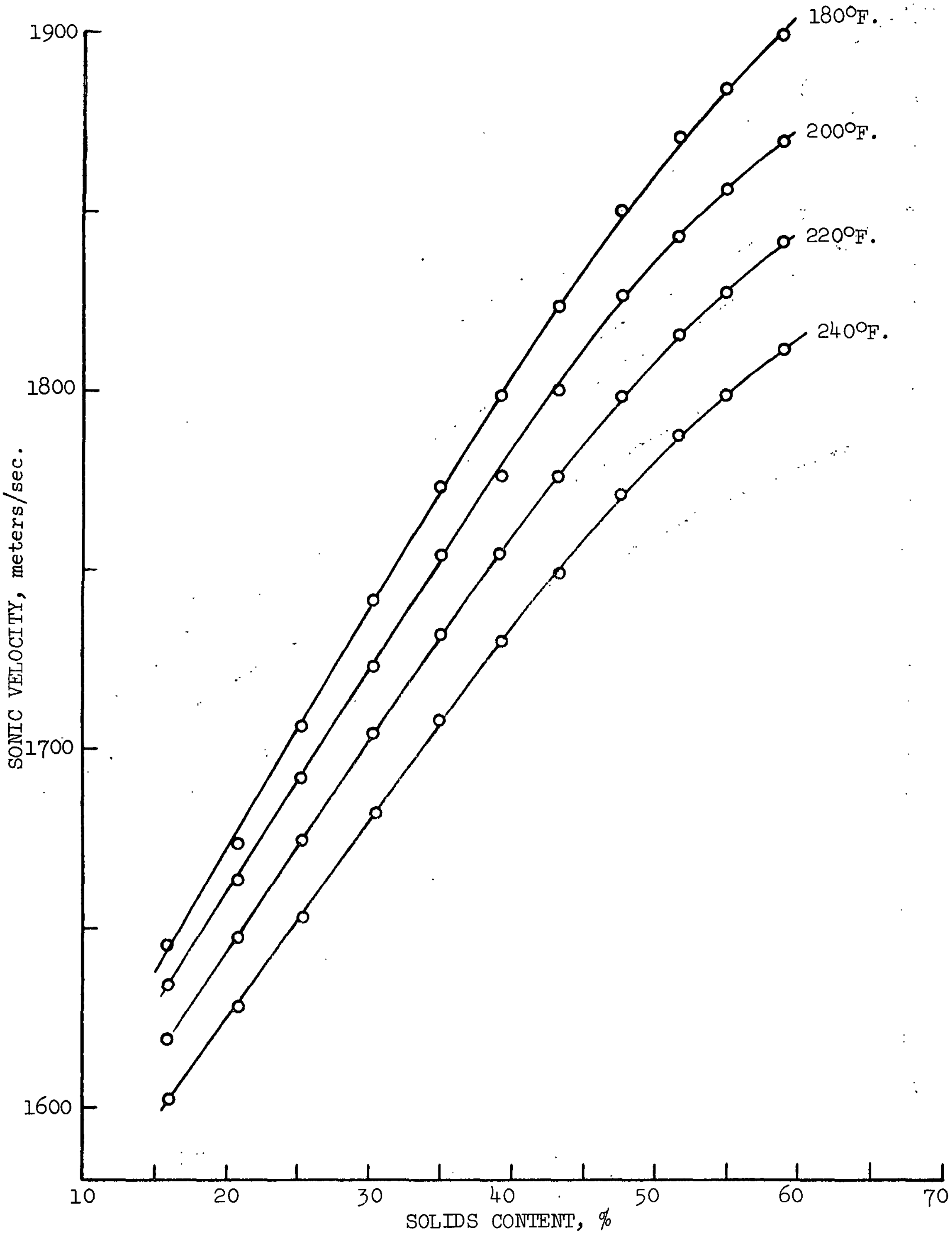


Figure 22. Sonic Velocity vs. Solids Content for Liquor A

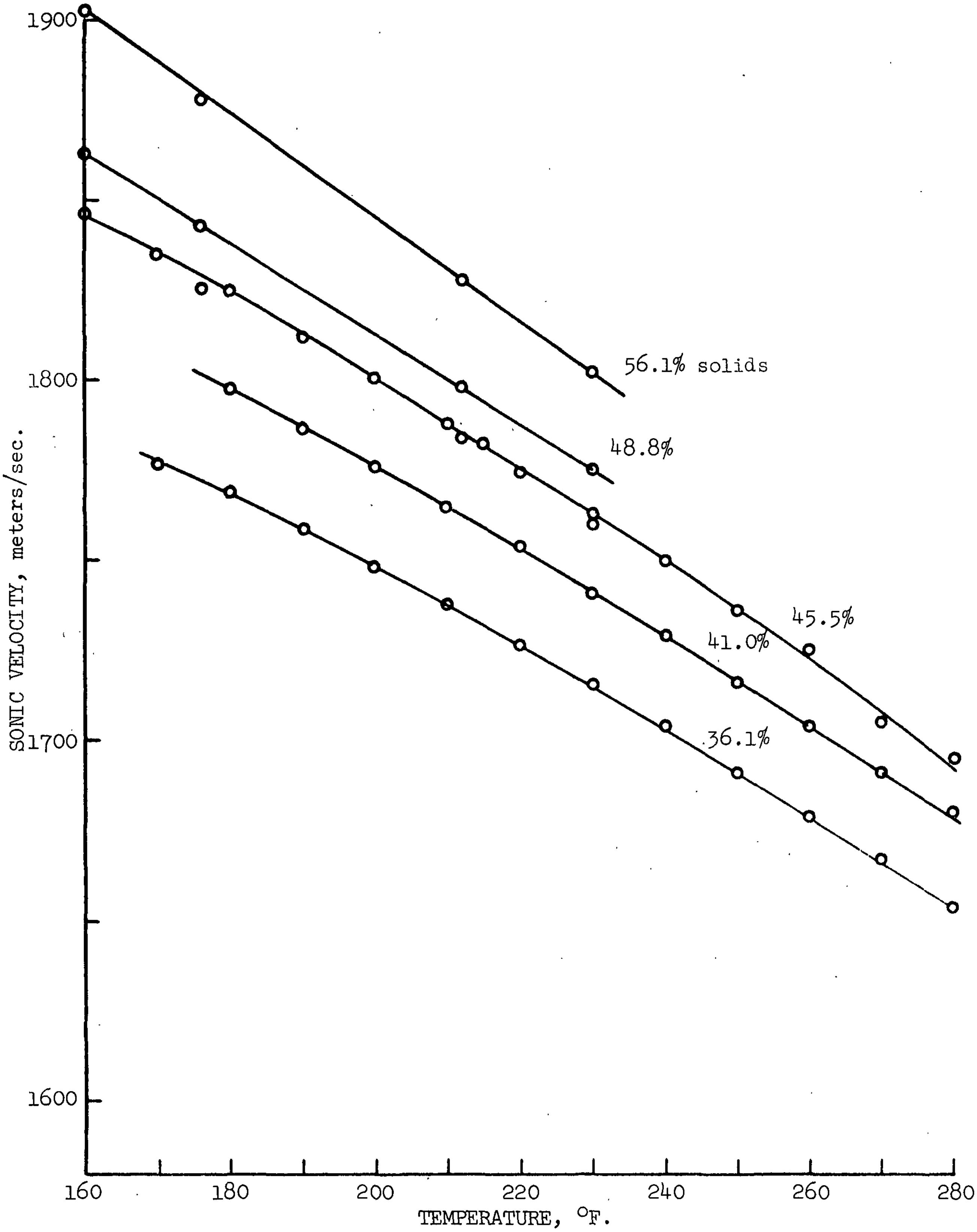


Figure 23. Sonic Velocity Data for Liquor B

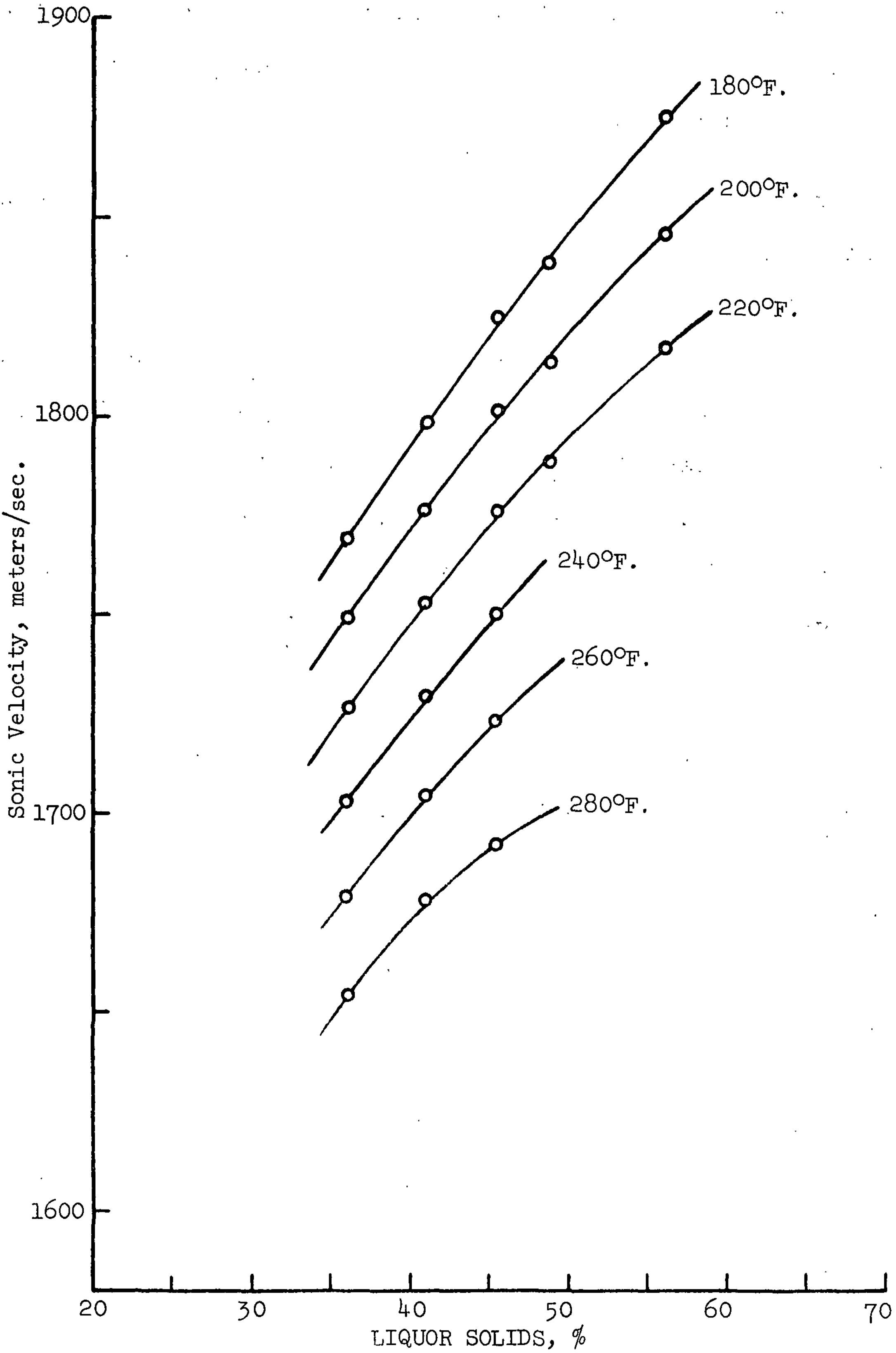


Figure 24. Sonic Velocity vs. Solids Content for Liquor B

of temperature dependence shown in these data should make it easy to provide temperature compensation because little error would be introduced by linearizing the curves over a 20-40°F. range.

The relationship between sonic velocity and solids content is shown in Fig. 22 and 24. The curves tend to be steepest and most linear at the low solids end and then bend over and become curved and less steep at high solids. Both linearity and steepness increase at lower liquor temperatures. Slopes of the response curves for Liquor A span the range from 6.7 to 3.0 m./sec./% solids. At the low solids end, linearization of the curves over a wide range of solids contents would be adequate. At high solids, linearization would be valid only over a small (say, ± 2.5% solids) range of solids contents. It is evident that the sonic velocity response of black liquor is sufficiently straightforward to permit its use for monitoring solids content.

A comparison of Fig. 22 with Fig. 24 shows that composition of the black liquor affects sonic velocity response also. The curves for Liquor B fall below and to the right of Liquor A. This means that at the same solids content and temperature Liquor A gives a higher sonic velocity than Liquor B. This effect of composition has several implications. First of all, it is fruitless to attempt to discover an algorithm for describing the concentration and temperature dependence of sonic velocity in black liquor because it would change with each change in liquor composition. Secondly, since liquor composition would be expected to vary, it would be necessary to continuously maintain calibration during on-line operation. Composition effects will be discussed in more detail a little later, as will the problems of on-line calibration.

TEMPERATURE COMPENSATION

The effectiveness of the temperature compensation circuitry which is provided in the velocimeter was checked over the specified temperature range of ± 10°C. using Liquor C and a midrange temperature of 90°C. The adjustments of the amount of compensation were made on a high solids content liquor which was then progressively diluted. Unfortunately, no direct determinations of liquor solids content were made for this series, and so all of the data are on a relative basis ranging from about 60% solids down to 30% solids.

The temperature compensation is not a factory calibration and it is necessary to set it up according to instructions provided in the instrument manual. The liquor is brought to the desired midrange temperature, and the TEMPERATURE NULL set so that the temperature deviation reads zero. The LOW END ADJUST switches are then set so that S/V deviation reads zero. The product temperature is then changed to an extreme point and the temperature COMPENSATION ADJUST turned to bring the output meter back to zero. This inserts the correct amount of temperature compensation.

The results of the compensation test are shown in Fig. 25. It is evident that for the sample for which the compensation was set up [number (1)] excellent compensation is obtained over the ± 10°C. range. There were no deviations over the compensated range. With the progressively diluted liquors, the instrument was overcompensating for temperature. This simply reflects the fact that the sonic velocity vs. temperature curves are not parallel but rather are steeper at high solids. Thus, the compensation settings are valid only for a narrow range of solids content. A comparison of the compensated and uncompensated response shows that the compensation circuitry is indeed important.

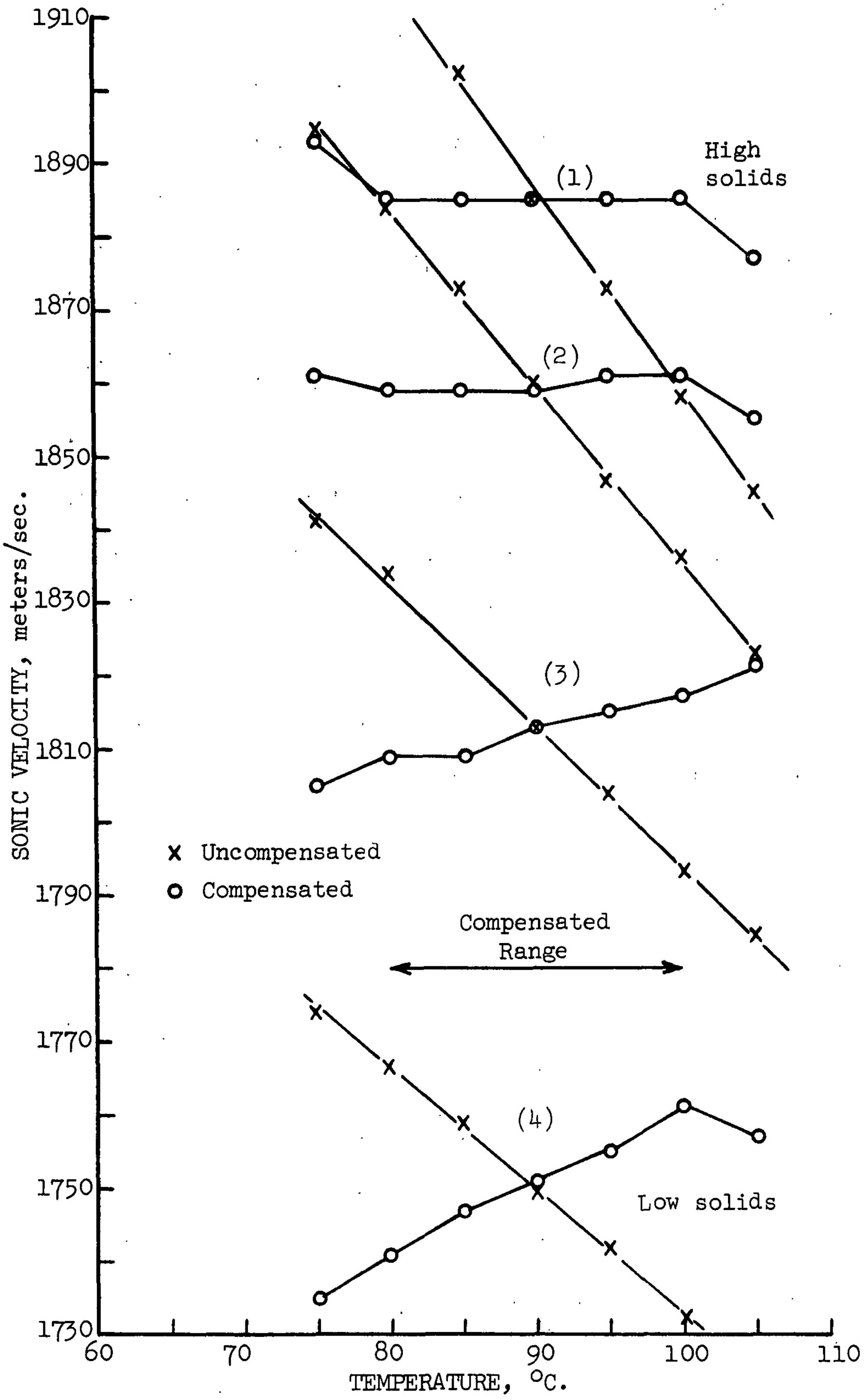


Figure 25. Temperature-Compensated Response of Velocimeter

COMPOSITION EFFECTS

The investigation of the effects of chemical composition on velocimeter response paralleled the study on the refractometer. Figure 26 clearly shows that composition effects are present. This curve shows the 180°F. lines for Liquors A and B taken from Fig. 22 and 24. The response curve for Liquor B lies below and to the right of the curve for Liquor A. This same behavior occurs at other temperatures. Thus, at the same temperature and solids contents, Liquor A gives a higher sonic velocity. Sonic velocity data for Liquor C are also shown in Fig. 26. Unfortunately, these data were taken at 40°C. (104°F.) so that a direct comparison with Liquors A and B cannot be made. In order to make such a comparison, the data in Fig. 21 were used to estimate the change in sonic velocity with temperature from 180 to 104°F. at various solids contents. These estimated values were then subtracted from the Liquor C curve to give an estimated curve for Liquor C at 180°F. This latter curve is shown as the dashed line in Fig. 26. This line indicates that Liquor C would give a higher value of sonic velocity than either A or B at the same solids content and temperature. Thus, the data indicate that sonic velocity decreases (at a given solids level and temperature) from C to A to B. It is of interest that this is essentially the same order in which refractive index <u>increases</u> (see Fig. 11).

In order to gain some insight into why these changes occurred, sonic velocity data were obtained on some simple solutions and mixtures. These data were obtained outside of the flow loop at 40°C. Sonic velocity data were obtained for Liquor C, various mixtures of sucrose and Na_2CO_3, Na_2SO_4, NaCl, oxalic acid, and phenol. These data are shown in Fig. 27. Several trends are apparent in these data. The general form of the curves is somewhat nonlinear, with an increasing slope at higher solids content. This may be contrasted with the data on black

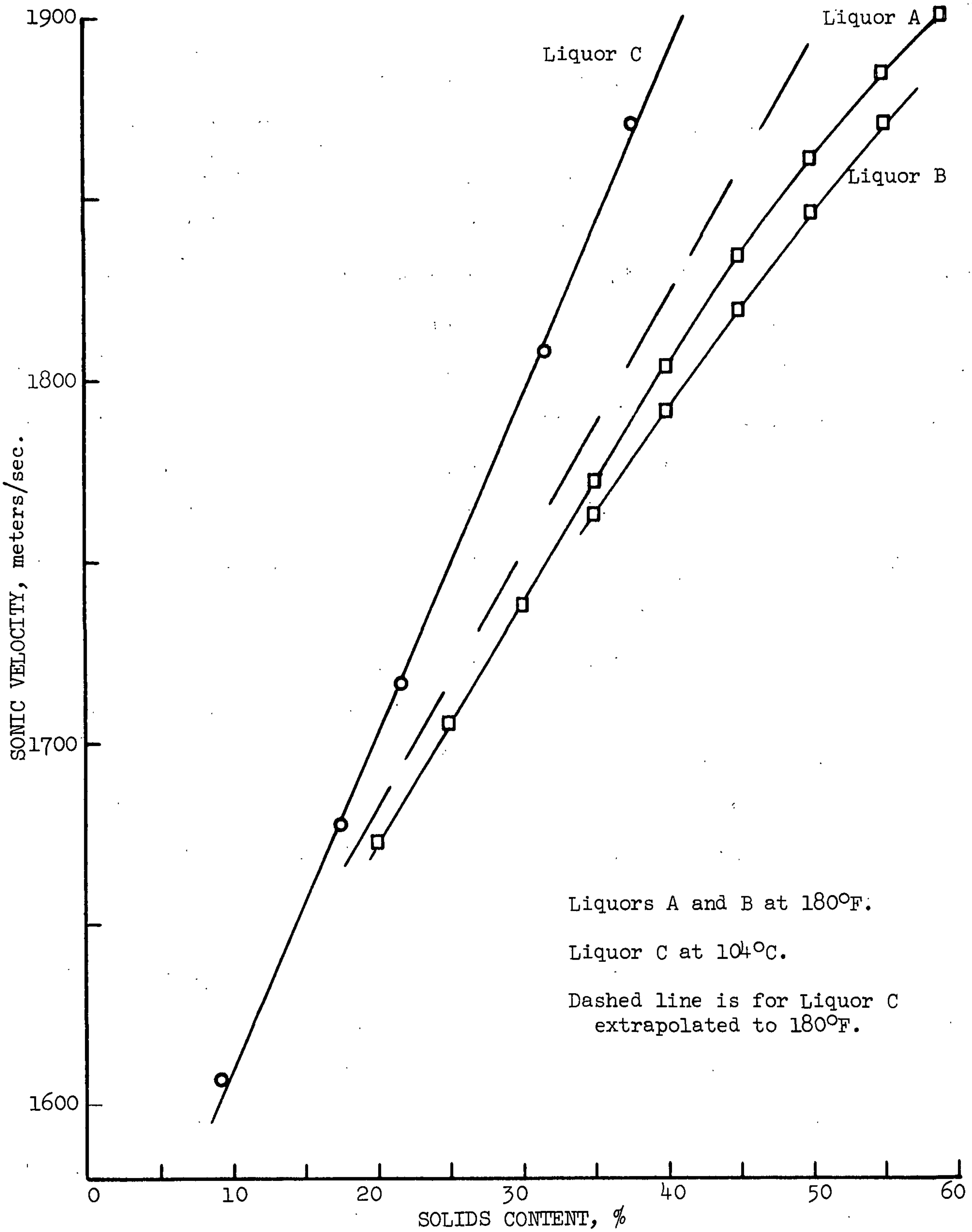


Figure 26. Effect of Liquor Composition on Sonic Velocity Response

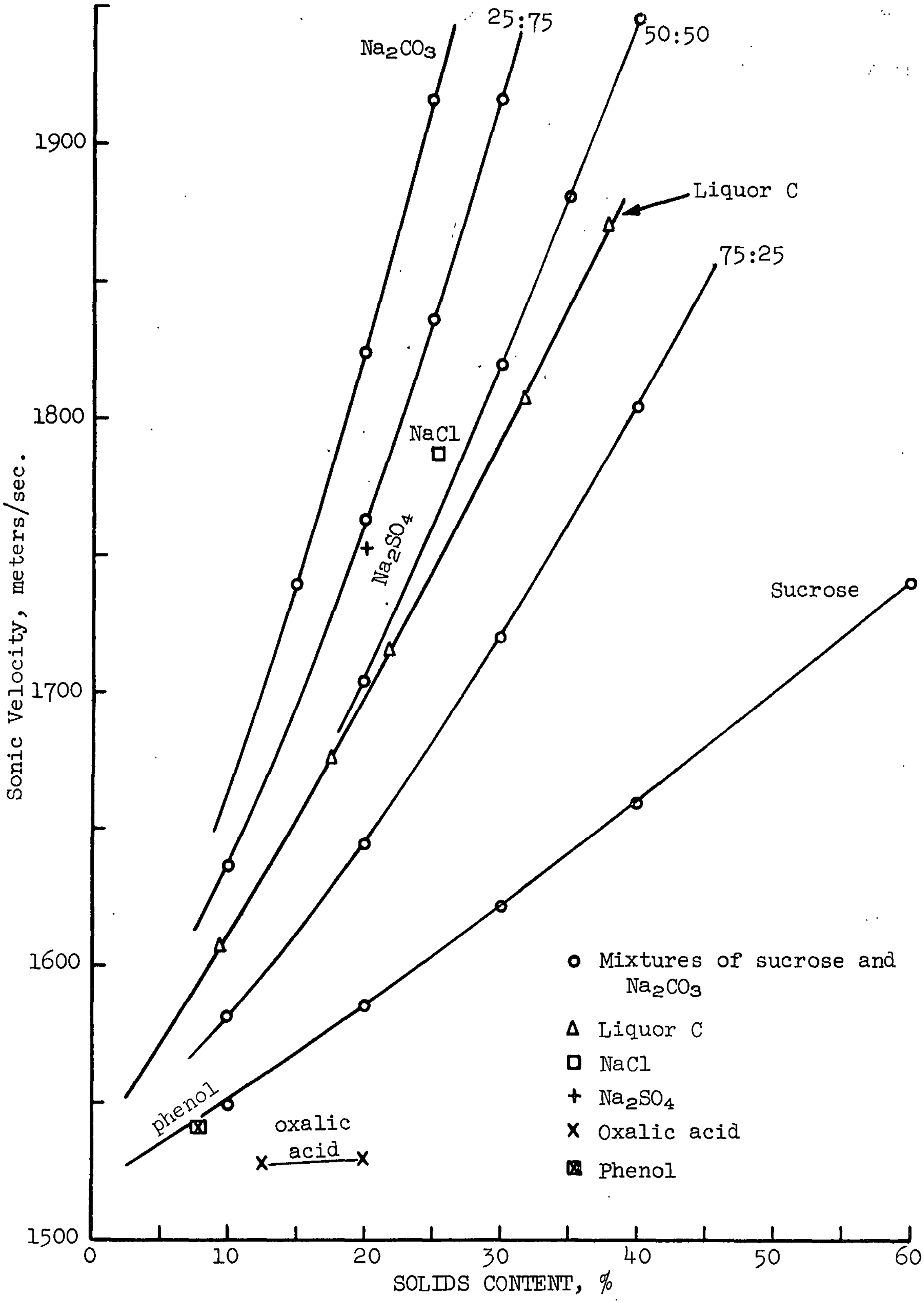


Figure 27. Sonic Velocity Data for Various Solutions

liquor in Fig. 22 and 24 taken at higher temperatures and solids levels showing a decrease in the slope at higher solids values. Another feature in Fig. 27 is that all of the curves seem to be converging to about a value of 1525 m./sec. at zero solids content, which is the approximate sonic velocity of water at this temperature. Perhaps the most striking feature of these data is the distinct separation between organic and inorganic compounds. Solutions of Na_2CO_3, Na_2SO_4, and NaCl all have high values of sonic velocity, while the organics – sucrose, phenol, and oxalic acid – all have relatively low values of sonic velocity. The curve for Liquor C, containing organics and inorganics, lies somewhere in between. This behavior may be contrasted with the index of refraction data on these same materials (Fig. 14) which did not show trends of this nature.

The data in Fig. 28 showing sonic velocities at various proportions of sucrose and Na_2CO_3 and those in Fig. 29 for mixtures of black liquor and sucrose and NaCl all show the same basic response. The sonic velocity of these organic-inorganic mixtures increases as the inorganic content increases in a linear manner. The sonic velocity of the mixtures is a linear combination of the sonic velocities of the pure components in all four curves. This may again be contrasted with the data on refractive index which tended to give nonlinear results. It should not be concluded that a linear combination law is generally valid for the sonic velocity of mixtures. However, it does appear that sonic velocity is more susceptible to linear addition of each component than refractive index.

On theoretical grounds, the sonic velocity, $\underline{c}$, in any liquid is related to density, ρ , and bulk modulus, $\underline{B}$, the reciprocal of compressibility, by the expression $\underline{c} = (\underline{B}/\rho)^{1/2}$. In order to gain some understanding of what changes occur in solutions, the sonic velocity data were plotted versus specific gravity as shown in Fig. 30. These data show that the sonic velocity increases as the specific

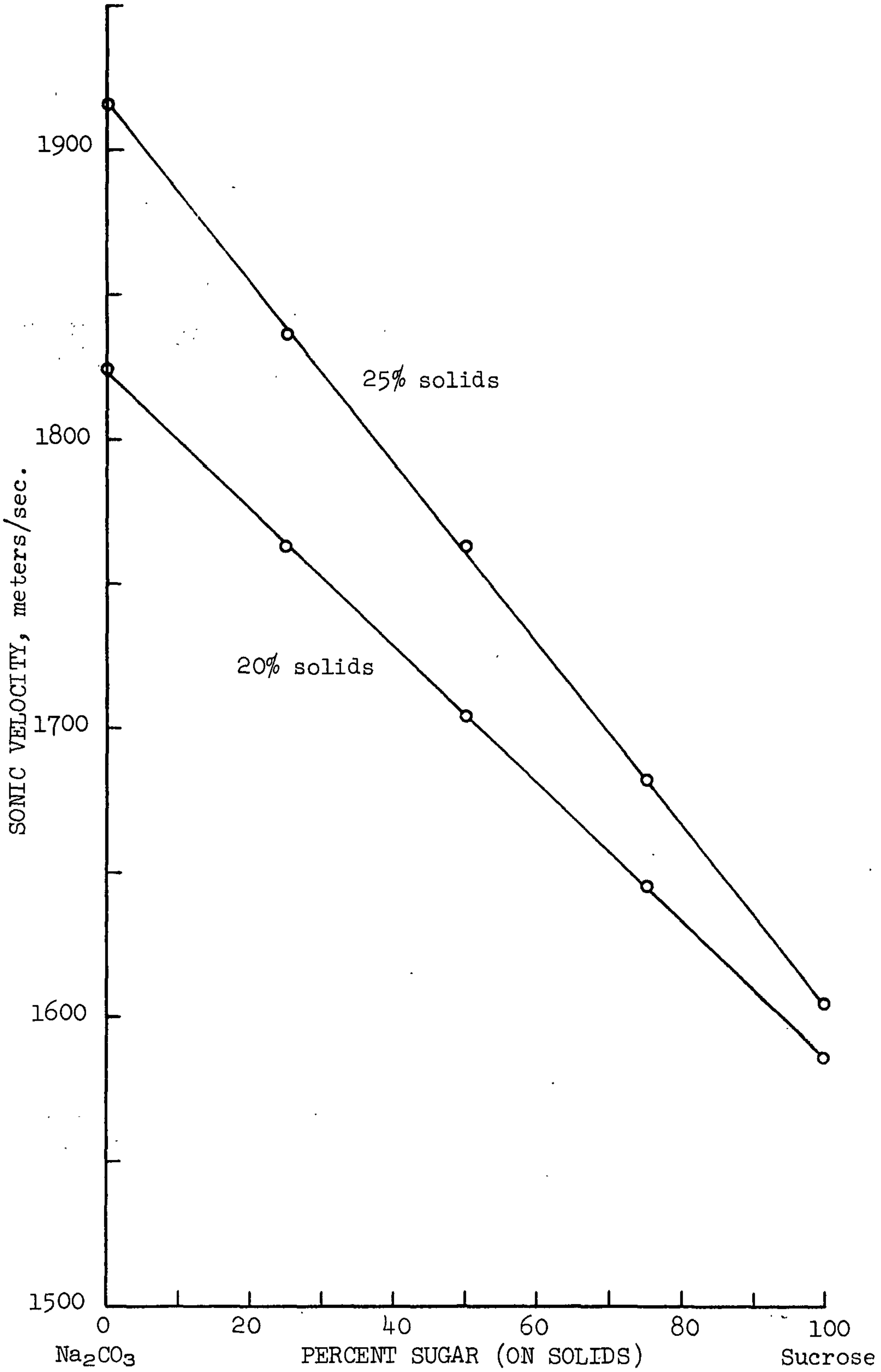


Figure 28. Sonic Velocities for Sucrose-Na_2CO_3 Solutions

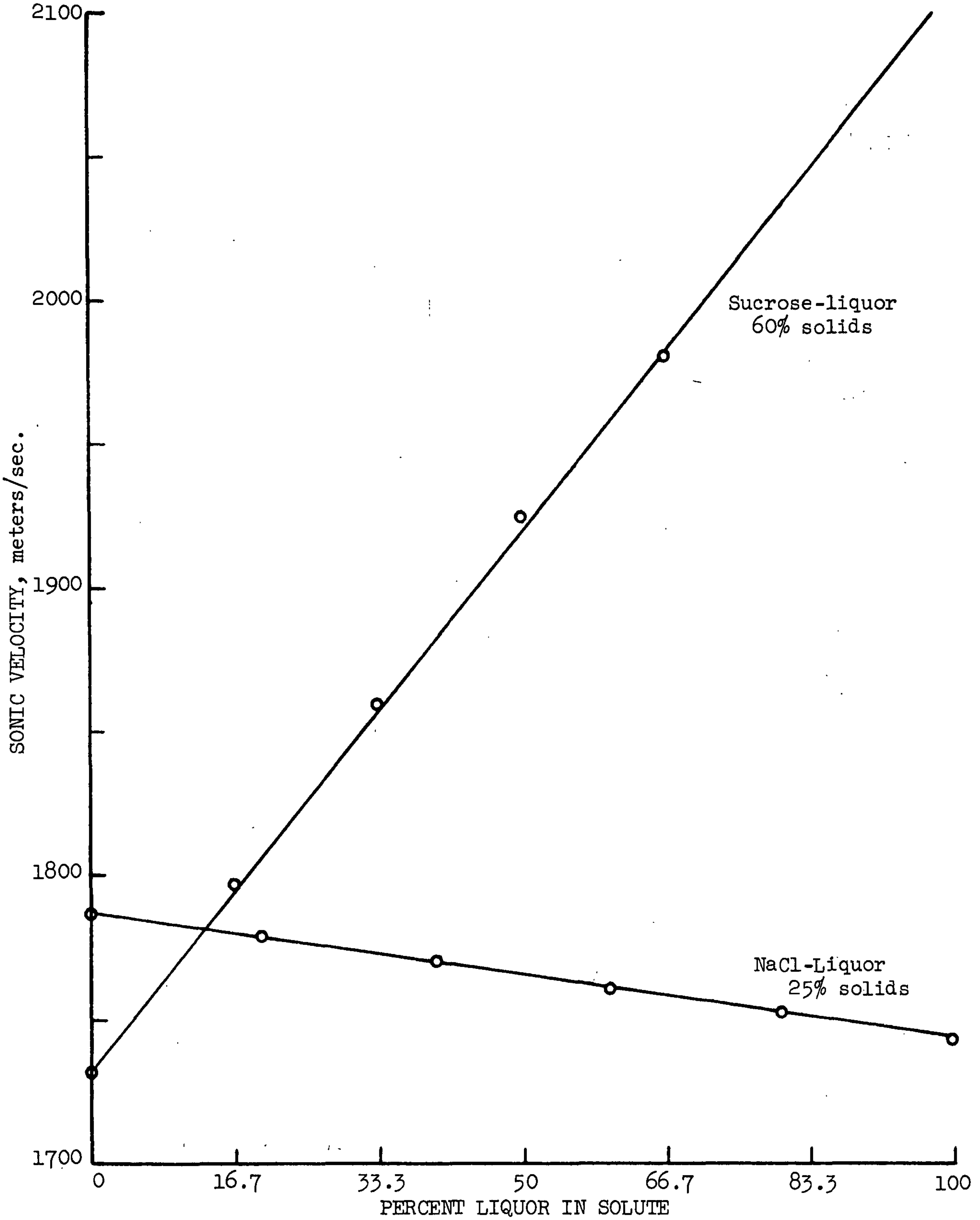


Figure 29. Sonic Velocities of Mixtures of Black Liquor and Other Substances

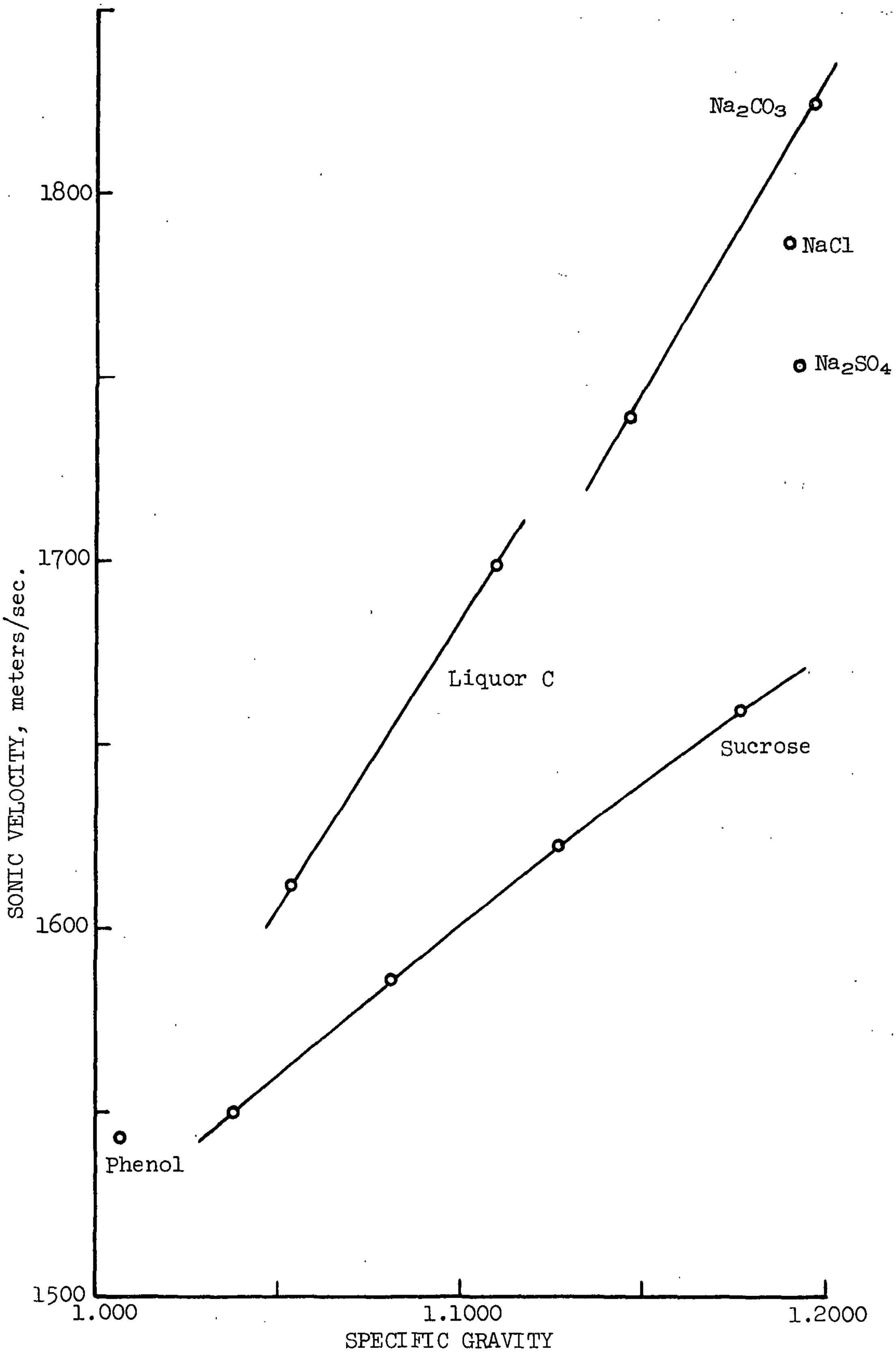


Figure 30. Sonic Velocities as Functions of Specific Gravity

gravity of the solutions increases, but along different curves for different substances. This is very interesting because the equation indicates that if the bulk modulus, B, remained constant, then the sonic velocity would decrease as specific gravity increased. The fact that the sonic velocity of solutions increases as specific gravity increases (both due to an increase in solids content) means that the bulk modulus increases more rapidly than density (B/ρ increases) as solids content increases. Hence, the measurement is responding more to changes in bulk modulus than to changes in density. In particular, this indicates that sonic velocity is a unique property of a given solution (like refractive index or density) and is not simply another way of measuring density. A sonic velocimeter and a densitometer are not equivalent.

The fact that the various methods of measuring solids content of liquor are susceptible to errors due to changes in liquor composition is a consequence of their employment of indirect methods for determining solids. The problem arises because the sonic velocity (or refractive index) at a given solids content and temperature of a solution is a function of its composition. This would be expected to be true at least to some degree for all indirect methods of determining black liquor solids content. In order to illustrate this point, some handbook data on specific gravity as a function of solids content are shown in Fig. 31. The data on black liquor are taken from the TAPPI data sheets. It is obvious that the use of solution density to determine solids content is fraught with the same problem as is the use of sonic velocity or refractive index.

One advantage to the sonic velocimeter may be that the interpretation of composition effects appears to be much more straightforward than it is for the refractometer. There seems to be a definite correlation between high sonic velocities for inorganic solutions and lower velocities for organic solutions.

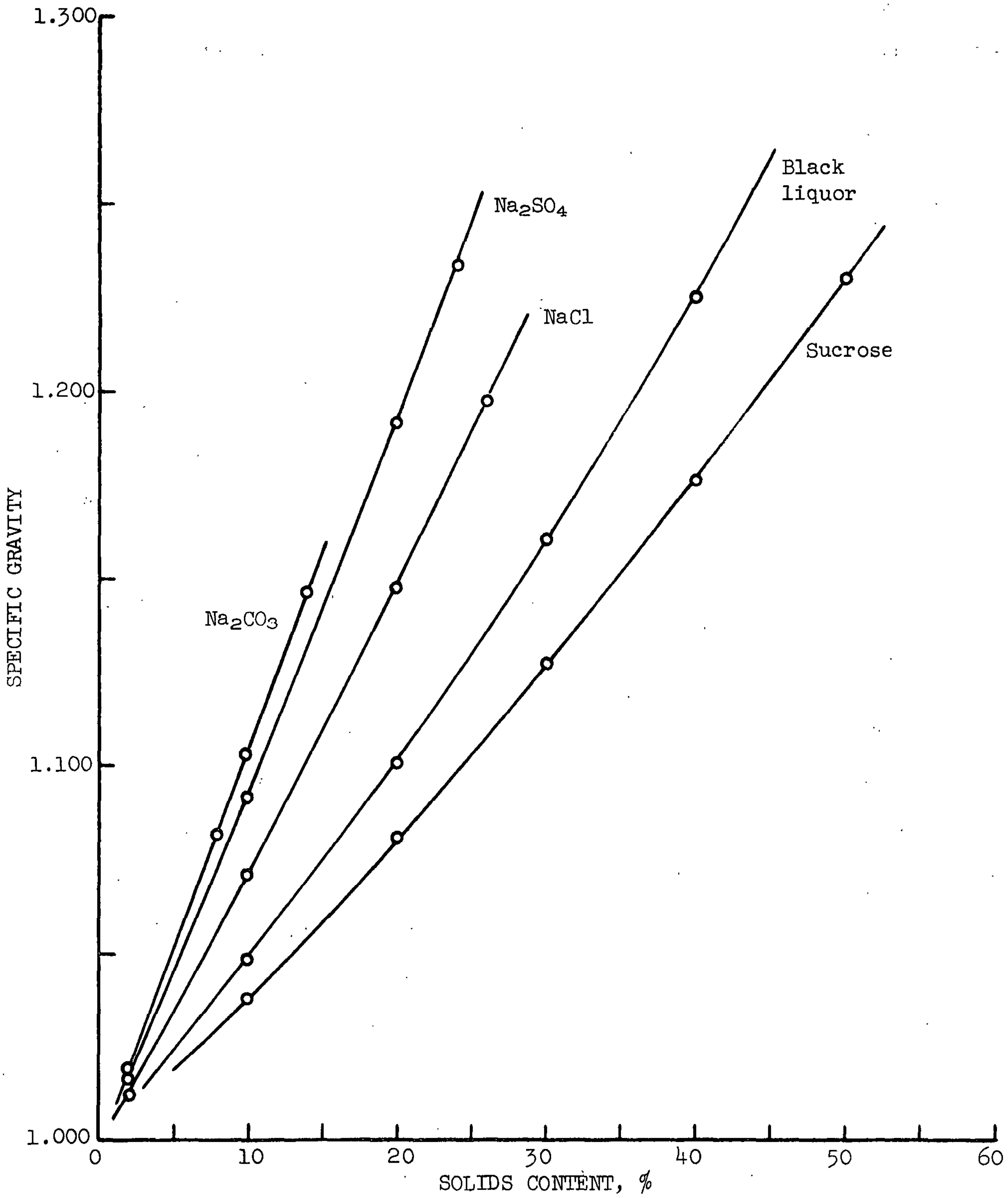


Figure 31. Specific Gravity Data for Various Solutions

It seems quite reasonable to assume that the major variable affecting sonic velocity in black liquor is the organic/inorganic ratio. Although refractive index also responds to changes in organic/inorganic ratio, the dependence is not as clear-cut or direct.

ON-LINE CALIBRATION

Since changes in liquor composition affect the sonic velocity response, and it is essential to avoid interpreting compositional changes as changes in solids content, it would be necessary to maintain instrument calibration during on-line operation. As with the refractometer, the major problem would seem to lie with changes in the functional dependence of sonic velocity on solids content and temperature rather than with drifts or other problems in the instrument itself. Thus, a program for on-line calibration is a major factor in obtaining reliable solids monitoring of black liquor.

The NUS velocimeter is a versatile instrument which can give several measurements on the solution under test. These include sonic velocity, temperature, and sound pulse attenuation in the solution. It can also be set up to read directly some other quantity (such as percent solids) which is a function of sonic velocity. This latter signal can be compensated for temperature variations. It is, of course, such an output which would be used in monitoring solids content of black liquor. This instrument is quite easy to use for measurement of sonic velocity and temperature. It is also easy to set up for reading solids content if the sonic velocity of the solution as a function of solids and temperature is known. Because of the effects which liquor composition may have on sonic velocity response, it is inadvisable to rely on a single set of curves (such as Fig. 21 or 22) in interpreting instrument response. It would be necessary to take periodic samples of the liquor and run a direct determination of solids content, and then use this information to adjust the calibration of the velocimeter.

The basic problem in on-line calibration is making the necessary adjustments on minimal information. Obviously, if a complete set of sonic velocity response data was obtained for each sample, the instrument could be easily readjusted. The calibrated dial settings on the velocimeter pots aid such an adjustment. However, it is not possible to run a full set of calibration curves on each sample, and less data would be available for changing the calibration. Normally, only the actual solids content of the liquor sample and the velocimeter readings would be known.

The adjustments needed to set a calibration are a zero, a span, and the amount of temperature compensation employed. The zero amounts to selecting a particular meter reading to correspond to a particular solids content (usually the lowest expected) and is basically determined by the LOW END ADJUST switch. The span is the change in output (meter reading) which corresponds to a given change in solids content (usually selected so that the meter covers the full range of solids expected) and is controlled primarily by the SPAN ADJUST pot. The amount of temperature compensation is determined by the gain applied to the temperature deviation signal which is controlled by the COMPENSATION ADJUST pot. The setting of the S/V RANGE switch affects both the zero and span and would not normally be changed during a minor adjustment of the calibration.

The adjustments required to maintain calibration depend on the degree to which the sonic velocity response function has changed. As with the refractometer, this could take on three forms: adjustment of zero only, adjustment of zero and span, and adjustment of zero, span, and temperature compensation. The first would require only a single-point calibration, and the second a two-point calibration. The third would normally require only two different concentrations to set zero and span plus the freedom to vary temperature; however, the manufacturer recommends a three-point calibration since the temperature compensation should be set at the mid-range concentration.

Examination of the data in Fig. 26 showing sonic velocity vs. solids data for the three different black liquors indicates that the major effect of composition changes will be a zero shift. The slope of the sonic velocity vs. solids curves (the span) appears to be less affected. If the instrument is set up to monitor solids over a reasonably narrow range (say, 50-60% solids), then the main effect of composition changes would be a zero offset. The proper corrective action in such a situation is a change in the LOW END ADJUST switches, and not a change of the SPAN ADJUST pot. When the liquor sample is taken for a laboratory measurement of the o.d. solids, the S/V deviation, temperature, attenuation and output readings should be recorded along with the settings on the pots and control switches. When the true solids content value becomes available, it should be compared with that obtained from the meter output. The sonic velocity difference associated with any discrepancy between the indicated and true solids content should be calculated and used to make the necessary change in the LOW END ADJUST switches. This would not be the simplest procedure because the switches are based on an octal code and a base conversion would be necessary. Over a period of time, this procedure may lead to significant error in the span, and the instrument should be taken off-line for full recalibration of zero, span, and temperature compensation according to the manufacturer's recommended procedure.

DIRECT MEASUREMENT OF SOLIDS CONTENT

A common theme running through much of the previous discussion is that the instrumental methods for determining solids content are indirect methods based on the measurement of some property dependent on solids content, and that these instruments must be calibrated by means of a direct measurement of solids content. Regardless of the stability and precision of these instruments, their ultimate accuracy is no greater than the accuracy of the solids determination employed in calibration. Since all methods for monitoring solids content are ultimately based on some direct method, some attention must be paid to this subject. This report on the refractometer and velocimeter would be incomplete without some discussion of direct measurement of liquor solids.

The use of the term solids content or concentration implies that black liquor can be considered to consist of two substances: something called liquor solids, and water. It is, of course, possible to make this distinction, and the solids are then identified with the total nonaqueous constituents of the liquor. However, it is important to make a distinction between the nonaqueous constituents and the residual solids remaining after evaporation of the moisture from the liquor. These are not normally the same since volatile matter other than water may be removed during evaporation. Because of the loss of volatiles, residual solids should always be less than the total nonaqueous constituents. It is a somewhat philosophical question to decide which quantity is truly desired, since black liquor is evaporated as part of the firing procedure. No attempt will be made to resolve that question in this report.

Parker _et_ _al_. (_2_) discuss the measurement of black liquor solids in some detail. They list two basic approaches to the problem. The first and most common is to measure the material in the liquor which is nonvolatile under specific test conditions. This might be called the residual solids approach. The second approach is to measure the water content of the liquor and calculate the solids by difference. Residual solids methods include those based on the use of drying ovens (e.g., TAPPI procedures) as well as the use of infrared lamps and a moisture balance (e.g., Cenco moisture balance). The amount of water in black liquor can be determined by titration using a modified Karl Fischer method (4). Another approach to determining the amount of water present is an azeotropic distillation with an organic solvent. Various procedures employing distillation for black liquor solids measurement have been developed.

RESIDUAL SOLIDS METHODS

The main problem in evaporating liquors to a solid residue for gravimetric determinations of solids contents are as follows:

1. The liquor may form a scum which greatly retards the rate of water removal. This results in excessive evaporation times and leads to erroneous high values for solids content due to unevaporated moisture.

2. There may be thermal decomposition of the liquor and subsequent volatilization of organic materials, especially if long drying times or excessive temperatures are employed. Volatilization would tend to cause measured values of solids content lower than the true values.

3. In the presence of air, oxidation of various components of the liquor may take place. Since the oxidation would not normally occur to the extent to which volatile combustion products are formed, the effect of the oxygen uptake would be to cause erroneously high values for solids contents.

Oven-drying procedures have been the basis for TAPPI methods for black liquor solids determinations. These procedures have evolved to try to overcome the problems mentioned above. Parker et al. discuss the latest Proposed Method in their paper. In this revised procedure, black liquor samples are dried at 105°C. for a minimum of six hours. An inert surface extender (such as sand or alundum) and a controlled flow of dried air are used to increase drying rate and eliminate moisture entrapment. Strong black liquors are diluted to allow volumetric handling and to reduce scum formation. The procedure can be summarized as follows.

1. Dry and weigh 25-30 g. of inert material in a wide, shallow glass container. Add sufficient liquor sample to give 1-3 g. of dry solids and weigh. Add 10-20 ml. of water to dilute and distribute samples in excess of 30% solids.

2. Dry the liquor for a minimum of 6 hours in a gravity convection oven controlled at 105°C. ± 3°C. with an air space of one cubic foot or less, adapted to pass dried, preheated air at a replacement rate of about twice per minute. After the initial drying and weighing, drying is repeated for one-hour intervals until the weight loss is less than 0.1% solids per hr.

3. Duplicate determinations on the same sample should differ by no more than 0.3% solids.

It is important, when using this procedure, to keep the sample size within the recommended range. An excessively large sample will lower the surface/volume ratio of the liquor and lead to scum formation. All tests should be run in duplicate. This procedure is not intended as a rapid or routine control method. It may be used to calibrate such procedures.

One of the big drawbacks to oven-drying procedures is the length of time needed to carry out the test. TAPPI Method T 625 ts-64 called for a 24-hour drying procedure. The revised procedure discussed above would still require from 7 to 10 hours to obtain results. In order to overcome this problem, moisture balances combined with an infrared lamp for heating the sample are used for rapid drying and simultaneous weighing. The weight loss can be followed continuously and the end point of very slow loss or constant weight easily determined. The scale on these devices can be calibrated to read solids content directly provided one starts with a fixed initial weight of sample. With such a balance, a solids determination can be made in a fraction of an hour, as opposed to the many hours required with the TAPPI procedure. It is thus suitable for use in the mill as a routine method to enable operators to run a recovery furnace efficiently and safely. However, the moisture balance should be considered a derived method requiring calibration and not as a primary standard method. The reason is that the high liquor surface temperatures which are associated with the higher drying rate may lead to thermal decomposition, formation of an impervious skin, or oxidation of the liquor. Parker _et al_. state that "use of the so-called moisture balances for rapid drying and simultaneous weighing have been evaluated with ambiguous results." It would appear that the moisture balance is suitable for monitoring the more indirect methods (refractometers, velocimeters, etc.) in order to detect drifts and as a check on sudden changes. However, actual changes in the calibration should be based on more accurate procedures.

DISTILLATION METHOD

Distillation methods for moisture analysis in pulp, paper, board, and other materials are well known, and have been applied to black liquor analysis. Basically, the approach consists of distilling off the water from the liquor in the presence of an organic solvent and collecting it in a trap. From the amount of liquor originally present and the amount of water collected, the solids content can be calculated.

A schematic diagram of the apparatus for determining solids content by the distillation method is shown in Fig. 32. A weighed amount of black liquor is introduced into the flask along with the solvent. The distilling trap is initially filled with solvent. Upon heating, both solvent and water are vaporized in the flask and recondensed up in the condenser. As the condensate drops down, the denser water collects in the trap and the solvent is refluxed to the flask. The procedure is continued until all of the water is distilled over. The connection between the flask and the trap should be insulated to prevent condensation of water at that point so as to facilitate capturing all of the water in the collecting trap. The temperature of the contents in the flask will remain close to the boiling point of water until essentially all of the moisture has been driven from the liquor. Then it will rise to the boiling point of the solvent. The end point of the distillation is signalled by the rise in temperature and when the volume of the water in the trap no longer increases with time. The volume of water in the trap is then read and the percent solids calculated. The precision of the test is such that duplicate determinations should agree within ± 0.5% solids.

Parker _et_ _al_. (_2_) make the following comments with regard to distillation methods. "Allowable sample sizes are normally small and vary directly with the sample solids content. Thus weak liquors with high moisture contents require smaller sample sizes to keep the amount of water distilled within the capacity of the collecting trap. Consequently, test accuracy varies widely as solids content changes. Calibration and cleanliness of the apparatus are of utmost importance in the distillation methods, rendering agreement between different laboratories somewhat difficult."

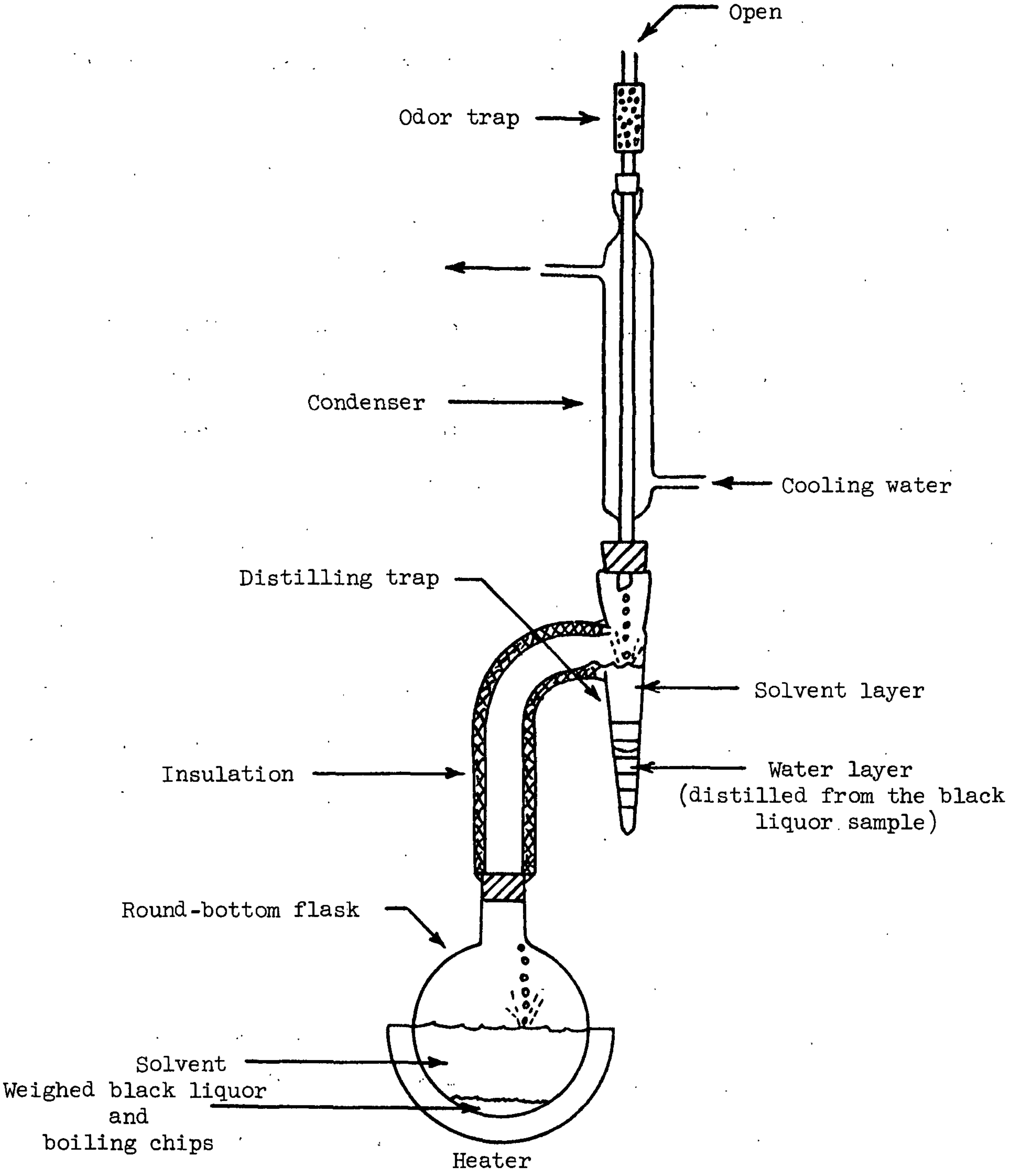


Figure 32. Distillation Apparatus for Solids Determination on Black Liquor

Proponents of the distillation method believe that it offers several advantages over residual solids methods. It is a faster method than oven-drying methods, since a distillation determination can be completed in about an hour. It is also more precise than a moisture balance approach. Among the advantages claimed for the method are the following:

1. With concentrated liquors, the relatively large-size sample of liquor used increases accuracy by permitting a more representative sample.
2. It is not necessary to weigh out liquor samples to a specific weight as with the moisture balance method.
3. Distillation is a direct means for determining water content. Solids can then be defined in an unambiguous manner as the total nonaqueous part of the liquor.
4. The black liquor is heated at a controlled temperature. The temperature remains close to the boiling point of water until evaporation is essentially complete. The maximum temperature is limited to the boiling point of the solvent.
5. Absorption of oxygen from the air is eliminated because the sample is covered by solvent. Since solids are determined from the amount of water present, oxidation of the liquor after the initial weighing would not cause error unless water were produced.
6. Results are independent of the time of distillation once the end point is reached.
7. The time for carrying out an analysis, about one hour, compares favorably with the long times needed for oven methods.

8. The distillation method is reproducible. Measured amounts of water added to black liquor can be recovered quantitatively.

The distillation method would seem to be sound in principle. It may be somewhat less precise than the TAPPI method because weighing the liquor and determining the amount of water are done only to within 0.1 gram. However, it should give correct results if carried out properly.

COMPARATIVE TESTS

In this work, both the ovendry and the distillation methods were employed for the direct determination of solids content. Although all of the data presented on the refractometer and velocimeter are in terms of ovendry solids values, the experience with the distillation method was quite good. There was nothing in the course of making the tests that directly indicated one method was inherently more accurate than the other.

It is interesting to compare values obtained by the two methods. Such data are shown in Table VII. One set of data was taken with Liquor C for a deliberate comparison of the two methods. The other set was taken with Liquor A during flow loop tests and includes a best estimate of the solids content taking into account the amounts of dilution water added. It can be seen that with Liquor C the distillation method tends to give consistently lower values of percent solids than does the ovendry method. The disagreement between the two methods is less in the data taken with Liquor A, although the distillation method does seem to give slightly lower values at high solids contents. It should be emphasized that these tests were not intended to be a conclusive comparison between the ovendry and distillation methods. No great pains to achieve maximum accuracy were taken.

Many of the tests were not run in duplicate. However, the tendency for the distillation method to give somewhat lower values does appear to be real.

TABLE VII

COMPARISON OF SOLIDS VALUES FROM OVENDRY AND DISTILLATION METHODS

	Ovendry Method	Distillation Method	Best Estimate
Data on Liquor C, % solids	69.9	68.2	
	61.3	59.2	
	53.5	53.1	
	42.5	40.7	
	36.9	35.1	
	28.3	25.5	
	15.9	13.1	
Data on Liquor A, % solids	--	61.2	58.9
	58.6	54.8	54.9
	52.7	--	51.7
	48.0	46.7	47.6
	43.2	42.8	43.3
	39.2	39.0	39.3
	35.2	35.6	35.0
	30.4	30.5	30.5
	25.4	24.6	25.4
	20.9	21.4	20.9
	15.8	--	16.0

In interpreting the meaning of the apparently lower values obtained with the distillation method, it must be borne in mind that the value is obtained from the amount of water collected. Thus, a lower value of solids content means a greater amount of water was collected. Most of the errors associated with the distillation method (stopping short of the end point, incomplete condensing, or trapping water droplets on the side arm) would tend to reduce the amount of water collected and hence cause an overestimation of solids content. The two errors which could lead to low solids values are either the solubility of some solvent in the water layer or a consistent underestimation of the initial weight of liquor. It may well be that consistently lower values by the distillation method are actually indicative of a systematic error in the oven-drying procedures. Such an error could be due to oxidation of the liquor during drying or to an inability to drive off the final amounts of moisture. These errors would tend to be greatest with heavy black liquors. Thus, it is possible that the distillation method is more accurate for high-solids liquors, while the ovendry method is more accurate for weaker liquors.

CONCLUSIONS

The results of this test program clearly show that both the refractometer and the sonic velocimeter are capable of effectively monitoring black liquor solids content on a continuous basis. In both cases, the response is a monotonically increasing function of solids content which can be linearized over reasonable concentration ranges. The effect of temperature on the response is sufficiently straightforward so that temperature compensation can be provided. Thus, with proper calibration, either instrument can be used to measure black liquor solids.

No major operational limitations were found regarding the refractometer. The response was not affected by changes in liquor flow or system pressure. Aeration of the liquor did not affect the response. No problems with deposits on the window were encountered; however, the loop was drained and washed with water frequently so the possibility of build-ups over a longer time period remains.

The only significant limitation to the use of the velocimeter was the effect of air bubbles in the liquor. It was practically impossible to obtain meaningful data with the velocimeter until the liquors (which were obtained already aerated) were deaerated. This would not hinder the use of the velocimeter within or after the multiple-effect evaporators, or a high-solids indirect concentrator, since the evaporation process would keep the liquor free of air. However, it is expected that a direct contact evaporator would aerate the liquor. Thus, the velocimeter would not be very applicable beyond the contact evaporator unless some means for on-line deaeration of the heavy liquor were employed.

Both the refractometer and the velocimeter are sensitive to changes in chemical composition of the liquor. The relationships of sonic velocity or refractive index to solids content and temperature are functions of composition.

Thus changes in chemical composition may be interpreted as changes in solids content of the liquor. This can easily cause an error of several percent in the solids content reading. The velocimeter tends to be quite sensitive to the inorganic/organic ratio of the liquor. The sonic velocity increases (which would be interpreted as an increase in solids content) as the inorganic content increases. The relationship appears straightforward and may eventually be susceptible to quantitative treatment of an empirical nature. The effect of composition changes on refractometer response was more difficult to interpret. It does appear that the refractive index tends to decrease (which would be interpreted as a decrease in solids content) as the inorganic content increases. This is the opposite direction from the velocimeter.

Because of the composition dependence of the response of both instruments, it is necessary to recalibrate them periodically to account for changes in liquor composition. The frequency of calibration would be dependent on the experience of a given mill; however, it would appear that the instrument should be checked at least once each shift. The procedures to be followed in changing the calibration "on-line" are discussed in the body of the report and need not be repeated here. If experience indicates that frequent adjustments of the calibration are necessary to maintain agreement between indicated solids and laboratory test values, the instruments should be taken off-line occasionally for a full recalibration.

It would appear that these two instruments could be effectively operated in tandem so as to make use of the fact that they tend to respond in opposite directions to changes in liquor composition. This would certainly permit a distinction to be made between changes in solids content and changes in composition. If both instruments responded together, it would indicate a real change in solids content. On the other hand, if they moved in opposite directions, it would indicate a composition change. It would appear possible that after a certain period of data logging, use of a refractometer and velocimeter in tandem would permit simultaneous monitoring of solids content and inorganic/organic ratio based on an empirical algorithm.

ACKNOWLEDGMENTS

The authors would like to acknowledge the following people who contributed significantly to this work. Mr. O. C. Kuehl and Mr. A. O. Johnson erected the flow loop and helped keep it running. Messrs. H. J. Grady, D. G. Sachs, and C. Piette assisted in taking data and running the liquor analyses. Mrs. E. A. Cary did her usual fine job in typing the manuscript. We would also like to thank the paper and instrument companies who supplied us with the instruments and the liquors which were used.

LITERATURE CITED

1. Black Liquor Recovery Boiler Advisory Committee (BLRBAC) Instrumentation Subcommittee. Report on use and application of black liquor solids monitoring devices. BLRBAC, Oct. 1, 1969.

2. Parker, J. L., Hensel, R. P., and Wagoner, C. L., Tappi 53, no. 5:874-7 (May, 1970).

3. Zacharias, E. M., Instruments and Control Systems 43, no. 9:112-113 (Sept., 1970).

4. Phillips, J. H., and Rubright, M. M., Tappi 36, no. 9:392 (Sept., 1953).

THE INSTITUTE OF PAPER CHEMISTRY

T. M. Grace

T. M. Grace, Research Associate
Division of Materials Engineering
and Processes

Robert N. Larsen

Robert N. Larsen, Research Fellow
Division of Materials Engineering
and Processes