



# NASA Technical Memorandum 58234

## JSC Systems Using Solid Ceramic Oxygen Electrolyte Cells to Measure Oxygen Fugacities in Gas-Mixing Systems

Richard J. Williams and  
Oscar Mullins

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National Aeronautics and  
Space Administration

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Houston, Texas

Measurement of Oxygen Concentration in Solid Ceramics Using  
Oxygen Cells to Measure Oxygen  
Concentration in Gas-Mixing Systems

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## SUMMARY

A system that uses a calcia-stabilized zirconia ceramic electrolyte oxygen concentration cell to continuously monitor the oxygen fugacity in a vertical-quench furnace has been designed, built, and tested. The construction makes extensive use of O-ring seals, commercial tube fittings, and simple solid-state electronic control and measuring devices.

Descriptions are given of a furnace using fibrous zirconium oxide insulation and molybdenum disilicide heating elements; a gas mixer using multiturn needle valves and a special gas-mixing chamber; the devices to monitor the electromotive-force output of the electrolyte cell; the devices to produce programmed rates of change of temperature and redox conditions; the techniques for preparation, mounting, and experimenting with various samples; the operation and maintenance of the system; the calibration of the system; and a thermogravimetric analysis method. This system is durable, highly accurate, and relatively inexpensive to construct. Because the redox conditions are measured directly, the system can be operated under conditions not possible in classical gas-mixing systems.

## INTRODUCTION

Geologists, chemists, and metallurgists commonly study problems in which the valence state of some elements is an important factor. At high temperatures, oxygen fugacity is most often used as the master variable that is manipulated, controlled, and measured during the experimental study of these problems. At atmospheric pressures and high temperatures, gaseous buffering, or gas mixing, is the most common method used to control the oxygen fugacity. This technique is extensively discussed in references 1 and 2. Briefly, two gases that undergo reactions to produce oxygen (such as carbon dioxide and carbon monoxide or hydrogen and carbon dioxide) are accurately mixed and flowed over a sample in a furnace. Depending on the temperature and the gases, oxygen fugacities between  $10^{-24}$  and  $10^{-3}$  can be produced. The oxygen fugacity is computed from the mixing ratios of the gases and the temperature by assuming equilibrium among the gaseous species (ref. 3); however, one investigator (ref. 4) has suggested that the gas reactions may not come to equilibrium under all conditions and thus that the actual oxygen fugacities may not be the same as those computed. Fortunately, the oxygen fugacity can be measured directly during gas-mixing experiments using certain ceramic electrolytes that can be made into oxygen concentration cells (ref. 2). Solid ceramic oxygen electrolyte cells have been used extensively in NASA Lyndon B. Johnson Space Center (JSC) studies involving thermodynamics (ref. 5), phase equilibrium (ref. 6), and crystallization of basaltic rock systems (ref. 7).

During the past 10 years, techniques and hardware have been developed and modified in response to the kinds of experiments required. These highly refined techniques and hardware permit gas-mixing studies to be conducted routinely and simply. This experience will hopefully be useful to other investigators who desire to undertake gas-mixing studies. The objective of this report is to describe the experimental systems and operating

procedures now in use at JSC; the report also supplements, expands, and corrects an earlier publication (ref. 8).

The authors gratefully acknowledge the contributions and significant suggestions of their coworkers including G. E. Lofgren, T. M. Usselman, R. V. Morris, and C. H. Donaldson of JSC; and D. Smith and E. Quinn of Lockheed. We also wish to recognize F. L. Gibbons and T. B. Byers of Lockheed for the development and construction of the electronic temperature programers and measuring devices and the signal analyzer, and T. Doebbler of Lockheed for the design of the balance stand for the thermogravimetric analysis system.

In compliance with NASA's publication policy, the original units of measure have been converted to the equivalent value in the Systeme International d'Unites (SI). As an aid to the reader, the SI units are written first and the original units are written parenthetically thereafter.

### THEORETICAL CONSIDERATIONS

Various ceramics may be used to construct electrochemical cells for the measurement of oxygen fugacity. Reference 2 contains a list of these materials and an extensive discussion of both their theoretical behavior and practical operation. This reference also reviews the literature on electrochemical cells of this type described here. A simple schematic of the cell is as follows.

Reference  $f_{O_2}$ , M|Electrolyte for  $O^{-2}$  ions|M, Unknown  $f_{O_2}$

where  $f_{O_2}$  is the fugacity of oxygen and M is the conducting contact. The net reaction at the cell is  $O_2 + 4e^- = 2 O^{-2}$  and the voltage across the cell is given by

$$E = \frac{RT}{4F} \ln \frac{f_{O_2(unk)}}{f_{O_2(ref)}} \quad (1)$$

where E is the voltage, R is the universal gas constant, T is the kelvin temperature, F is the Faraday constant, and (unk) and (ref) are unknown and reference, respectively. If pure oxygen at 100 000 N/m<sup>2</sup> (1 bar) is used as a reference gas, the equation can be reduced to

$$\log f_{O_2} = \frac{20.159}{T} E \quad (2)$$

Several types of ceramic become oxide ion electrolytes at high temperatures. The two that are most extensively used at JSC are calcia-stabilized zirconia ((CaO)<sub>0.15</sub> (ZrO<sub>2</sub>)<sub>0.85</sub>) and yttria-stabilized zirconia ((Y<sub>2</sub>O<sub>3</sub>)<sub>0.07</sub> (ZrO<sub>2</sub>)<sub>0.93</sub>). The latter type is more useful because it has a lower cost and a wider temperature and  $f_{O_2}$  range.

The utility of these ceramics as oxygen electrodes depends on the presence of anionic conduction. For the two types of ceramics mentioned, the range of temperatures and oxygen fugacities over which anionic conduction accounts for more than 99 percent of the conduction is quite broad; temperatures as low as 873 K (600° C) and as high as 1773 K (1500° C) and oxygen fugacity as low as  $10^{-23}$  and as high as 1 at 873 K are within the 99 percent limit. Beyond these limits, either electronic or cationic conduction contributes significantly to the electrical output of a cell. There is no sharp change in the behavior of the ceramic electrolytes as these other conduction mechanisms begin to operate. Consequently, if these ceramics are used under conditions different from those for which confirmed results have been obtained, care must be taken that the electromotive forces (emf's) obtained are externally and internally consistent.

## SYSTEM DESCRIPTION

The components of the JSC system for control and manipulation of oxygen fugacity are illustrated in block diagram form in figure 1. The system is capable of controlling temperatures and oxygen fugacity, of automatically varying temperature during experiments, and of recording both temperature and oxygen fugacity as a function of time. A modification of the basic system that incorporates an electronic balance (fig. 2) permits the system to be used for thermogravimetric analysis experiments. The following subsections briefly describe the construction and operation of the various components of the basic gas-mixing system and the modifications necessary for operating it as a controlled atmosphere thermogravimetric analysis system.

### Furnace

Furnaces with hairpin molybdenum disilicide heating elements are used rather than platinum-wound furnaces. These heating elements are less expensive than those using precious metal wire, are useful to much higher process temperatures (up to 1848 K (1575° C)), and have nominal lifetimes in excess of 24 months. Particularly when zirconia-based insulation is used, lightweight rugged high-temperature furnaces can be constructed (fig. 3) that have an indeterminately long lifetime if operating conditions are restricted to temperatures less than 1723 K (1450° C).

The radially symmetrical distribution of the hairpin heating elements about the muffle tube produces a large uniform hotspot (fig. 4). Since the heating elements are wired in series and are nearly symmetrical with respect to the location of the oxygen electrode, electrical shielding of the electrode is unnecessary in this system.

## Temperature Control

The molybdenum disilicide furnace elements have low resistance and a matching transformer is needed. Consequently, the temperature controller must be compatible with inductive loading. Although it is possible to build such control systems, commercial systems of high quality are available. (Complete furnaces with compatible temperature control systems can be obtained from several commercial sources.)

## Temperature Programing

Because two thermocouples (one to control the furnace and another to measure the process) are used, a simple method for programing temperature increases or decreases can be used. In general, the method developed at JSC consists of adding or subtracting a controlled voltage to the furnace control thermocouple.

Most temperature controllers compare the output of a furnace control thermocouple to an internally generated reference voltage that is established by the controller set point. As the control thermocouples output (i.e., the temperature of the furnace) approaches that established by the set point of the controller, the controller supplies less and less power to the heater by either reducing the current or increasing the off-time of an on-off cycle. Thus, depending on the type of control system, one of two situations occurs. If the thermocouple output exceeds the set point of the controller, either current is decreased or off-time is increased; if the thermocouple output is less than that of the set point, either current is increased or off-time is decreased.

If a calibrated voltage source is placed in series with the control thermocouple so that an additional voltage can be added to or subtracted from the thermocouple output, the controller senses that the process is either over or under temperature and adjusts its output accordingly, causing the actual process to either cool or heat. Finally, if the amount of extra voltage is controlled by a clock, a controlled time-varying change of temperature can be produced. The same result can be accomplished, though perhaps less efficiently, with cams, gears, motors, and potentiometers.

A block diagram of the temperature programmer is shown in figure 5. A crystal-controlled 1000-pulse-per-hour clock goes to a startup delay circuit that allows up to 79 hours (in 1 hour increments) before any change will occur. This allows experiments to remain at an isothermal temperature for up to 79 hours or to be started at a time such that the end of the experiment will occur during normal working hours if melt time is not critical.

The 1000 pulses per hour also go to a clock divide circuit that sets the duration of the run. The output of the clock divide circuit goes to a 1000-count counter and its output goes to a count-to-voltage converter. When the temperature change starts, the counter and voltage converter are at zero. As counts accumulate, the output voltage increases or decreases depending on the position of the "up-down" switch. The voltage generated causes the controller to either heat or cool the furnace. The converter

output goes to the "nonlinear" card that controls offset, zero, and full-scale millivolts as well as up, down, polarity, and curve shape.

Independently controllable functions and outputs are as follows.

Startup delay range:	0 to 79 hours
Temperature change time:	1 to 999 hours
Output millivolt change:	0 to 50 millivolts
Output direction:	Up or down
Output polarity:	Plus or minus
Output curve shapes:	Linear, exponential, or square root of time

Because the thermocouple emf is not strictly a linear function of temperature and the output of the program is strictly linear with time, a very minor deviation from a linear temperature-time change is produced. In practice, this nonlinearity is less than 2° over week-long time periods.

#### Furnace Heads

To maintain the controlled gas atmosphere in the furnace, gastight O-ring seals are needed. Because of the high-process temperatures, these O-rings need to be water cooled. Figures 6, 7, and 8 illustrate the construction of the water-cooled heads needed to keep the O-rings from burning up. Details of the end plates that hold and position the sample rods and cells are not shown because they may be modified to suit the requirements of the individual experiment. The O-ring grooves in the heads must be cut so that all the metal parts can be brought into tight contact with each other and thus be effectively water cooled. Because ceramic tubes vary in size, precise matching dimensions cannot be given.

These heads have been successfully used with muffle tubes as large as 6.6 centimeters (2.6 inches) in diameter. However, for the larger sizes, heat transfer to heads is so large that either a second cooling ring (fig. 9) or a radiation shield should be used. Most JSC systems are of a 3.8-centimeter (1.5-inch) bore, a size that permits sufficient space for experiments while ameliorating heat-transfer problems. Water flow is connected in series and flows through the top head first. Interlocks are incorporated so that furnace power is turned off if either the coolant flow or the power is interrupted (fig. 10).

#### Gas Mixers

The gas mixer (fig. 11) is constructed with hard tubing using appropriate tube fittings. The total flow through the furnace is fixed primarily by the total output of the two metering valves and thus careful setup

and operation is required to obtain stable operation. A key design feature in the JSC systems is the use of low-pressure gas regulators to produce small highly stable gas pressure differentials across the metering valves and isolate one furnace system from another. The filter (a tube filled with glass wool) in the return line prevents the blow-by of fine particulate carbon, which is produced in the gas reactions in the furnace, into the flowmeter. Clogging of this flowmeter produced a significant maintenance problem for early designers.

A device that replaces the mixing chamber (fig. 12) is particularly useful in those situations in which one of the gases is in lower concentration than the other. The minor component is fed through the small-diameter inner tube; the major component is fed through the side port. The device works somewhat like a carburetor to produce a more complete mixing of the gases and to prevent the flow of the major gas from affecting the flow of the minor gas.

### Electrolyte Cell

The construction and mounting of the electrolyte cell are illustrated in figure 13. O-ring seals are used to produce gastight seals against the ceramic while permitting enough slippage to accommodate the differential expansion of the components during heating. A compression spring is incorporated to ensure that the inner electrode contact remains firm as temperatures are changed. There are two ways of mounting the assembly in the furnace. The system at JSC is mounted so that the sensing head of the electrode and the sample are symmetrically disposed about the axis of the furnace; however, in small-bore systems, a coaxial arrangement is necessary. The coaxial design precludes vertical quenching.

Several points relevant to the construction of the cell are not obvious in figure 13. Inner and outer electrode contacts are easily made of metal tubing that is made to fit the ceramic tube. Lead wires are spotwelded to the contacts. The contacts and leads may be made of any metal that does not react with the ceramic; e.g., platinum. However, both inner and outer contacts and leads should be of the same metal. One leg of the thermocouple may be used as the reference lead for the cell if a thermocouple is placed inside the cell itself to simplify wiring. Heavy lead wires (0.76 centimeter (0.30 inch)) and contacts (0.0102 centimeter (0.004 inch)) extend cell lifetime. The process thermocouple placed inside the cell is protected from adverse effects of the furnace gas; but, because of this isolation, it may be at a slightly lower temperature (up to 6 K (6° C)) than the actual process temperature.

A second thermocouple may be placed inside the sample rod near the sample for more precise measurement but must be calibrated frequently because of its exposure to the furnace gases.

The reference gas for the cell is provided by an oxygen gas purge in the interior of the cell. This flow should be delivered to the inner electrode contact; therefore, the inner ceramic tube that supports the leads and inner contact must be continuous. Flow rates of 0.00085 to 0.0017 stdm<sup>3</sup>/h (0.03 to 0.06 stdft<sup>3</sup>/h) are sufficient to provide a stable refer-

ence. Oxygen is vented to the laboratory from the base of the cell through the holes carrying the lead wires out of the cell.

The electrode is introduced from the bottom of the furnace and the atmosphere-control gas flow is directed from top to bottom. This procedure provides for a stable operation; any volatiles that condense on the cell (water from hydrogen-containing mixtures) will flow to the bottom of the furnace, and any leaks of reference gas from the cell will be flushed out of the system without affecting the charge.

The electrolyte ceramic cells are available in several sizes. Those of 0.635-centimeter (0.25-inch) outside diameter (OD) and 0.953-centimeter (0.375-inch) OD were used in the system described here. These larger tubes are preferred because they are less sensitive to thermal and mechanical shock.

### Electrode Measurement System

The electrolyte cell is a high-impedance device at low temperature (approximately  $10^{14}$  ohms at 873 K (600° C)); however, at high temperature, its impedance decreases to a few thousand ohms at 1773 K (1500° C).

A matching circuit (fig. 14) provides the high-input-impedance interface between the cell electrode and a common lower input-impedance voltmeter. A high-input-impedance low-input-current device is needed as a buffer between the electrolyte cell and the lower impedance measuring circuitry to prevent premature cell failure. In addition, a powerline-frequency notch filter was found to improve the accuracy of fugacity readings because 60 hertz more easily finds its way into the high-impedance circuit.

The input buffer, BB 3528 CM, is a Burr-Brown Research Corporation<sup>1</sup> field effect operational amplifier with a room-temperature input current typically at  $7.5 \times 10^{-14}$  amperes. A buffer with a gain of one drives a tuneable notch filter. The filter can be tuned to reduce 50- or 60-hertz noise by a factor of 30 (minimum) and the notch is no wider than about  $\pm 9$  hertz when using  $\pm 10$  percent capacitor values. A deeper narrower notch can be obtained by lowering the value of the 68-ohm resistor and using matching capacitors. The output of this matching circuit is then the input for an inexpensive digital voltmeter; millivolt resolution is thus easily obtained and is more than sufficient.

### Calibration

Temperature.— Temperature calibrations are performed by the use of thin gold wire (0.127 millimeter (5 mil)) placed across the two sample

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<sup>1</sup>Although a specific manufacturer's part has been cited, suitable replacements can be used. We have retained the manufacturer's name not as a certification of that part but rather as a convenient way of completely specifying all the required characteristics.

wires; a relay/buzzer is connected in a series with this wire. The furnace is brought up to the melting point of the gold (1337.6 K (1064.4° C)) very slowly. When the gold melts, the relay opens and the buzzer sounds; calibrations within  $\pm 1$  K ( $\pm 1^\circ$  C) are easily obtained. Other methods can be used but all calibrations should be under actual run conditions; i.e., gas flow normal, sample rod in place in the hot zone, quench port closed, etc. Additional calibration points are possible (again in the actual run configuration) using convenient thermometric calibration materials (sodium chloride, 1073 K (800° C); gold, 1337 K (1064° C); lithium metasilicate, 1475 K (1202° C); diopside, 1668 K (1395° C); anorthite, 1828 K (1555° C).

Numerical monitoring of temperature with automatic compensation for ambient temperature is very convenient. Temperatures should occasionally be checked with a potentiometer.

Electrode.- The electrode should be checked for correct emf response. Most errors in calibration are due to incorrect electronic hookup or to incorrect placement of the sample relative to the electrode. The three most convenient calibrations are against air, the nickel-nickel oxide (NNO) buffer, and the iron-wüstite (IW) buffer. The electromotive forces of the cell in millivolts with pure oxygen gas as a reference are given by the following equations:

$$\text{Air: } E = -0.0337T$$

$$\text{NNO: } E = -1231 + 0.462T$$

$$\text{IW: } E = -1350 + 0.326T$$

where T is in kelvin. (Note that the electromotive forces are always negative within the operational temperature range. The polarity of the electronic setup can be rapidly checked.) The best procedure is to reverse the metal/metal-oxide buffer reactions using metal foils as a starting material and duplicating actual run configurations as far as possible. The use of foils is convenient because the calibration is a tarnish technique and the tarnish forms or dissipates in approximately 15 minutes.

#### Run Procedures

Starting from a completely down condition, the first step is to begin the oxygen reference flow to the electrode. The temperature of the furnace is then increased slowly to approximately 1473 K (1200° C). The emf from the electrode is monitored during this procedure; with the furnace open to air, the electromotive forces are near those of the air/oxygen couple. In a dynamic system, the precise electromotive forces are rarely attained but an approximately correct response indicates that the electrode and electronics are functioning correctly. At approximately 1473 K (1200° C), the furnace is sealed and carbon dioxide is flowed through the furnace for a few hours to degas the system. Finally, pure carbon monoxide is run through the furnace and the emf output of the electrolyte cell should exceed 1000 millivolts at 1473 K (1200° C). If it does not, either an air leak exists

in the system and all the seals must be checked or the electrical contacts within the cell are loose and must be tightened.

After this "baking out," the gas flow is adjusted to run conditions. The exhaust valve from the furnace is set full open and the mixing needle valves are each set half open. The gas feed pressures are set between 6.9 and 27.6 kN/m<sup>2</sup> (1 and 4 psig) on the low-pressure regulators. The needle valves controlling the input gases are adjusted until the desired total flow is obtained: 0.0085 to 0.01416 stdm<sup>3</sup>/h (0.3 to 0.5 stdft<sup>3</sup>/h) is sufficient. The exhaust valve is closed until the flow is just affected. This procedure slightly pressurizes the furnace, minimizing leakage of air into it. To change the oxygen fugacity, the mixing ratio is adjusted by turning both needle valves, opening one while simultaneously closing the other, except for minor changes (3 to 5 millivolts). The calibration procedures for the thermocouple and cell are then performed.

A description of the sample preparation and mounting techniques that are routinely used in the JSC laboratory is contained in reference 9. The loop technique described in that publication is used for samples that will melt during the experiment. For experiments below the solidus, a basket formed by wrapping wire (platinum, silver, palladium alloy, etc., as appropriate) around the tapered end of a pencil is used. Both holding techniques permit the maximum exposure of the sample to the furnace atmosphere with minimum contact between the sample and its holder.

A sample attached to the sample rod is inserted into the furnace through the sample port. When initially inserted, the sample is held near the top of the muffle. It is gradually lowered (in steps) into the hot zone over a 10- to 15-minute period to permit the sample to degas and gradually adjust to the high-temperature environment. The temperature and  $f_{O_2}$  may change slightly after the sample is inserted because of degassing of the sample and sample holder and their thermal mass. Conditions should return to the original settings within 5 to 10 minutes; if not, only the slightest adjustments should be necessary. Fluctuations of  $\pm 1$  to  $\pm 3$  millivolts over daylong periods are normal. If the quench port is opened, the orientation of the sample and the electrode can be examined with a mirror. Because of the gas-flow pattern, the redox conditions near the sample are not affected by opening this port. The quench is accomplished by electrically burning the fine platinum wire and dropping the sample through the quench port or removing the sample, still attached to the sample rod, through the sample port.

#### CONTROLLED ATMOSPHERE THERMOGRAVIMETRIC ANALYSIS SYSTEM

By modifying procedures and constructing some additional hardware and electronics, an analytical balance may be integrated with the gas-mixing system to make a thermogravimetric analysis system. The descriptions are based on a particular type of balance; however, modification to other types should be rather direct and obvious.

## System Description

A block overview of the system is shown in figure 2. Many of the electronic and mechanical components are identical to those described above and will not be described again. A generalized drawing of the balance stand is shown in figure 15 and hardware for coupling the balance to the furnace is shown in figures 16 through 19.

For the type of balance used for this system, the rounded end of the pyrex cap on the sample side is cut off. An adapter of aluminum or brass that fits the diameter of the hang tube joins it to the water-cooled furnace heads (fig. 16). O-rings are used to provide a gastight seal. Because the basic designs use a symmetrical offset about the axis of the furnace for use with the electrolyte cells, an adapter plate (fig. 17) is used to produce a consistent and mechanically stable offset. If no cell is used or if physically large samples are to be run, the adapter plate may be eliminated and a purely axially aligned sample configuration may be used.

Most of the gases used for atmosphere control are quite reactive and cannot be allowed to contact the balance itself. An iris diaphragm (from a camera) has been incorporated into the adapter plate of the furnace (fig. 18) and a gas system (bottle, regulators, and flowmeter) provides an inert atmosphere in the balance chamber (fig. 2). The iris is opened for inserting or removing samples and closed during an experiment, and a very slight (less than  $0.00028 \text{ m}^3/\text{h}$  ( $0.01 \text{ stdft}^3/\text{h}$ ) flow of argon prevents the furnace gases from entering the balance chamber.

If carbon monoxide-carbon dioxide gas mixtures are used to control the oxygen fugacity in the furnace, a special problem arises due to the precipitation of graphite from the reacting gases onto the hang wire. The weight changes observed on the balance become meaningless when this happens. The ceramic tube through which the hang wire passes (fig. 19) may be used to overcome this problem. A small flow of argon down the tube prevents the furnace gas from contacting the hang wire before it emerges from the tube. This tube arrangement, however, makes the insertion and removal of samples more difficult.

Samples as light as 55 milligrams may be used; however, turbulence in the gas atmosphere causes both the oxygen fugacity and the apparent weight to fluctuate. Cyclical random weight changes as large as  $\pm 100$  micrograms with very small samples under extreme conditions are produced. This noise can be minimized by using heavy samples or by weighting the hang wire near the sample. By weighting the hang wire, samples as small as 55 milligrams can be used and fluctuations reduced significantly. The remaining noise can be reduced by passive filtering; if the signals are filtered too much, however, response to real changes is slowed. Since the noise is random and cyclical, it may be averaged over time to provide an accurate quantitative measure of  $f_{\text{O}_2}$  and weight. This is accomplished by using time-averaging electronics. A recorder and passive filter network are used to provide a visual monitor of the weight and oxygen fugacity changes.

## Signal Averager<sup>2</sup>

The emf output from the electrolyte cell and the electronic balance is read once every second and accumulated in two registers of a micro-processor while the number of readings is accumulated in a third register. At the end of a set time (0 to 99 minutes), the accumulated emf is divided by the number of readings. At the completion of each time period, the time-averaging circuit records the averaged values of both channels and the time of day and the next time period begins. The input range for channel 1 (weight) is 0 to +10 millivolts and the input range for channel 2 (oxygen fugacity) is 0 to -1 volt.

The basic components are shown in figure 20. Five different cards are involved.

1. Analog card - This card accepts the input signals and performs a voltage-to-frequency conversion. Each channel is first multiplied by an amplifier to obtain a 0- to +10-volt signal. The gain on channel 1 is +100 and on channel 2 is -10. Each signal is then input to an Intech 8400 V/F converter. The output of the converter ranges from 0 to 16.67 kilohertz full scale. This is followed by a pair of  $\div 10$  counters that drop the rate to 166.7 hertz (10 000 counts/min), which is used as the output.

2.  $\div N$  card - This card provides normalization of the count rate by dividing the count rate by the time period set on the digi-switches. A 1-minute time period does not affect the count rate, whereas a 2-minute period divides it by two, a 3-minute period divides it by three, etc. In this way, the final full-scale count is always 10 000, regardless of how many minutes were used to accumulate the counts.

The card consists of two down counters that are preloaded with the numbers set on the digi-switches and then clocked down by the pulses from the analog card. When the counters count down to zero, a one-shot fires to preload the counters and the cycle starts again. The one-shot pulse is used as the output pulse from this card.

3. Logic card - This card consists of three sections, counters and display, real-time clock and display, and processor. The counters consist of Ferranti-type ZN1040E chips, which are four-decade devices. The 1040's then drive Hewlett-Packard-type 4700 displays. There is a separate display for channels 1 and 2.

The real-time clock consists of a National-type MM5312 clock chip that also drives the Hewlett-Packard displays to provide time-of-day information. The 60-hertz reference for the clock chip is provided by a National-type MM5369 using a 3.58 megahertz crystal.

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<sup>2</sup>Although specific manufacturer parts are mentioned in this section, this is not to be construed as a recommendation; other parts with the same specifications would be acceptable.

The processor is a MOS Technology 6502. The program is stored in RAM memory located on the memory card. RAM memory is provided as part of the 6530 peripheral interface adapter (PIA) that serves as the interface between the processor and the printer card. Two other PIA's are used to connect the processor to the two counters, the real-time clock, and the time-interval digi-switches. A 555 timer acts as a master clock for the digit multiplexing and interrupts the processor to tell it when a new digit is available.

4. Printer Card - This card accepts data from the output PIA on the logic card in a bit-parallel digit-serial pattern and inputs it to shift registers to provide a 24-bit parallel output for the printer.

5. Memory card - This card contains the three 1702 EPROM's that contain the operating program. This program controls data acquisition and transfer.

The only controls that the operator can set are on the analog card. There are six potentiometers; two amplifier offset potentiometers are used to make the outputs of the amplifiers zero (when the input is zero) and the other four potentiometers are used to set the range and offset of the final displays.

### Operation

Temperature, oxygen fugacity, and hotspot calibrations are done as previously described. The balance, hang tube, and furnace assembly must be carefully aligned. It is essential that the sample and hang wire do not touch any portion of the system and that the balance moves freely. This alinement is done with the furnace cold.

After alinement, the distance between the attachment hook on the balance arm and the sample position (adjacent to the electrolyte cell and in the center of the furnace hotspot) is measured. A length of platinum wire approximately 2.5 centimeter (1 inch) longer than this length is cut. Loops are made in each end of the wire and it is hung from a hook with an approximately 50-gram weight attached to the free end. The wire is very carefully heated with a propane torch to anneal, straighten, and stretch the wire. Finally, the wire is remeasured and cut so that when a sample is attached, it will hang at the desired position. (It is more efficient to prepare several of these wires at one time.)

The furnace is brought to temperature and the oxygen fugacity adjusted to the desired initial condition. The balance is raised off the furnace and argon flow into the balance is begun. If the iris adapter is being used, it is closed tightly. The sample is attached to the balance arm, weights are added to the other arm of the balance until the two are balanced, the iris is opened, and the balance is lowered and locked into the final position and sealed. The iris is closed as tightly as possible without touching the hang wire. If the hang tube is being used, the procedure is the same except for the opening and closing of the iris and the more difficult insertion procedure of the sample.

It will take several minutes for the oxygen fugacity and temperature to recover from the effects of sample insertion and the weight may take several hours to stabilize. If the hang tube is in use, the argon flow must be carefully adjusted by shutting off the argon and then slowly increasing the flow until it just effects the emf output from the cell. The flow is then reduced slightly.

After the weight has stabilized, it is electronically balanced to zero. The null position is then the reference point from which subsequent weight changes can be measured. If the sample has been weighted accurately before the experiment, absolute weights can be obtained; but usually differences in weight are the most important measurement.

The oxygen fugacity or temperature may now be changed and the changes in the sample weight recorded either graphically or digitally or both. Operation of the gas-mixer and temperature-control system is as described in previous sections.

An experiment is terminated in one of two ways. If the iris is in use, it is opened and the balance with the sample attached is carefully withdrawn through the top. If the hang tube is being used, the furnace temperature is lowered; then the balance is raised slightly and the hang wire is detached from the balance with a pair of tweezers and held in place while the balance is raised out of the way. Then the hang wire and sample are carefully pulled through the ceramic tube.

#### PRECAUTIONS

The ceramics used to make the electrodes are very sensitive to thermal shock at temperatures above approximately 773 K (500° C). Once the electrode is in place and the heating process is begun, it is best to restrict the movement of the electrode to an absolute minimum. This is accomplished by mounting the electrode so that the sensing head is in the center of the hot zone of the furnace. Any subsequent alinement is accomplished by adjusting the sample position only. To prevent thermal shocking, the reference gas-flow rate is kept as low as possible.

Finally, during the cooling of the furnace, the furnace must either be opened to the air or the gas flow must be continued during the cooling; otherwise, a substantial vacuum can be created.

#### COMMON PROBLEMS

##### Erratic emf Output

All shielding, grounds, and electronic connections must be checked. Leads should be firmly connected to the electrode and it should be ensured that there is no short circuit to the temperature-measurement system.

## Incorrect emf Output

All ground loops must be eliminated and all metal surfaces must be grounded. If these sources of error have been eliminated, the only other sources of incorrect electromotive forces are miscalibration and misalignment of sample and electrode.

In recent years (since about 1978), electrolyte cells that produce systematic offsets in emf from the theoretical values have been found. This problem has also been noticed in other laboratories. Although some procedures have been developed that can eliminate the offsets in some cases, no general procedure exists. Indeed, sometimes several different cells have been tried randomly until one that gave an acceptable response was found and then calibrated to actual response (usually offsets of 3 to 5 millivolts).

## Drift

At highly reducing conditions, graphite or water (or both) form in the system. These clog the output flowmeters and lines affecting the gas flow. To prevent this from occurring, a filter containing silica wool is placed in the exhaust line between the furnace and the exhaust flowmeter. The filter should be checked for carbon and cleaned. The needle valves used for mixing can wear out and may slip. Drift caused by changes in gas composition will be noted when the bottles begin to be depleted, particularly if gas mixtures are used; e.g., hydrogen in nitrogen or carbon monoxide in nitrogen. Drift may also occur if the metallic contact to the electrode is not firm. A spring-loaded electrode that keeps the inner contact of the cell firm eliminates most problems of this type.

## Overshoot

In adjusting the mixing ratio, changes of the gas mixture take a finite time to be effective in the furnace. This time varies with the flow rates used and with the construction of the gas mixer. It is best to adjust the mixing ratio slowly and in small steps to prevent overadjustments. Changes in  $f_{O_2}$  are not linear with the mixing ratio; so, depending on the particular conditions of the experiment, varying amounts of adjustment are needed to cause a similar change.

## Old Age

After a cell has been used for several months, metal from the contacts migrates through the ceramic to produce a partial short circuit. Erratic emf outputs, incorrect emf response, and drift can occur unpredictably. This problem is seen only in cells that have been in continuous use for several months and the solution is to replace the cell with a new one. Also, sample material can sometimes be dropped on the top of the electrode rendering it useless.

## MAINTENANCE

Although the lifetime of the system is theoretically very long, in practice the system functions only for 8 to 12 months before some component breaks down. When this occurs, a complete maintenance check of the system should be made that includes the following.

1. Replace all wiring and contacts in the cell.
2. Check all O-ring seals and grease or replace, if needed.
3. Check plumbing and clean flowmeters and valves.
4. Check and clean water-cooling system.
5. Recalibrate for temperature and oxygen fugacity.

By following this procedure, it is possible to reduce downtime significantly. All items used for maintenance are relatively inexpensive.

The furnace, under some conditions of use, may become saturated with water or graphite. The result is drifting electromotive forces, sluggish response, and general instability of redox conditions. The situation can be remedied by opening the top and bottom ports of the furnace and allowing it to operate at about 1473 K (1200° C) for approximately 24 hours. This procedure dehydrates the furnace and "burns out" the graphite. It is necessary to do this every 4 to 6 weeks if highly reduced experimental conditions are used constantly.

## CONCLUDING REMARKS

This experimental system for measuring oxygen fugacities in gas-mixing systems should be useful to investigators engaged in research in which control of redox conditions is necessary. The system was developed in conjunction with a variety of studies performed at NASA Lyndon B. Johnson Space Center where the capability and utility of the system have been verified. Investigators at Lyndon B. Johnson Space Center have established and validated the procedures for operating, calibrating, and maintaining the system. These researchers believe that the system is the simplest and least expensive one available and that it should be useful in a variety of experimental applications.

Lyndon B. Johnson Space Center  
National Aeronautics and Space Administration  
Houston, Texas, January 16, 1981  
152-85-00-00-72

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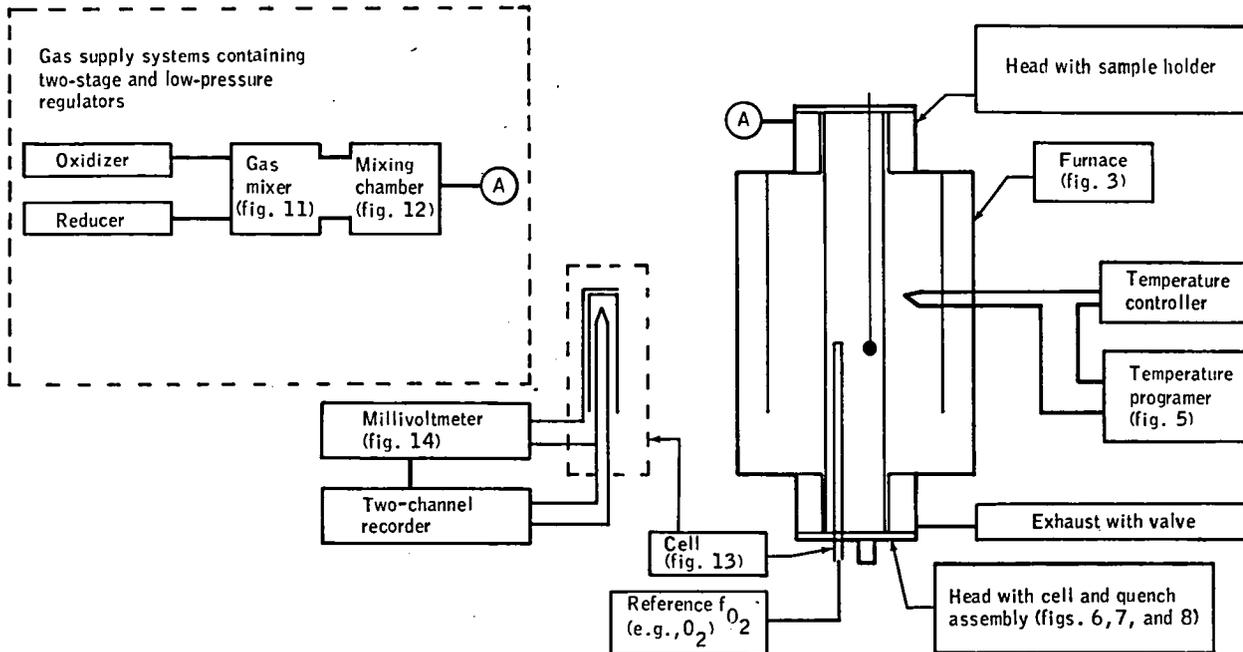


Figure 1.- Block diagram of JSC gas-mixing system. Components of the system are shown in greater detail in the figures indicated in parentheses.

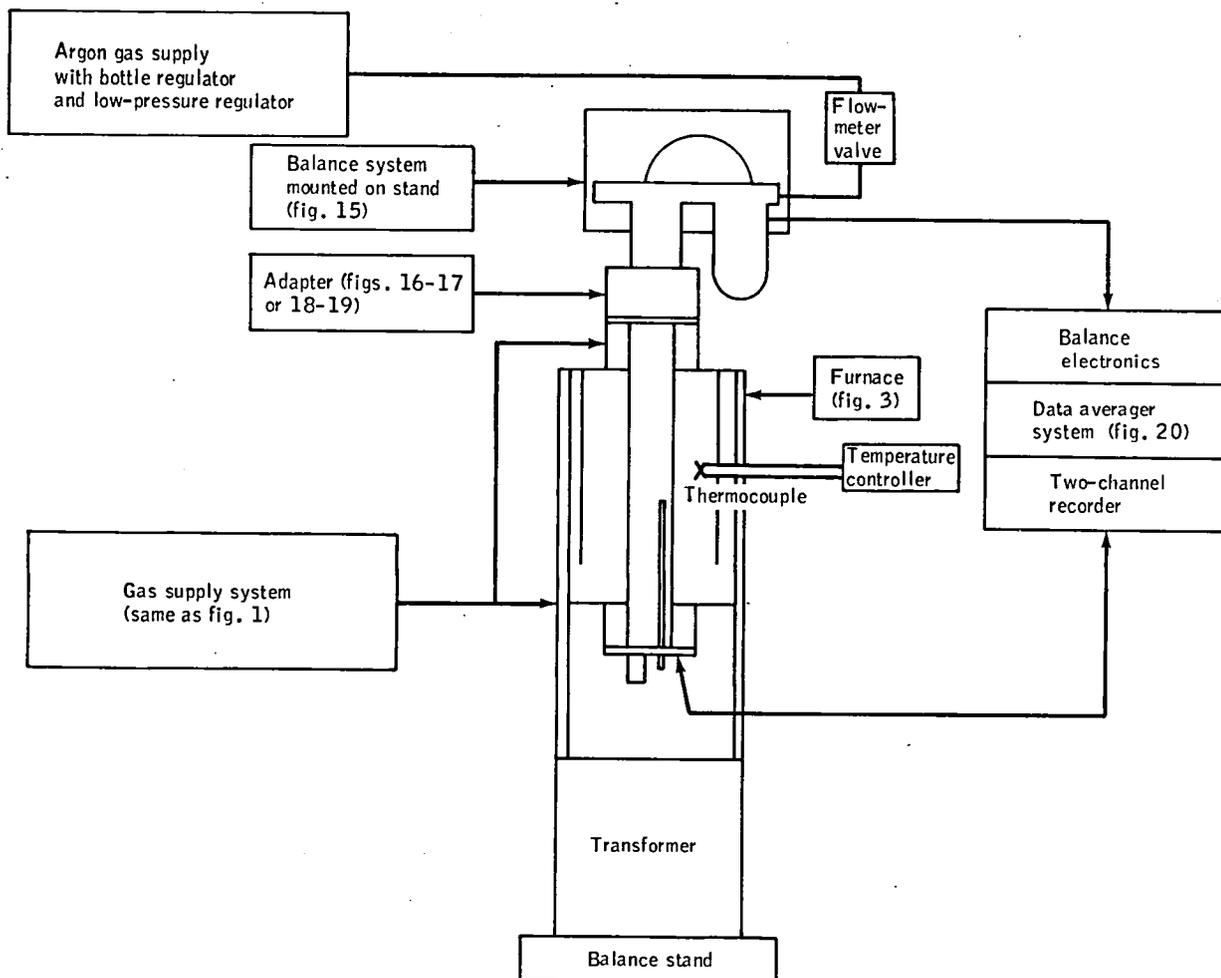


Figure 2.- Block diagram of controlled atmosphere thermogravimetric analysis system. Components are shown in greater detail in the figures indicated in parentheses.

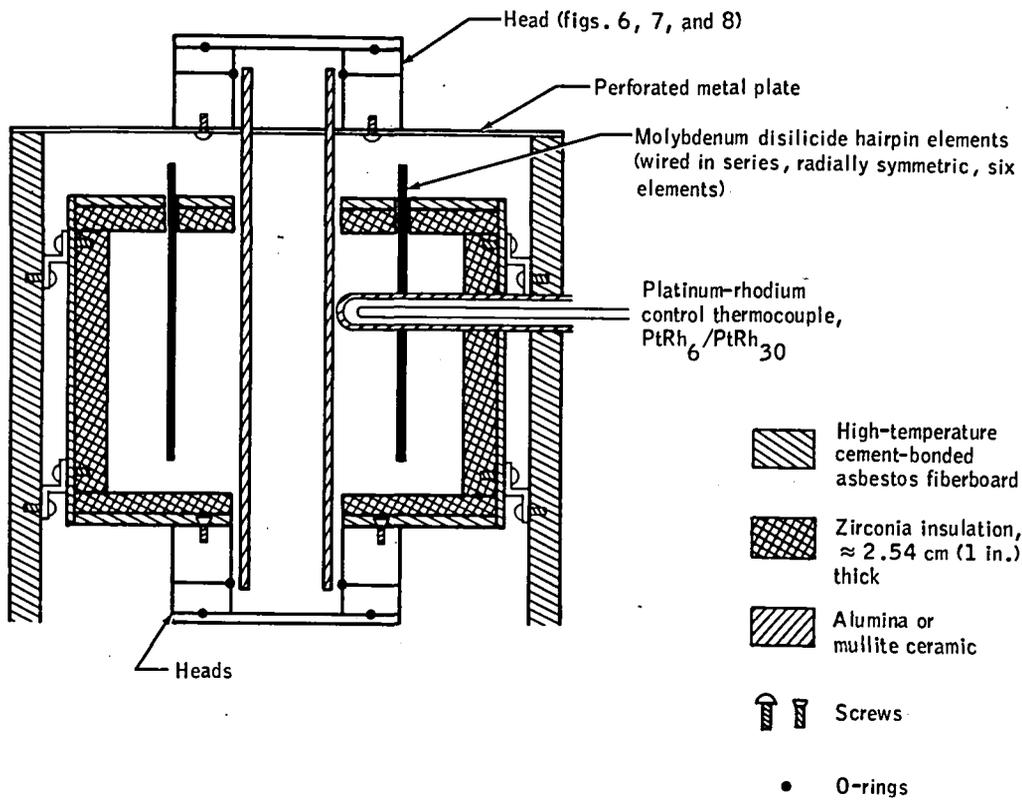


Figure 3.- Cross-sectional view of construction of high-temperature furnace (not to scale).

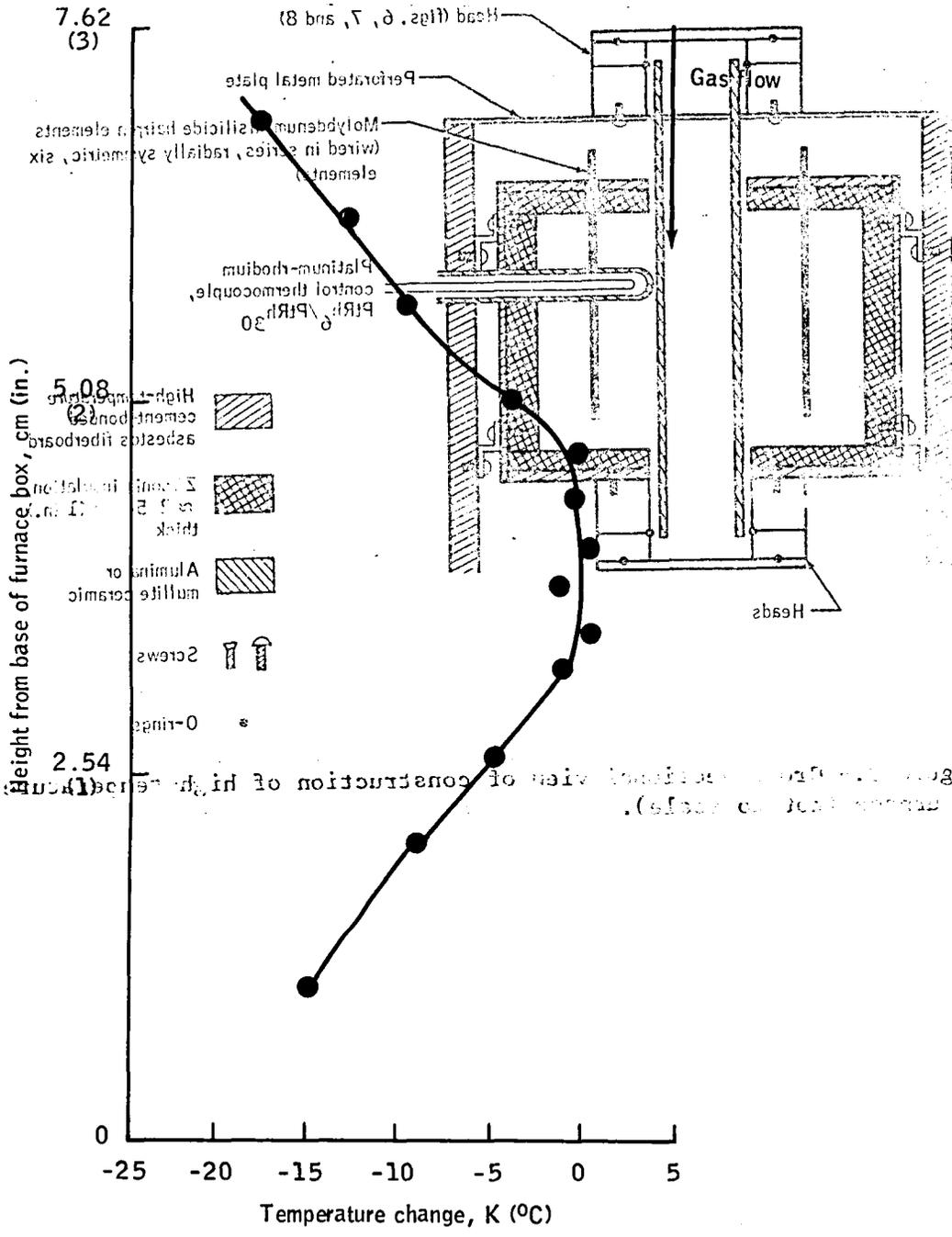


Figure 4.- Profile of hot zone. Average results from 1273, 1473, and 1673 K (1000°, 1200°, and 1400° C) hotspot temperatures.

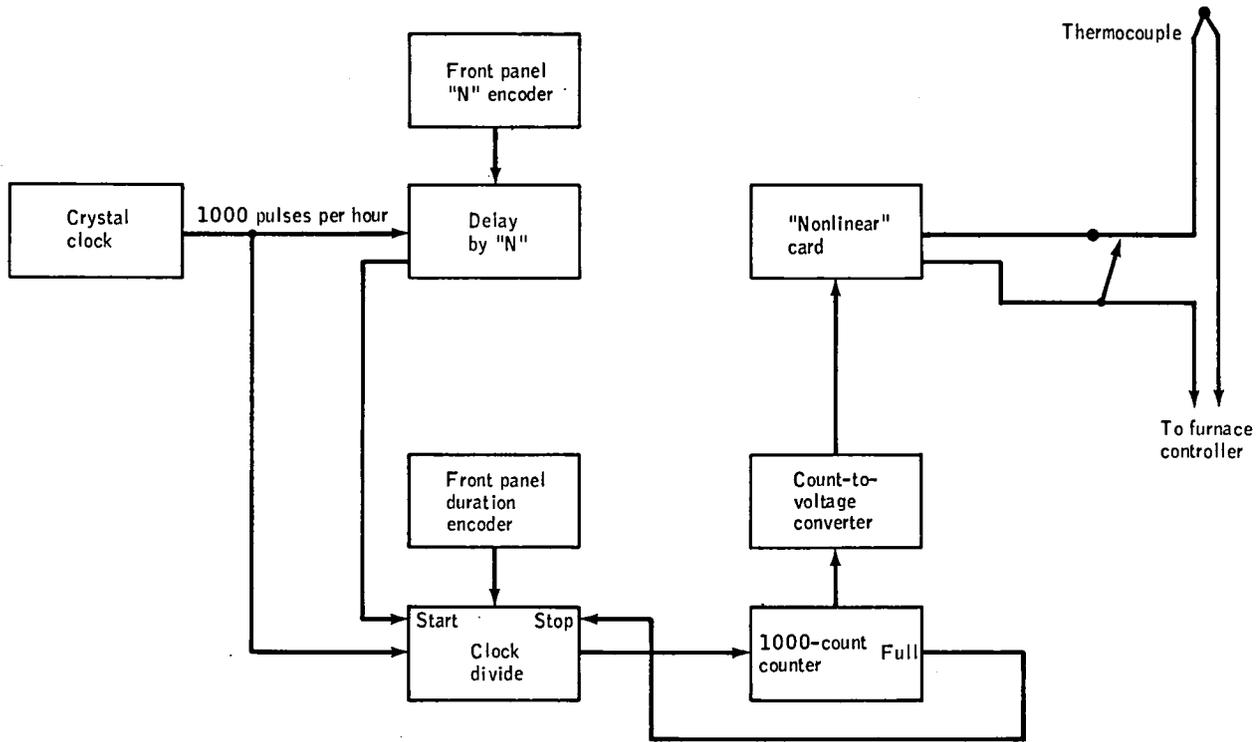


Figure 5.- Block diagram of temperature programming circuit.

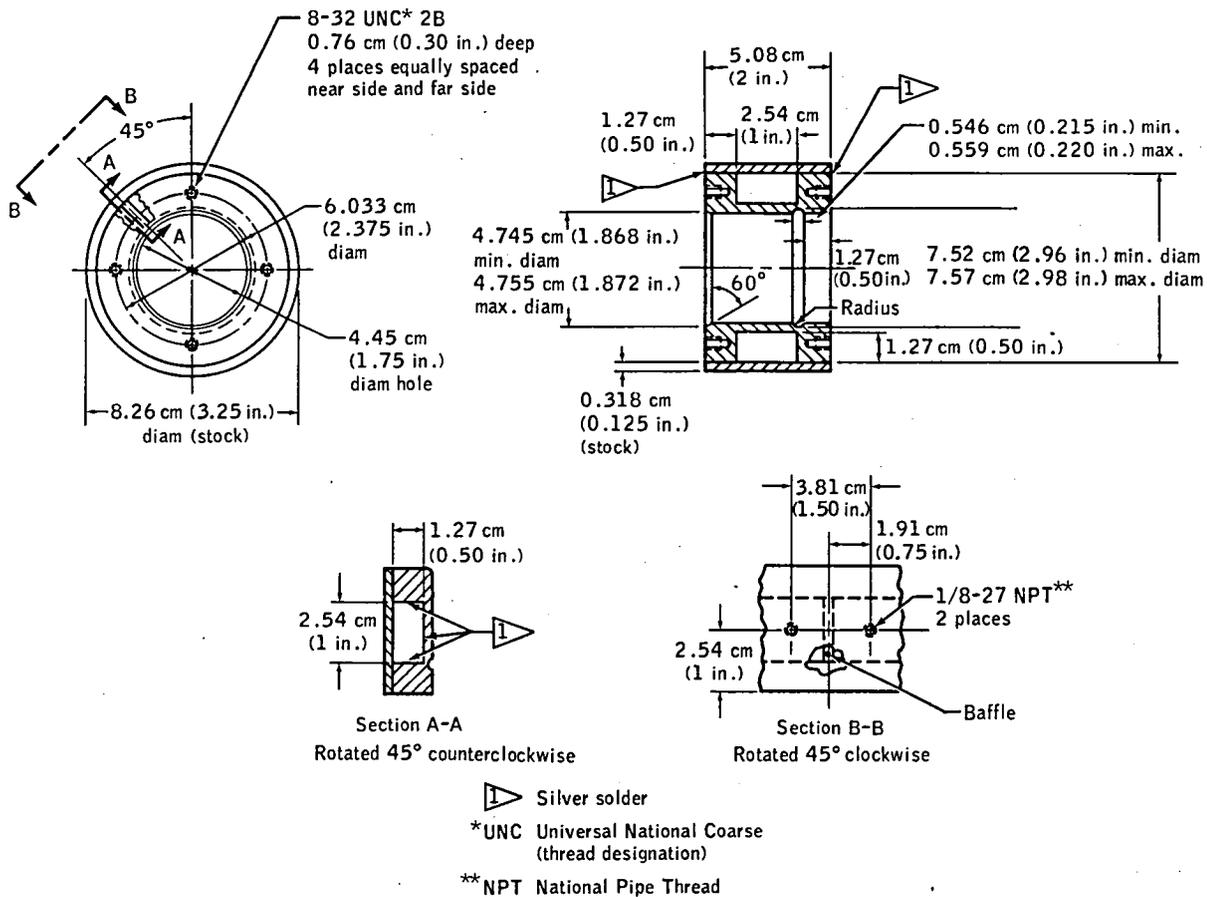


Figure 6.- Detail of water-cooling head. To obtain uniform water flow, a baffle is soldered between the input and output fittings inside the head (section B-B) before the water jacket sleeve is soldered in place.

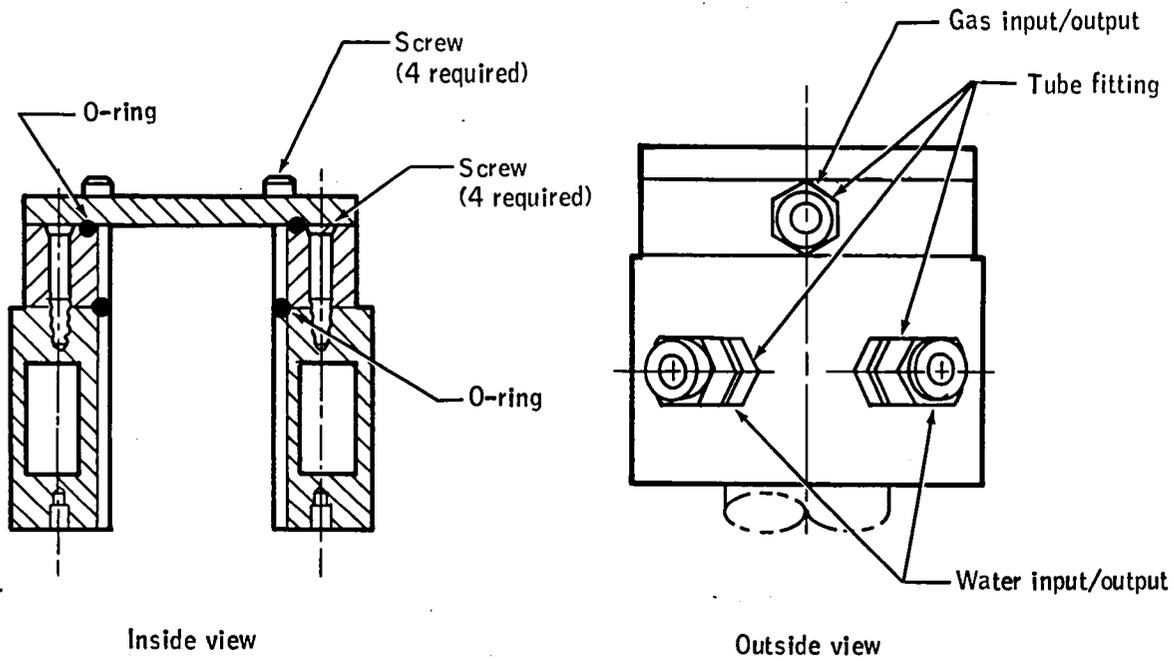
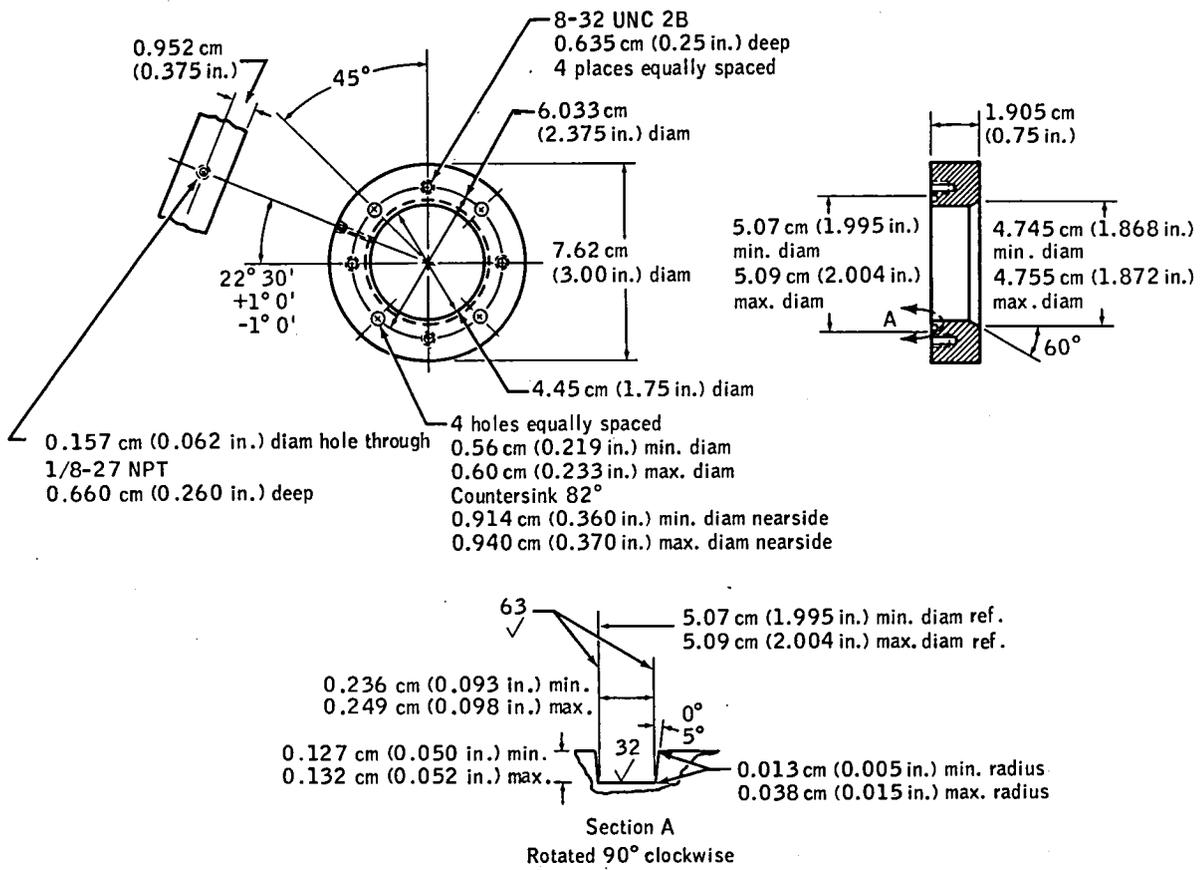
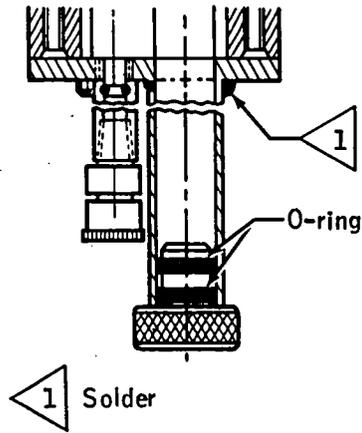


Figure 7.- Water-cooled furnace seals.

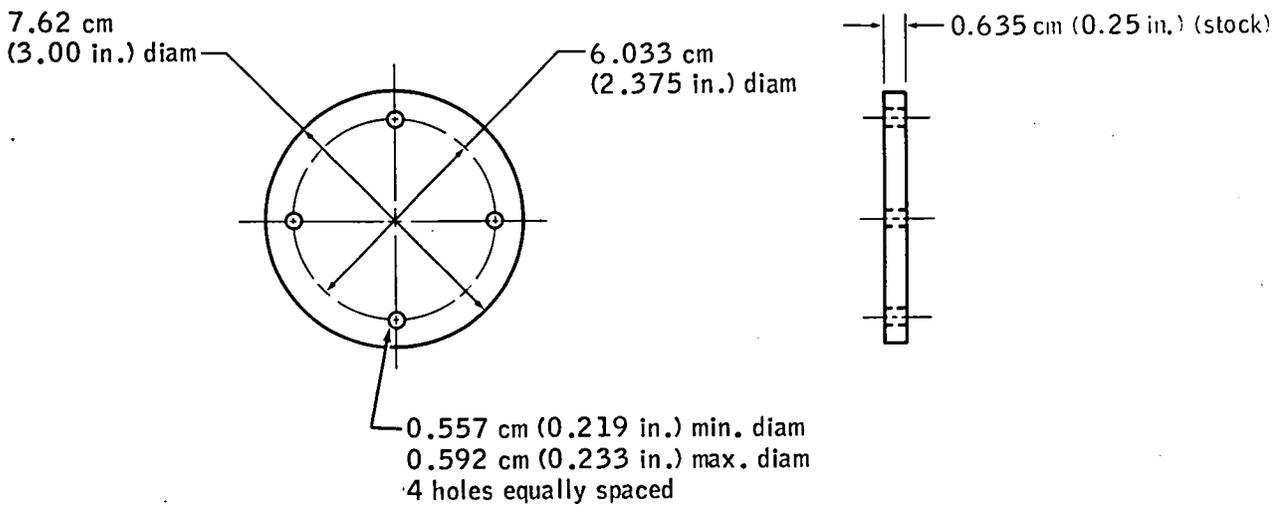


(a) Detail of gas seal.

Figure 8.- Furnace-head designs.



(b) Detail of end plate.



(c) Cross section of bottom head and end plate configured for vertical quenching with axially offset electrode, quench port, and plug.

Figure 8.- Concluded.

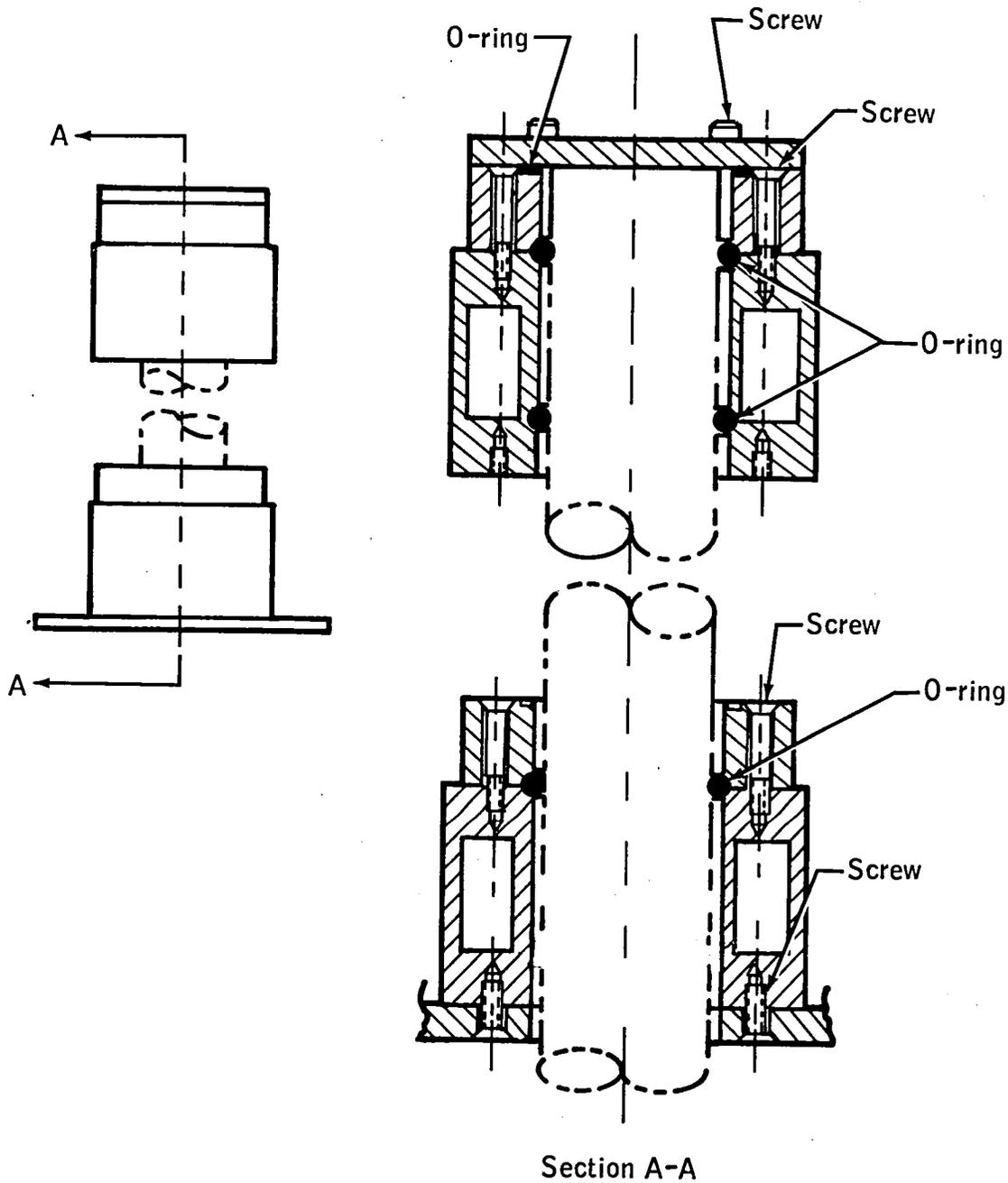


Figure 9.- Dual-head arrangement for large-bore furnaces. Note that the two O-rings are required in the top head to ensure alinement.

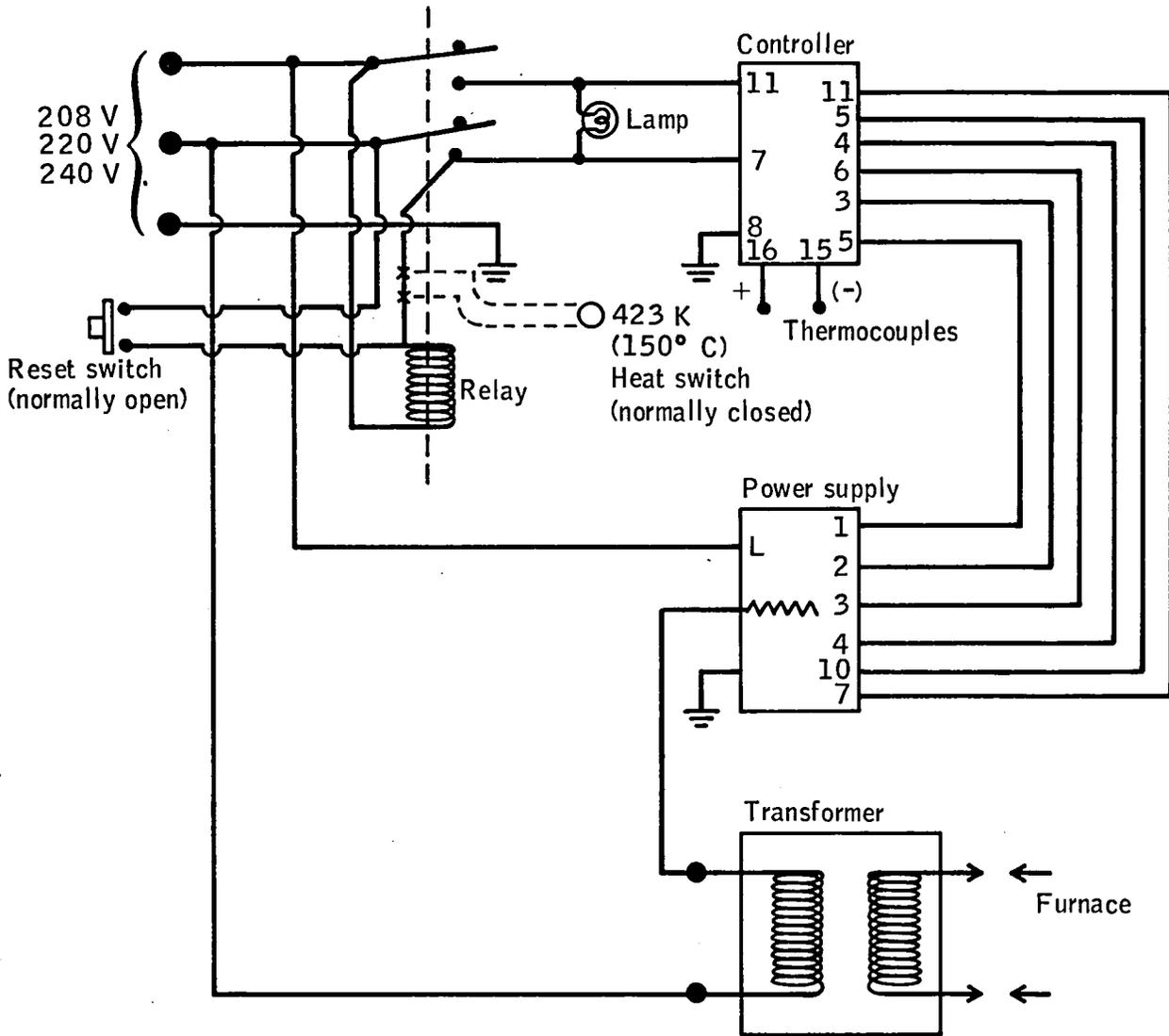


Figure 10.- Power wiring for furnace-controller system, including interlocks.

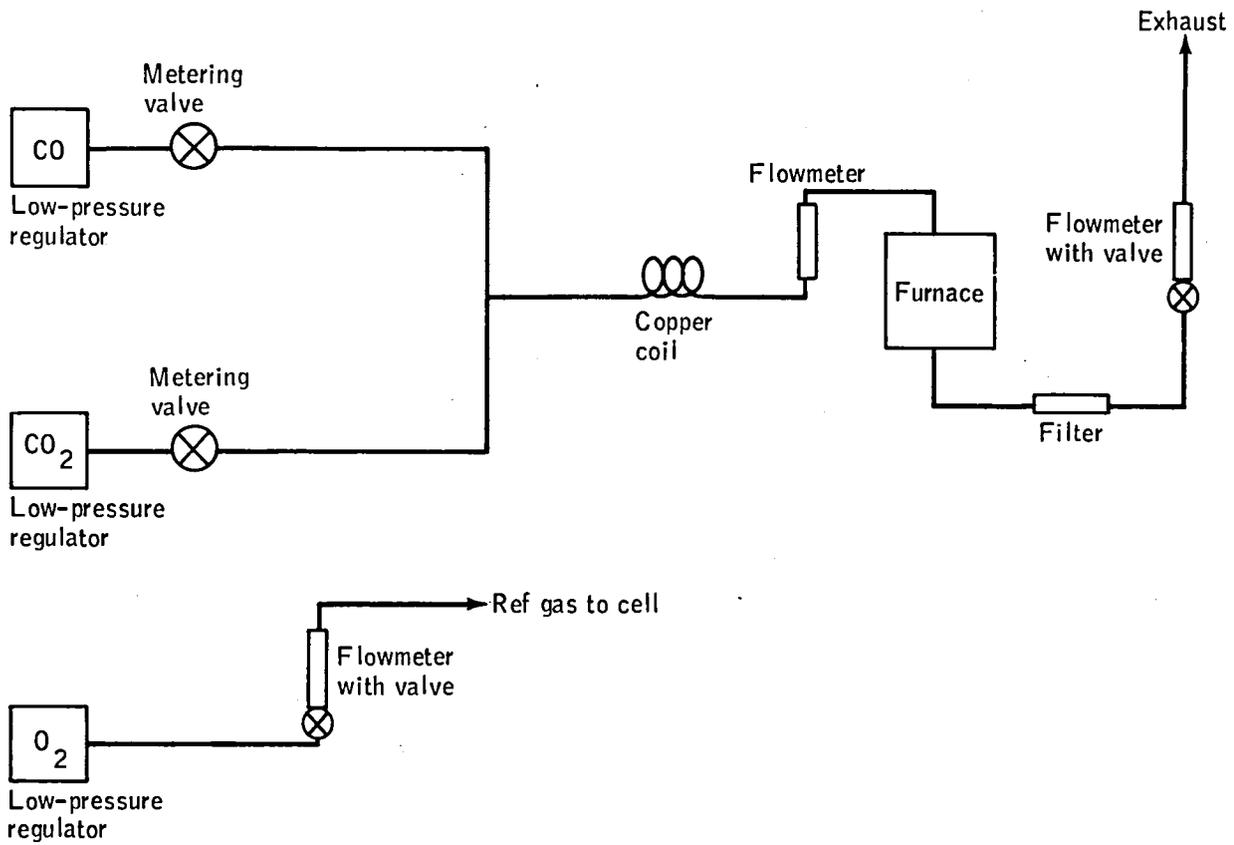


Figure 11.- Gas supply, mixing, and distribution system.

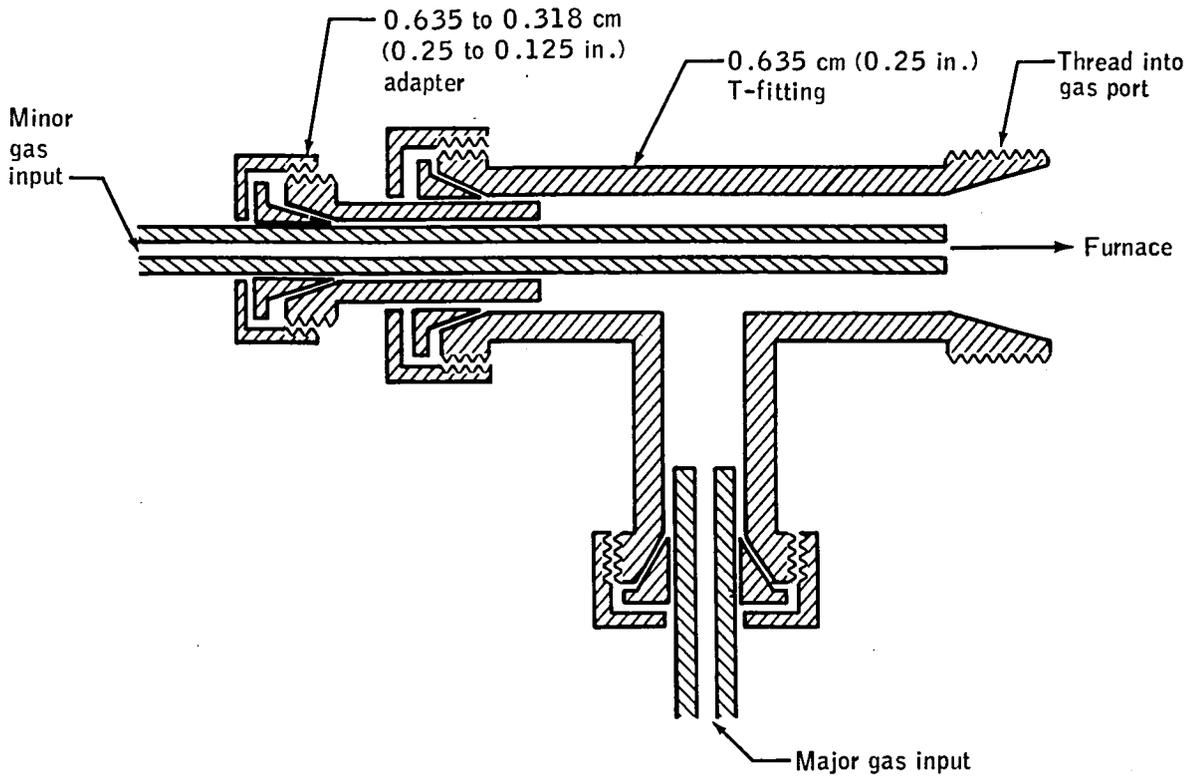


Figure 12.- Mixing chamber (not to scale).

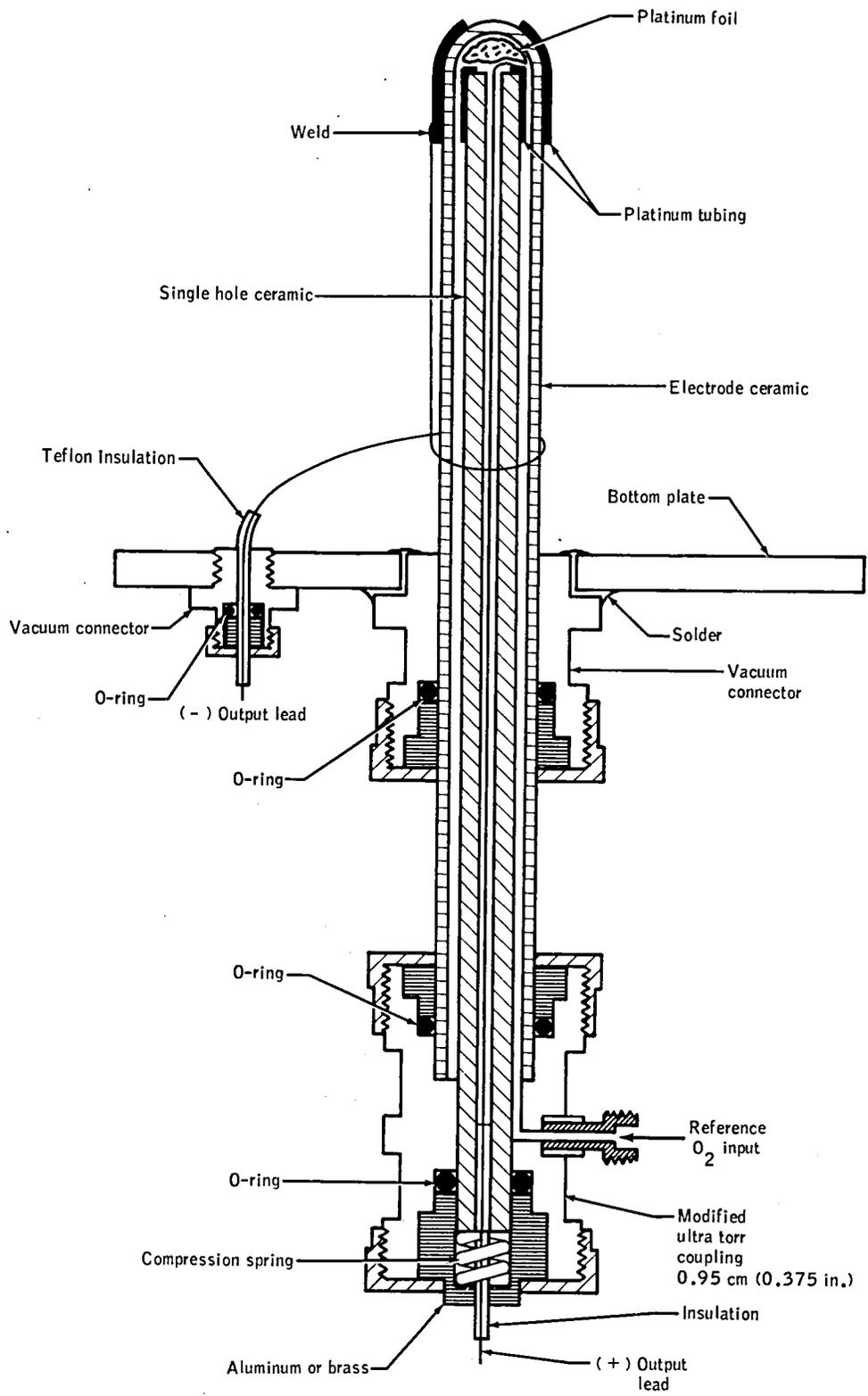


Figure 13.- Detail of electrolyte cell configuration showing spring-loaded design.

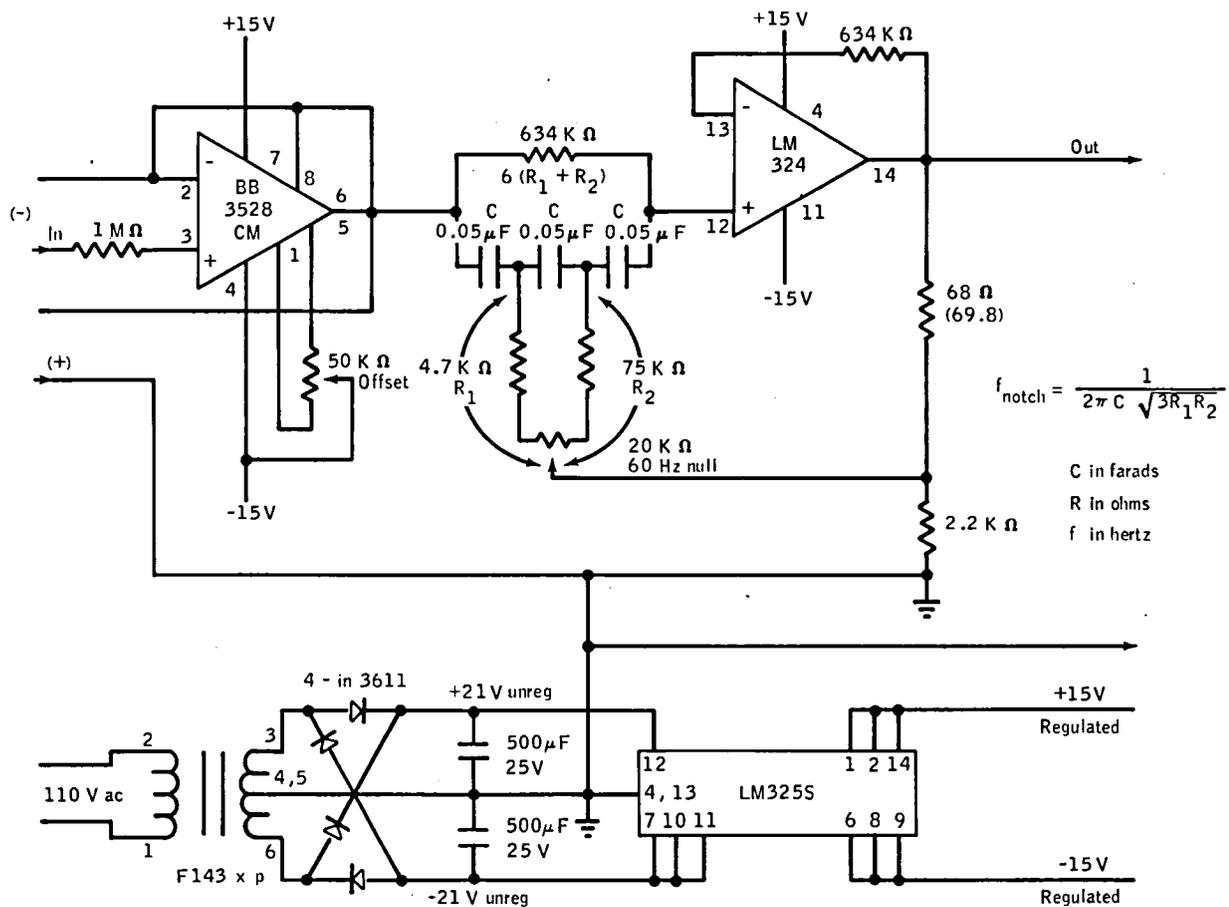


Figure 14.- High-Z/notch filter schematic (after F. Gibbons). (Note: Although specific manufacturer parts are cited, suitable parts from different manufacturers exist and may be substituted.)

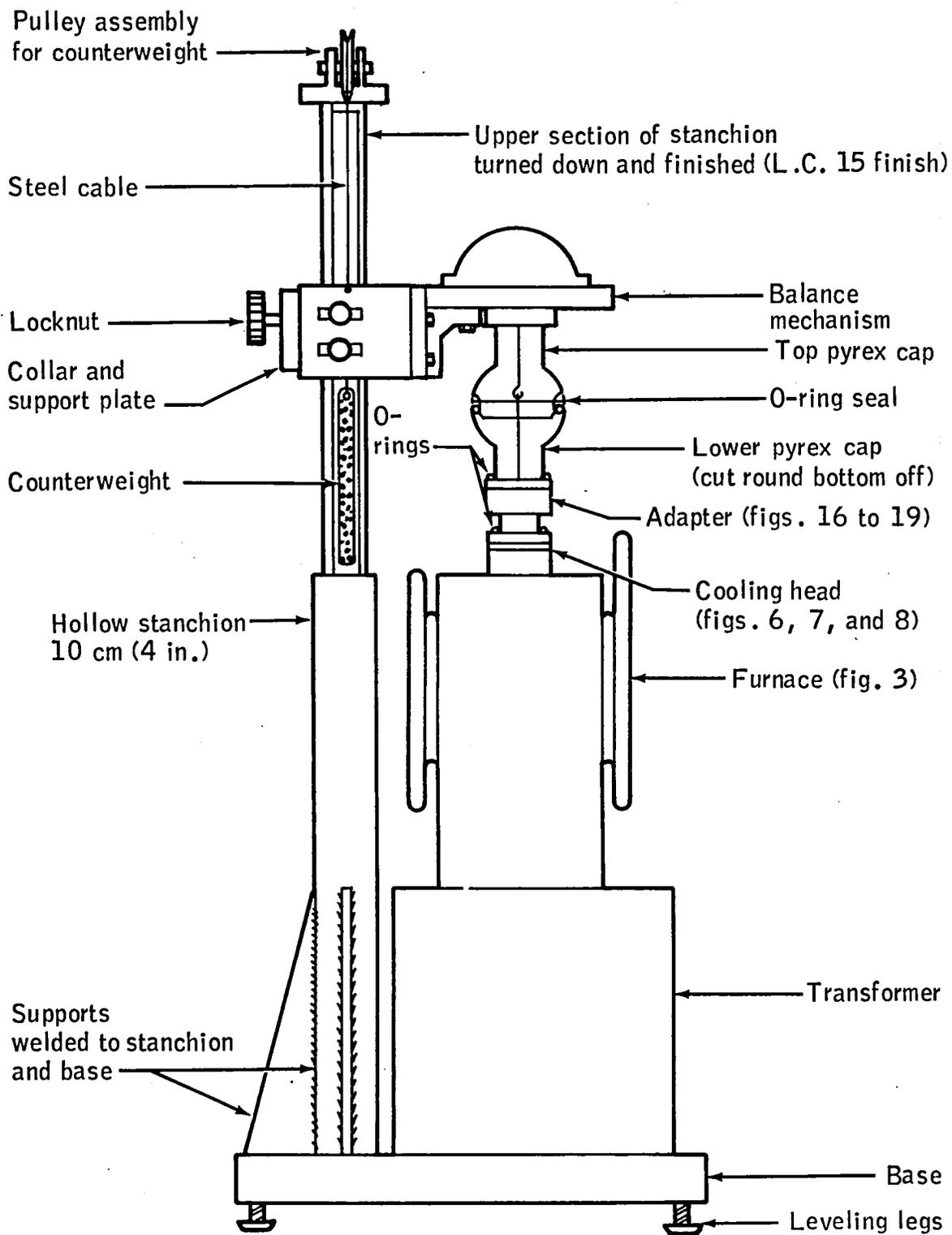


Figure 15.- Balance stand overview (after design by T. Doebbler).

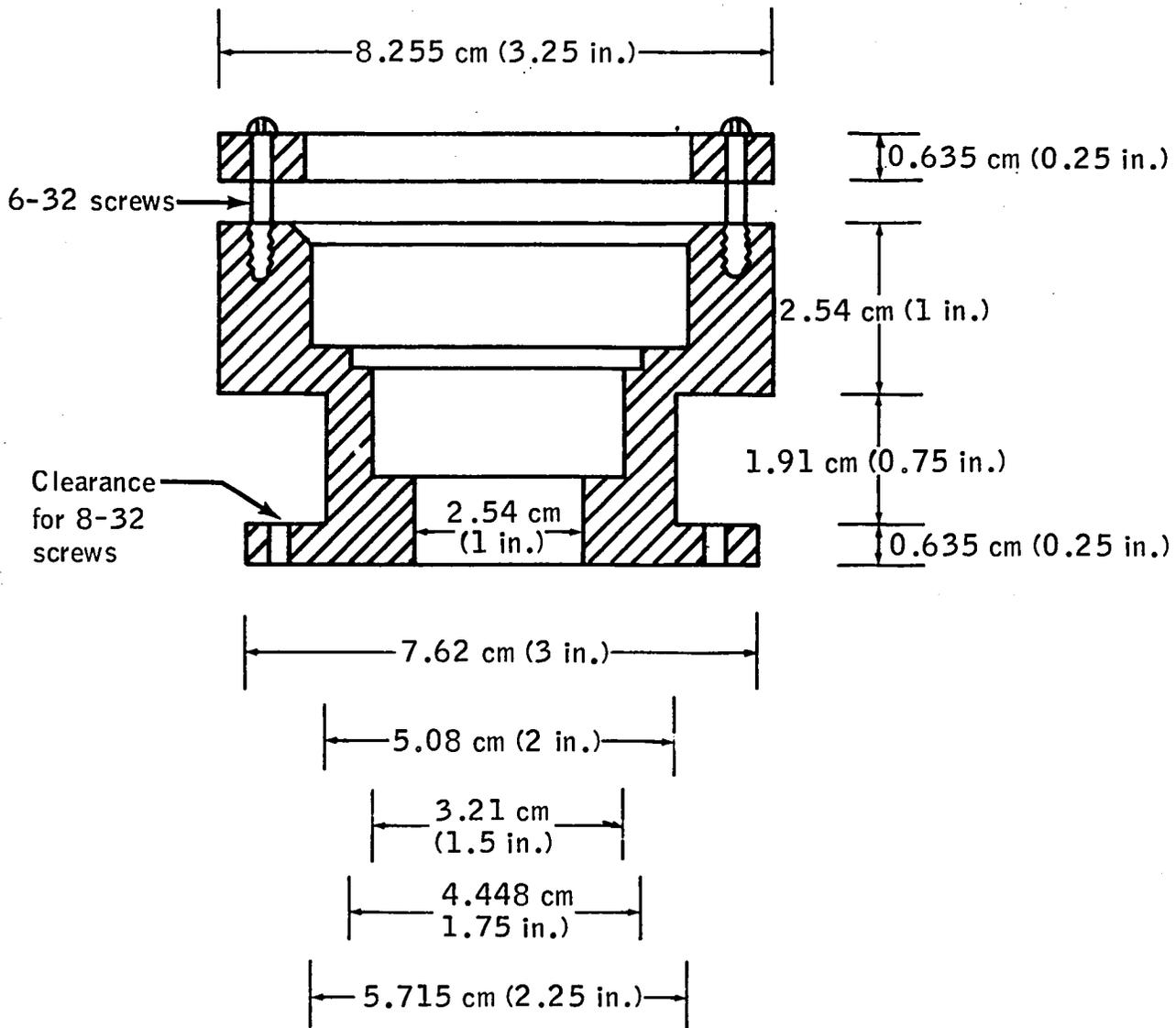


Figure 16.- Coupling used to attach balance assembly to furnace heads.

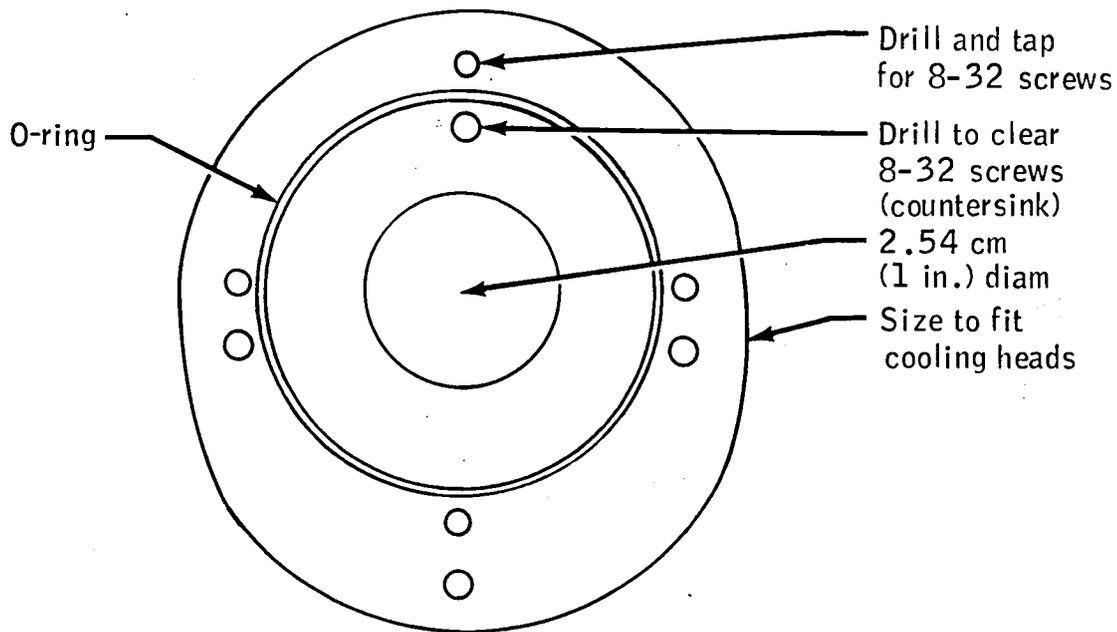


Figure 17.- Adapter plate to offset sample from the center line of the furnace in the thermogravimetric analysis system. This offset is required so that electrode and sample cannot touch.

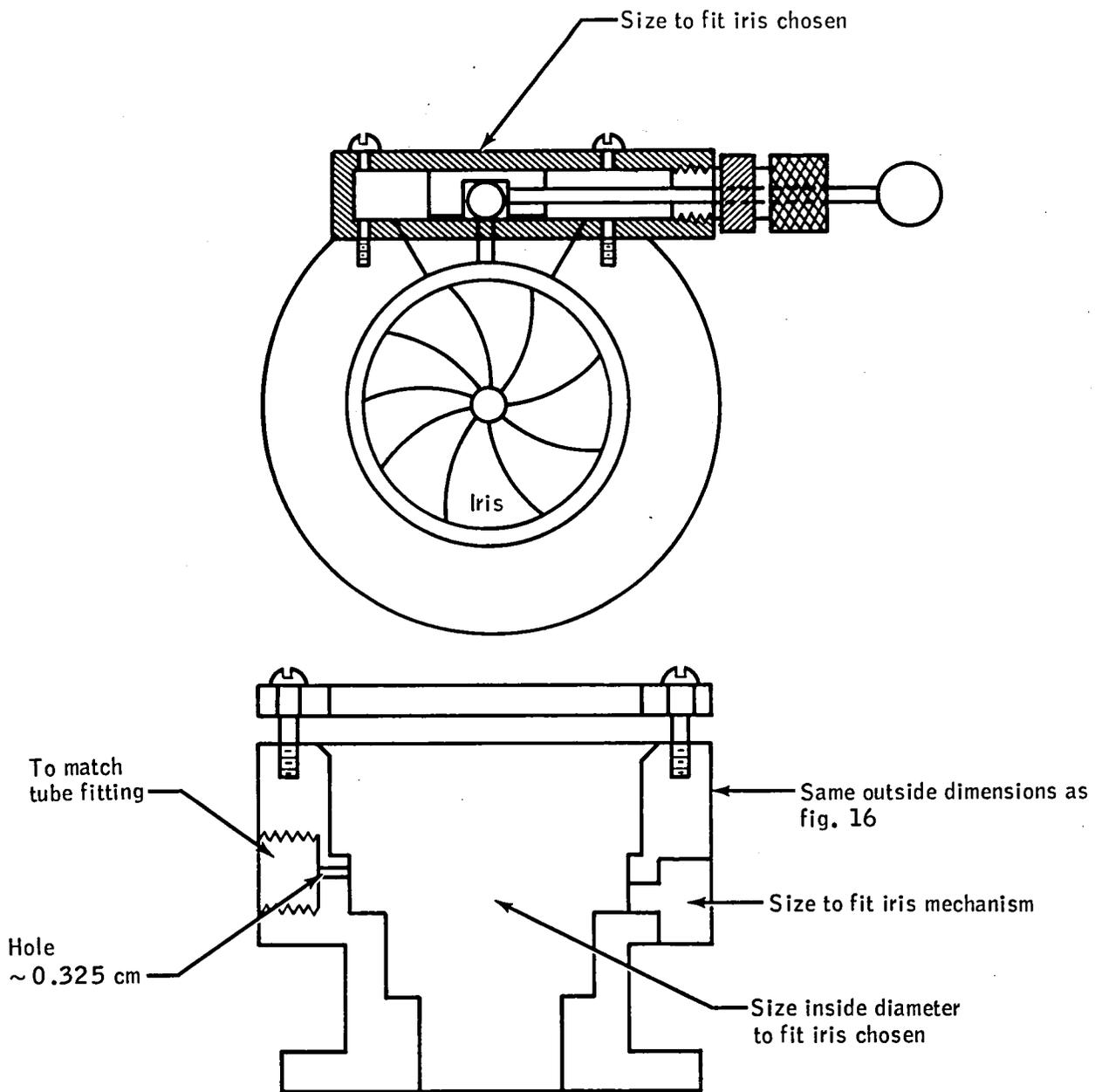


Figure 18.- Iris adapter used to isolate the balance from the furnace atmosphere.

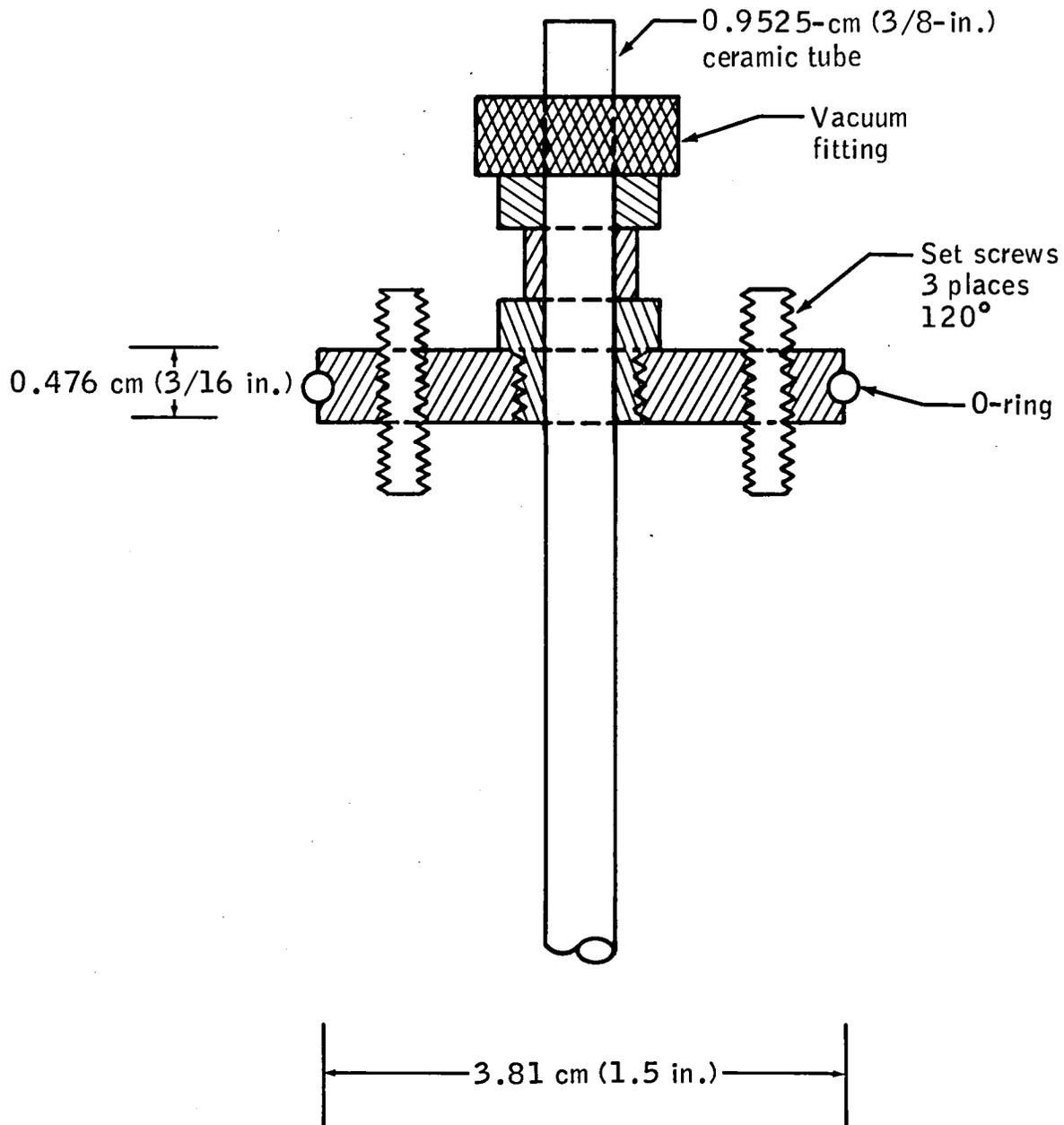


Figure 19.- Detail of hang tube that is used with the coupling shown in figure 16. The tube prevents the accumulation of graphite on the balance hang wire.

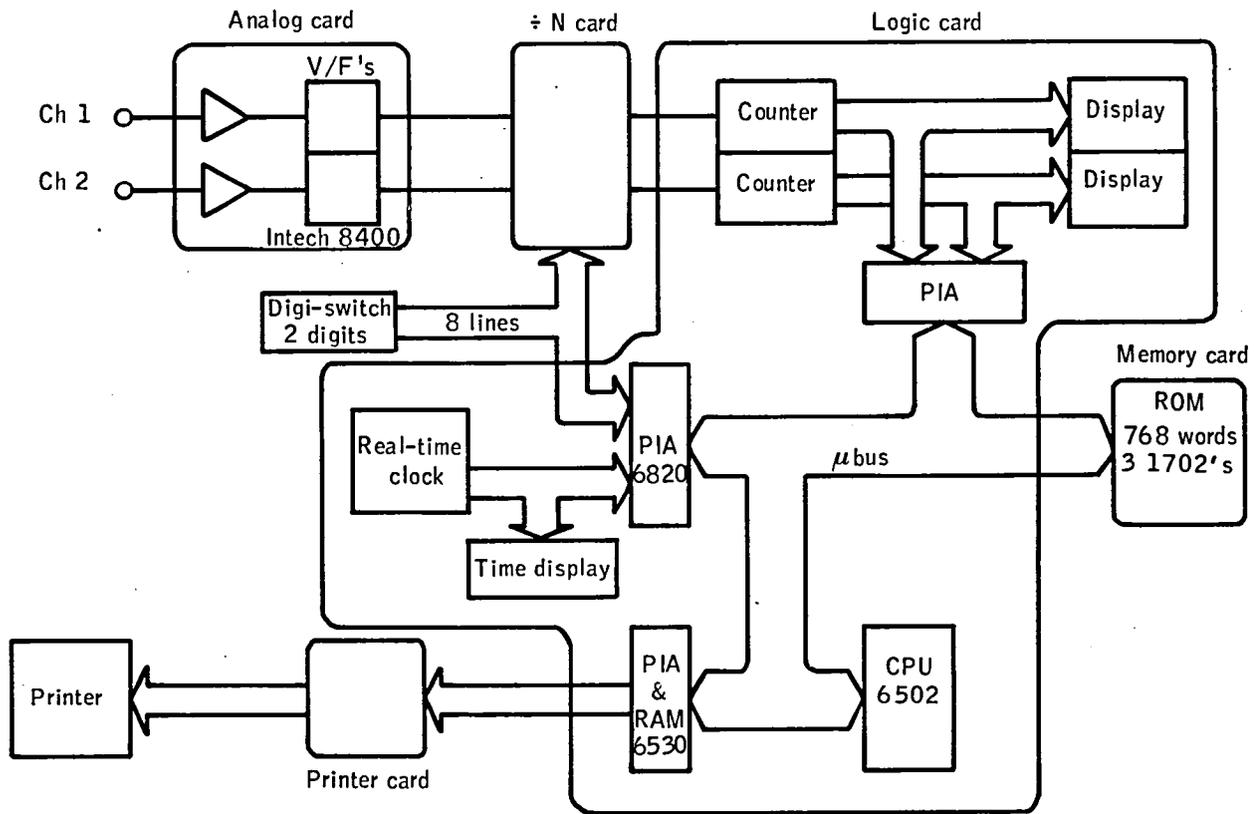
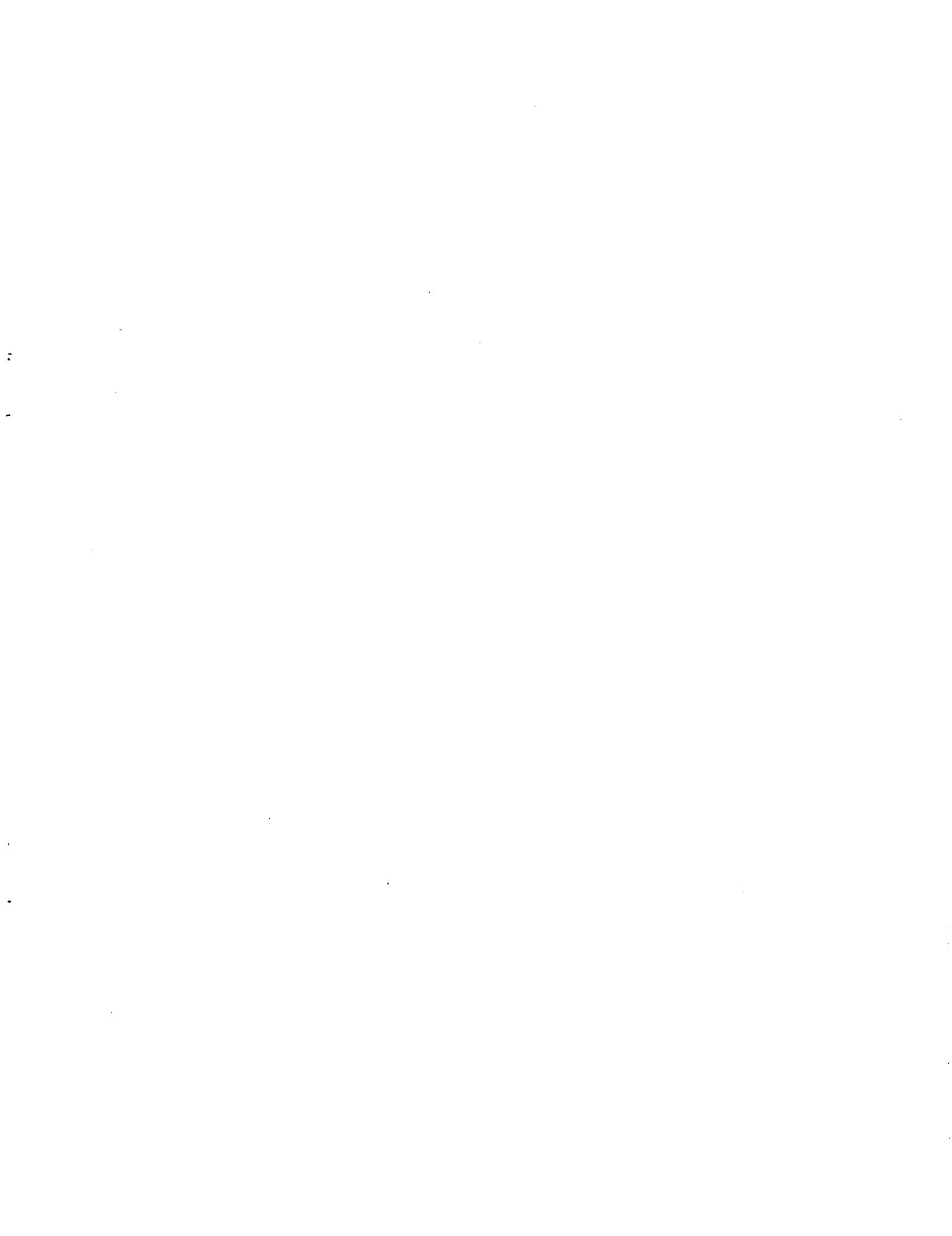


Figure 20.- Block diagram of signal averager (after T. Byers).

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