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Development of an Automatic H_2SO_4 Monitor

Interagency Energy/Environment R&D Program Report

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July 1979

Development of an Automatic H_2SO_4 Monitor

by

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CONTENTS

		Page
Acknowledgement		iv
List of Figures		v
List of Tables		vi
Sections		
I	Introduction	1
II	Monitor Description	3
	2.1 General Operation	3
	2.2 Component Enclosures	3
	2.3 The Sampling Train	10
	2.4 The Sequencer	15
	2.5 Electrical Control Panel	17
	2.6 Temperature and Flow Control	25
	2.7 Conductivity Instrumentation	30
	2.8 Additional Equipment	34
	2.9 Umbilical Connections	38
	2.10 General Timing Sequence	39
III	Laboratory Tests	43
	3.1 Sequencer Timer Settings	43
	3.2 Calibration of Conductivity Cell	44
	3.3 Coil Rinse Efficiency	46
	3.4 Acid Injection Tests	47
	3.5 SO_2 Tests	48
	3.6 System Collection Efficiency	49
	3.7 Endurance Test	49
	3.8 Results of Laboratory Tests	49
IV	Field Test	51
	4.1 The Test Facility	51
	4.2 Test Description	51
	4.2.1 Equipment Set-up	51
	4.2.2 Initial Testing	52
	4.2.3 Endurance Test	57
	4.3 Test Results and Conclusions	59

Section		Page
V	Recommendations	67
	5.1 Size Reduction	67
	5.2 Impinger System	67
	5.3 Gas Flow Measurement	67
	5.4 Organic Removal	68
	5.5 Filter Redesign	68

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This document describes the apparatus developed on Task 47, "Development of a Continuous SO_3 Monitor," on EPA Contract No. 68-02-2165, "Sampling and Analysis of Reduced and Oxidized Species in Process Streams." The Energy Technology Department, Applied Technology Division was responsible for the work performed on the task. The work was conducted under EPA Project Officer Mr. Frank E. Briden of the Process Measurement Branch of the Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina. Dr. R. F. Maddalone was the Program Manager and the Task Manager was Mr. E. F. Brooks.

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LIST OF FIGURES

Number		Page
1	Sulfuric Acid Monitor Showing the Probe Unit (A) and Control Unit (B) Enclosures	4
2	Control Unit Enclosure, Front Doors Open	5
3	Control Unit Front Panels	7
4	Control Unit, Back Doors Open	8
5	Umbilical Connections	9
6	Glass Sampling Train	13
7	Sequencer	14
8	Electrical Control Panel	19
9	Terminal Strip Connections	20
10	Electrical Circuitry Schematic	22
11	Function Circuitry Schematic	23
12	Temperature and Flow Control Panel	27
13	Air Flow Meter Calibration	28
14	Conductivity Instrumentation	31
15	Conductivity Cell Calibration, X1 Scale	32
16	Conductivity Cell Calibration, X10 Scale	33
17	Control Unit Pump Compartments	35
18	Filter Compartment	37
19	Schematic of SO_3 Monitor	41
20	Probe Unit at Scrubber Inlet	53
21	Probe Connections at Sampling Port	54
22	Filter Element After Test	56
23	Conductivity Recorder Output	60

LIST OF TABLES

Number		Page
1	Function Designations	16
2	Sequencer Input/Output Connections	18
3	Fuse Sizes and Circuits	24
4	Thermocouple Locations	29
5	General Timing Sequence	40
6	Sequencer Timer Settings	45
7	Temperature Control Data	58
8	Field Test Results	64
9	Analysis of Shawnee Power Plant Coal	65
10	Particulate Loadings During Field Test	66

SECTION 1

INTRODUCTION

This report has been prepared for the Industrial and Environmental Research Laboratory of the Environmental Protection Agency, Research Triangle Park, North Carolina as part of Task 47 of Contract No. 68-02-2165, "Sampling and Analysis of Reduced and Oxidized Species in Process Streams." The technical objective of this task was to develop a device capable of automatic measurement of the mass emission rate of sulfur trioxide (H_2SO_4 vapor) within a precision of ±20%. This document summarizes the results of the development of a single prototype unit, including a description of the monitor as well as the results of laboratory and field tests of the unit.

Currently only manual methods are available for the purpose of monitoring sulfuric acid emissions: EPA Standard Method 8 and the Controlled Condensation System (CCS). In the latter system, sulfuric acid is selectively condensed out of a sample gas stream by cooling the gas in a water-jacketed coil to a temperature below the dewpoint of H_2SO_4. The condensed acid is then titrated and the acid concentration determined through a wet-chemistry procedure. The disadvantages of the manual systems are that they require extensive manpower, they cannot provide continuous measurements, and there are long delays associated with sample analysis.

The automatic monitor described herein was designed to eliminate these problems. The prototype device which was constructed and tested is an automated Controlled Condensation System, with acid concentrations being determined by measurement of the electrical conductivity of a sulfuric acid solution. The monitor is capable of continuous unattended operation for a 24-hour period in streams of moderate (5 g/m^3) particulate loadings. Readings of solution conductivity are recorded continuously, and new samples of the gas stream being studied are obtained every 10 minutes. Sulfuric acid concentration can be determined from the instrument and associated calibration curves within 5 minutes of sample acquisition; determination requires only reading recorder output

and sample gas volume, obtaining values from calibration curves, and inserting these values into expressions for ppm concentration in the gas stream.

The prototype device constructed is capable of detecting sulfuric acid concentrations in the range from 0.5 ppm to 500 ppm, at temperatures up to 300°C (527°F) with 3000 ppm SO_2, 8 to 16 percent H_2O, and up to 9 g/m^3 of particulate matter in the gas stream. Field tests of the unit indicate a system accuracy of ±7% at 10 ppm concentration under high (11 g/m^3) mass loadings and high (4000 ppm) SO_2 concentration.

Because of the success of the present prototype and the demand for a system capable of this type of operation, continued development of the monitor is highly recommended. Optimization of packaging and filtration system design are the two major areas where modifications are needed. The potential demand for the device, coupled with the successful operation of the present prototype, make continued development very desirable.

SECTION 2

MONITOR DESCRIPTION

2.1 GENERAL OPERATION

The automatic sulfuric acid mist monitor consists essentially of a heated Vycor probe, a cyclone and filter, a modified Graham condenser (condensation coil), a conductivity measuring cell, three pumps, and an orifice meter. In operation, the system condenses sulfuric acid out of a sample gas stream by cooling the gas in a water jacketed coil which is maintained at a temperature below the dewpoint of H_2SO_4 but above the H_2O dewpoint. The coil is then rinsed with deionized H_2O into a conductivity cell which measures the conductance of the H_2O-H_2SO_4 solution and outputs the conductance on a 0-10 mv scale. To automate the procedure, a sequencer controls the operation of the various components and steps in the sampling process. The entire sampling train temperature is controlled to prevent condensation of the H_2SO_4 aerosol on the component walls prior to the condensation coil. The gas sample volume flowrate can be controlled with a maximum sampling rate of 28 l/min provided by a 4-stage diaphragm pump. Provision is made for the washing and drying of the glass sampling train, so that measurements of sulfuric acid emissions can be made on a semi-continuous basis unattended for a period of time determined primarily by the particulate concentration encountered in the gas stream and its effect upon the monitor's filtration system.

2.2 COMPONENT ENCLOSURES

The components of the monitor are housed in two environmentally resistant all-steel cabinets, which are shown in Figures 1 and 2. The probe unit shown in Figure 1 is a Nema Type 4 enclosure manufactured by Hoffman Engineering, Anoka, Minnesota (Model A-36H30DLP). The enclosure size is 91 x 76 x 31 cm (36 x 30 x 12 in.) and its weight is 41 kg (90 lbs). This unit contains the glass sampling train and probe connections, and in operation must be positioned at the stack sampling port.

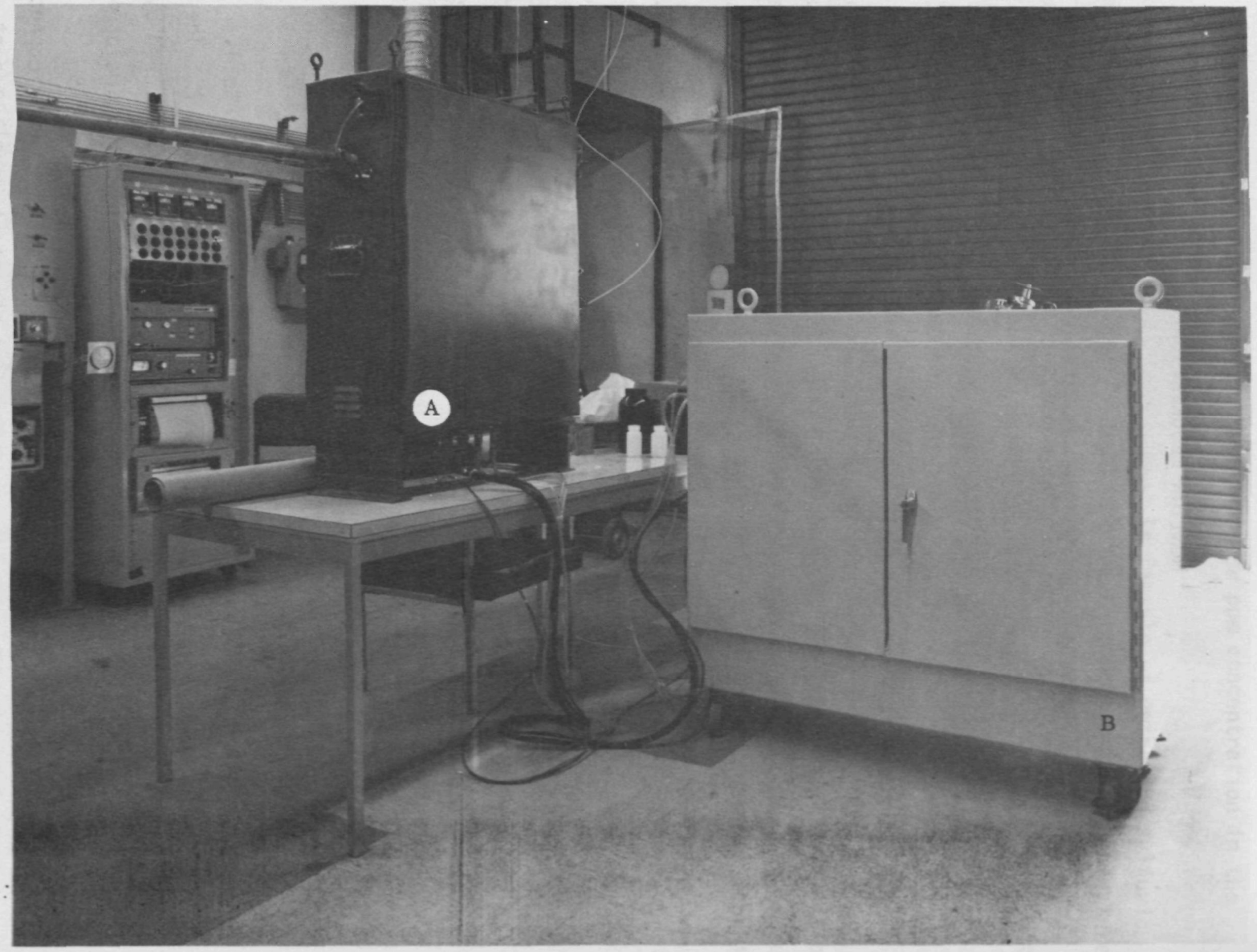


Figure 1. Sulfuric acid monitor showing the probe unit (A) and control unit (B) enclosures

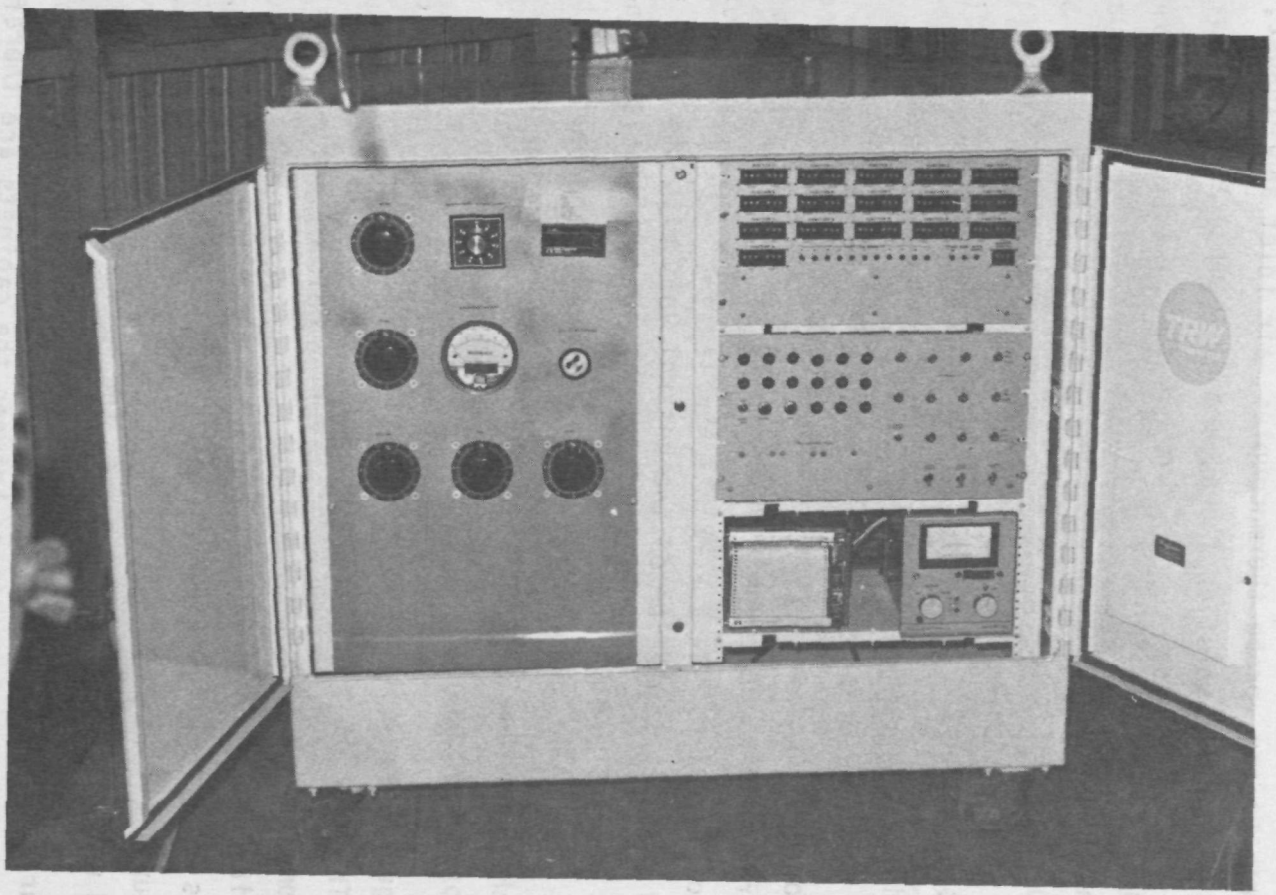


Figure 2. Control unit enclosure, front doors open

Lifting lugs are provided at the top of the cabinet for use with a hoist for applications where the sampling port is located on a platform above ground level. Handles are provided on two sides to aid in manipulation of the unit. Openings through the cabinet are provided for the probe inlet, probe heater, probe thermocouples, air inlet and exhaust, sampling train thermocouples, solution flows, and gas sample flow.

Figure 2 shows the control unit cabinet which is a Nema Type 12 free standing two door dual-access enclosure. This enclosure was custom manufactured by Hoffman Engineering of Anoka, Minnesota and is based upon the model number A-724824FSDAD. It is 183 x 122 x 61 cm (42-1/16 x 48-1/16 x 24-1/16 in.) in overall dimensions and weighs 136 kg (300 lb). This cabinet contains all the control systems for the operation of the monitor, fluid reservoirs, pumps, filters, and instrumentation. It is a two door dual access enclosure; one set of doors provides access to the control panels, the sequencer, and the conductivity instrumentation, and the other set of doors provides access to the pumps and fluid reservoirs. Figure 3 shows the interior of the control unit with the front doors open. The left panel contains the temperature and flow controllers and temperature readout. The right side contains the sequencer, the main electrical control panel, the conductivity meter, and the conductivity recorder. This arrangement provides access to all controls from one position.

Figure 4 shows the interior of the control unit with the rear doors open. The rear of the cabinet is divided into 4 main compartments. The right compartment houses the deionization column, the deionized water reservoir, air filter, air drier, and an orifice meter. The left side contains 3 compartments; the first houses the purge air pump and 24 VDC power supply, the second houses a peristaltic pump for transfer of the deionized water, and the third houses the main sampling pump.

During normal operation, the probe unit will operate remotely from the control unit. Connections between the cabinets are therefore provided for gas flow, solution flow, waste flow, power, and thermocouples. Figure 5 shows the connections which are mounted on the bottom of the probe unit and the side of the control unit. The tube fittings are all quick release double-end shut-off fittings to facilitate removal without loss of fluid.

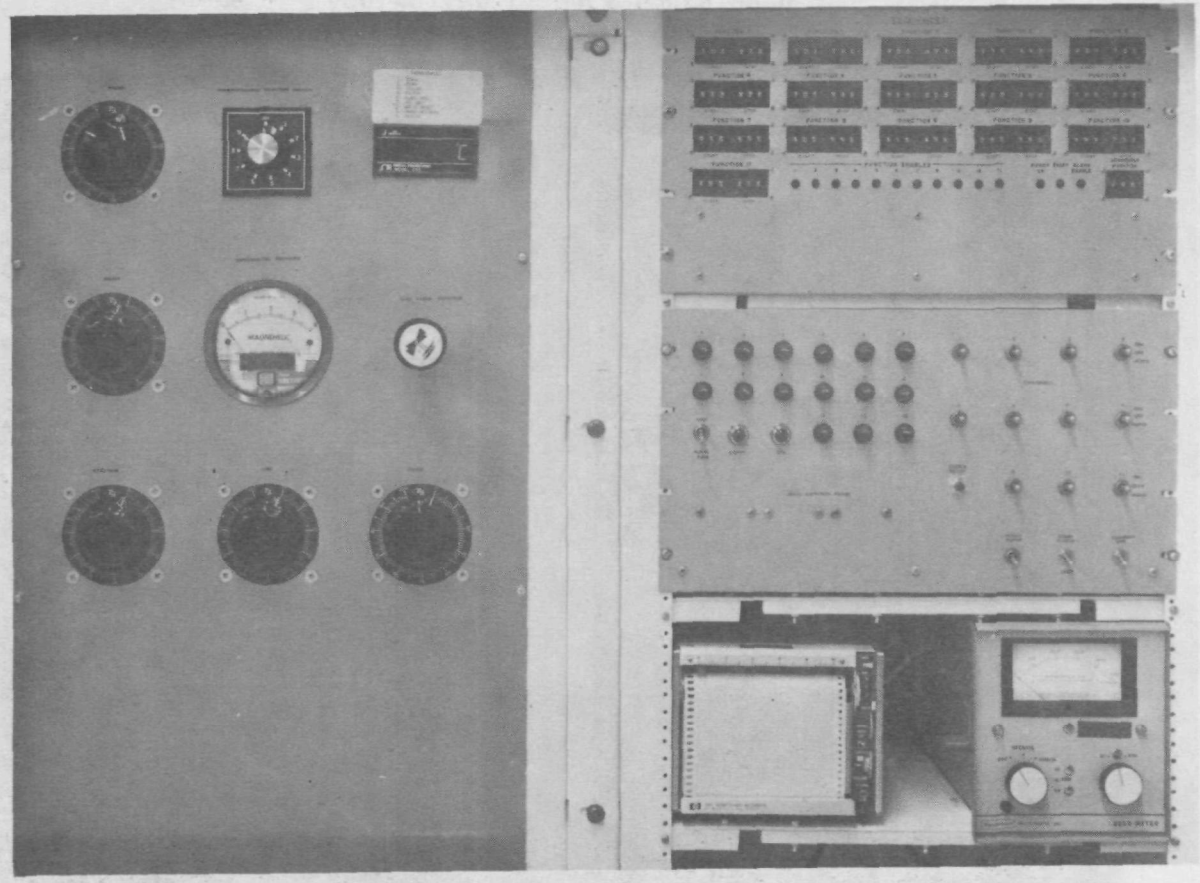


Figure 3. Control unit front panels.

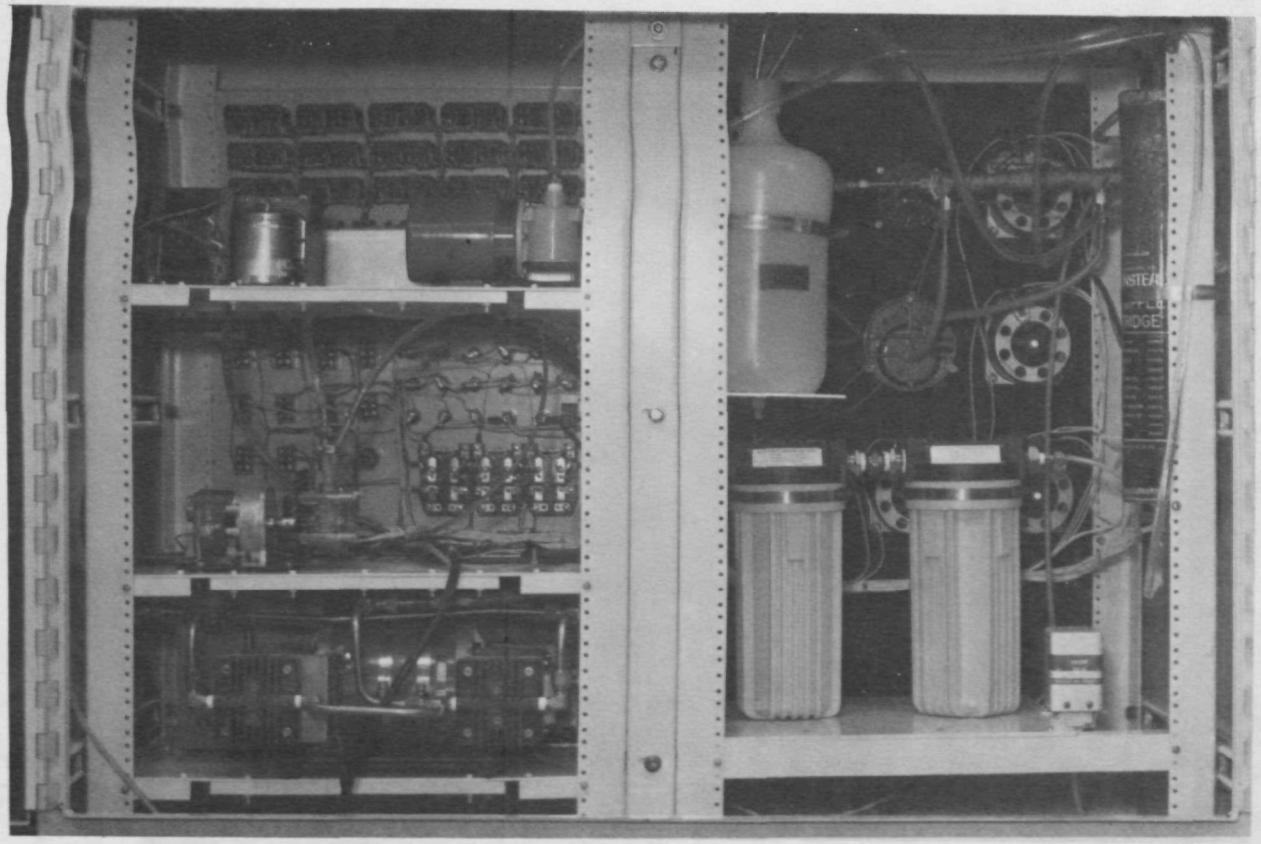


Figure 4. Control unit, back doors open

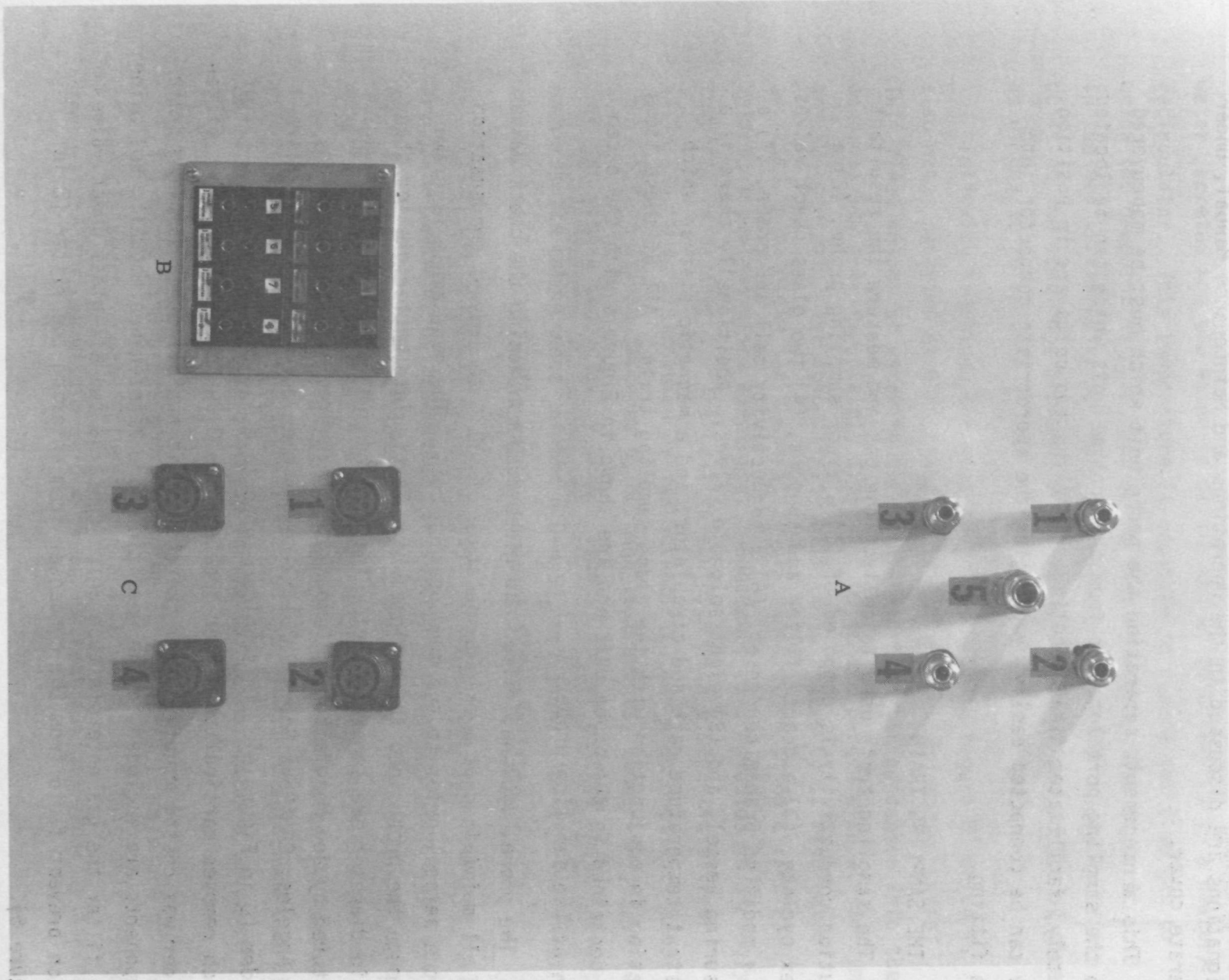


Figure 5. Connections between enclosures: (A) Sample and Fluid Flow Connections, (B) Thermocouple Connections, and (C) Power Connections

The power connections are provided by four 6-conductor shielded cables which connect to multi-pin environmentally-resistant connectors. The pin designations are discussed in the Operations and Maintenance Manual, under separate cover.

This arrangement, separating the probe unit which must be maneuvered into the sampling port location from the control unit which can be located remotely, facilitates field handling. Once the two units are in position, they can be connected easily by plugging the appropriate connector into each fitting.

2.3 THE SAMPLING TRAIN

The sampling train used to collect the gas and measure the resultant solution conductivity is composed of (1) a Vycor sampling probe, (2) a pyrex cyclone, (3) a quartz filter and support, (4) two glass check valves, (5) a modified Graham condenser, (6) a conductivity cell and probe, (7) a measuring vessel, and (8) eight solenoid valves. Additionally there is a constant temperature bath and circulator, and a magnetic stirrer which function in conjunction with the glass sampling train. All of these items are contained in the probe unit and are shown in Figure 6 with the exception of the sampling probe.

The probe, cyclone, filter and glass tube containing the check valves are all maintained at a skin temperature of 300 °C to prevent condensation of the aerosol prior to the condensation coil. The gas sample is drawn through the probe into the cyclone where particulate matter greater than 10μ in diameter are separated out. The cyclone (B in Figure 6) is manufactured by Joy Manufacturing Company, Western Precipitation Division, Los Angeles, CA (Part No. A-2070). The gas then enters the quartz filter holder (C in Figure 6). This holder supports a 113 cm^2 Tissuequartz filter which removes particulate matter greater than 0.2μ in diameter. This filter holder was custom manufactured; sketches of it and all other sampling train components are included in the Operations and Maintenance Manual. Following the filter the gas enters a tube which contains two all-glass check valves which prevent fluid from the condenser from entering the filter (D in Figure 6).

The controlled condensation coil (E in Figure 6) consists of a Graham condenser modified to accept a medium quartz frit. The coil is water jacketed and the water is maintained at 60°C (140°F) by a heater/recirculator. This temperature is adequate to reduce the flue gas to below the dewpoint of H_2SO_4 but above that of water. The sulfuric acid in the gas stream is selectively condensed on the inner surfaces of the coils during sampling; sampling continues for a specified period of time as discussed in Section 3.1.

Following sampling, the measuring vessel (F in Figure 6) which is also water jacketed at 60°C (140°F), is filled with deionized water. This fixed volume of water is then rinsed through the condenser into the conductivity cell immediately after the coils are purged with air to remove any SO_2 present. The conductivity cell (G in Figure 6) is also water jacketed to maintain the temperature of the solution at 60°C (140°F). This is important since electrical conductance of a solution is strongly temperature dependent. The cell is equipped with a magnetic stirrer (I in Figure 6, distributed by VWR Scientific) and a conductivity probe (H in Figure 6, manufactured by Beckman Instruments, number K-1). In conjunction with a conductivity bridge located in the control unit, the probe measures the conductance of the H_2O-H_2SO_4 solution. The stirrer keeps the solution well mixed while the measurement is being taken.

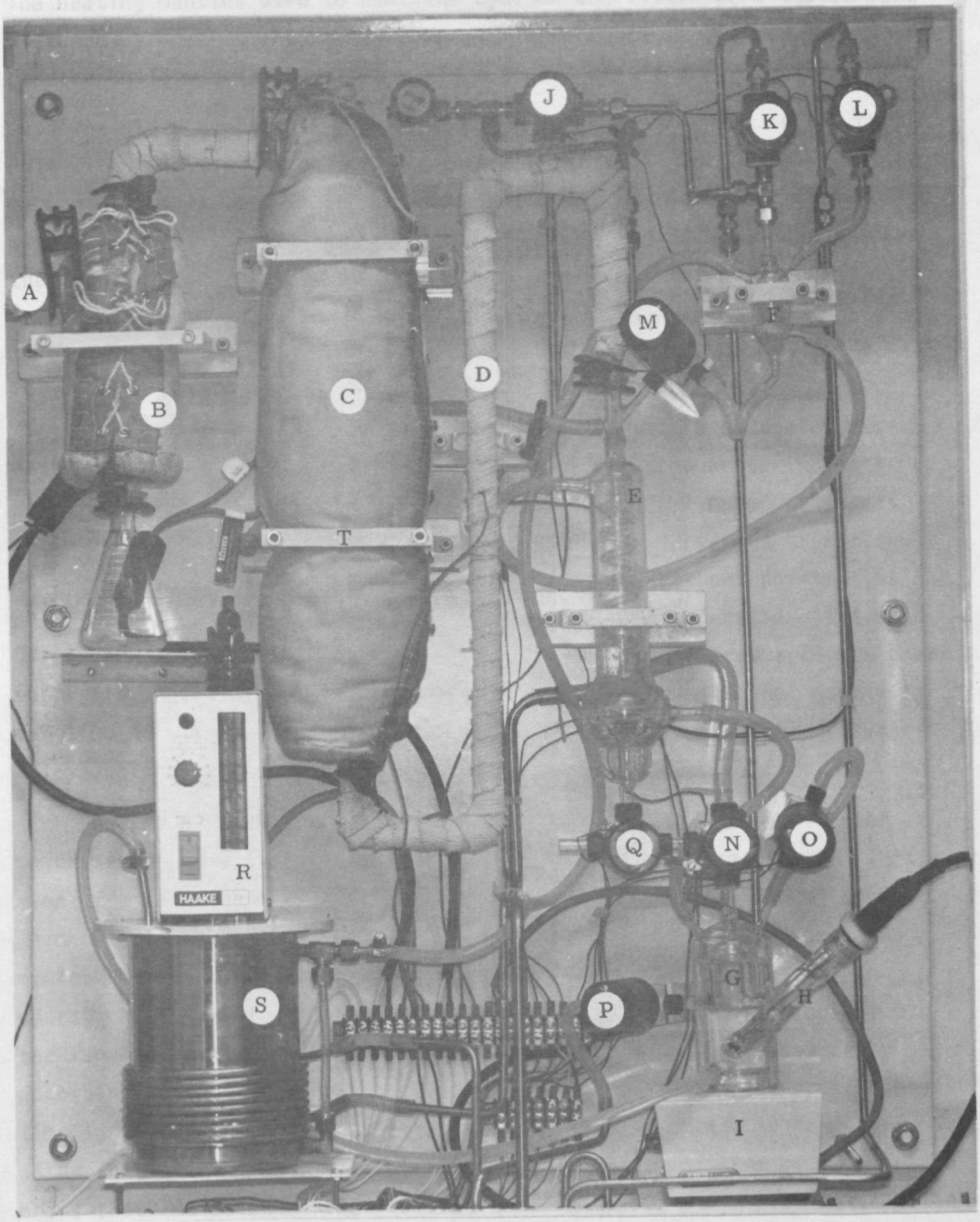
After the conductivity measurement is taken, the condenser and cell are washed with deionized water for several minutes and then dried with 60°C (140°F) air which has been filtered and dried. The actions of sampling, purging, rinsing, washing, and drying are automated through the use of 8 solenoid valves as shown in Figure 6. These valves are of all-Teflon construction to avoid the corrosive effects of sulfuric acid, and operate on 24 VDC. The operation of these valves is controlled by a sequencer, as described in Section 2.4 below.

The water bath used to maintain the 60°C (140°F) temperature of some of the glassware is manufactured by Haake (Model E52). This unit provides temperature control within ±1°C with a 1000 watt maximum capacity heater.

Figure 6. Glass sampling train

LEGEND:

- (A) PROBE INLET
- (B) CYCLONE AND MANTLE
- (C) FILTER SUPPORT AND MANTLE
- (D) GLASS TUBE WITH CHECK-VALVES
- (E) CONDENSATION COIL
- (F) MEASURING VESSEL
- (G) CONDUCTIVITY CELL
- (H) CONDUCTIVITY PROBE
- (I) MAGNETIC STIRRER
- (J) SV-1
- (K) SV-2
- (L) SV-3
- (M) SV-4
- (N) SV-5
- (O) SV-6
- (P) SV-7
- (Q) SV-8
- (R) WATER BATH CONTROLLER
- (S) WATER BATH COILS
- (T) GLASSWARE MOUNTING SUPPORT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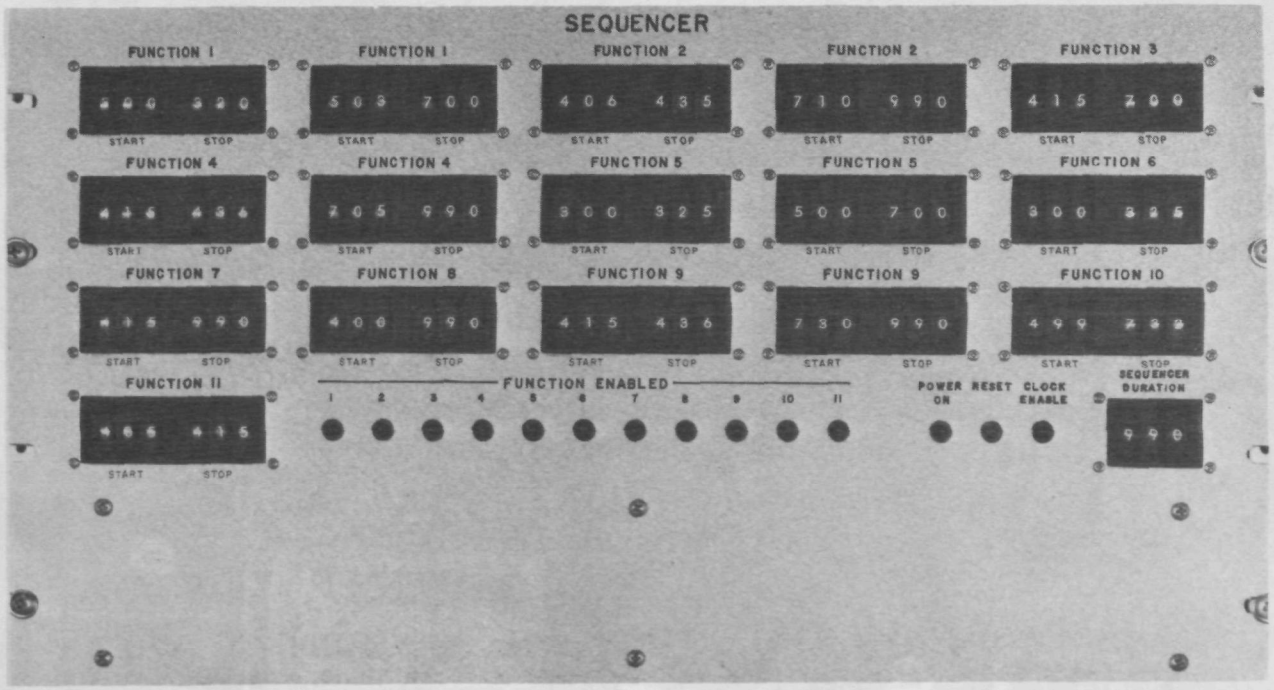


Figure 7. Sequencer

The heating mantles used to heat the cyclone and filter were custom manufactured by Glas-Col Apparatus Company, Terre Haute, Indiana. They provide uniform heating with a minimum amount of electrical power input.

The glass components of the sampling train are mounted in the probe unit with fixtures which were designed to reduce mechanical shock to the components. Each mount is insulated from the glass component it supports with a layer of asbestos insulation. The height of each component above the mounting plate can be adjusted to provide alignment between adjacent components.

2.4 THE SEQUENCER

To automate the operation of the sampling train, a sequencer was designed to time and control the operation of key components in the sampling process. Shown in Figure 7, the sequencer has 11 output channels which supply power to each of 11 components which are termed "Functions". The control panel of the sequencer contains 33 3-digit set point units which control the time in a sampling cycle in which a function is turned ON or OFF. When a function is in the "ON" mode, power from a 24 VDC power supply is provided at the output terminal associated with that particular function. This power switching is provided by a series of solid-state relays which are incorporated within the sequencer itself.

Powered by a 24 VDC supply, the sequencer contains an oscillator which serves as a timing base for the individual function timers. Initiation of a sampling cycle is accomplished by activating a "Clock" circuit which starts the timers. De-activation of the clock circuit stops the cycle. A reset circuit resets all timers to 000 when activated. In operation, the various components of the system are turned on or off by the function timers which activate or deactivate the associated relay according to the time (in seconds) selected on the set-point unit. The time indicated on the set-point unit is the time an event is to occur after initiation of a cycle. A "Function No. 1 START" time of 100 seconds means that 100 seconds after initiation of a cycle, power will be supplied at the Function 1 output terminal. The power will stay on until such time as is indicated by the "Function No. 1 STOP" time. This type of operation continues until a period of time determined by the "Sequence Duration"

Table 1. FUNCTION DESIGNATION

FUNCTION NUMBER	COMPONENT CONTROLLED
1	Peristaltic (water) pump
2	Purge air pump
3	Magnetic stirrer
4	SV-1
5	SV-2
6	SV-3
7	SV-4
8	SV-5
9	SV-6
10	SV-7
11	SV-8

timer. Whenever the cycle duration reaches this time limit, the internal clock automatically resets to 000 and a new cycle begins. In this manner, once the "Clock Enable" switch is activated with the sequencer power on, the eleven functions controlled by the sequencer will operate in the selected timing sequence continuously until such time as the "Clock Enable" switch is turned off. Once the "Clock Enable" switch is turned off, the "Reset" button must be pushed to stop the operation of any functions which were activated whenever the "Clock Enable" switch was originally turned off.

Table 1 shows the components which are controlled by each of the function timers. Because the sequencer operates on 24 VDC power, the first three functions which control the peristaltic pump, purge air pump, and the magnetic stirrer, operate separate relays which switch 115 VAC power to those components. Examination of Figure 7 shows that several of the functions have two sets of START and STOP timers. This is necessitated by the requirement that during a complete test cycle, several of the components must operate more than once. The timers are grouped under each function according to their normal sequence of operation; the first set of timers controls the operation of a function, and then the second set of timers controls the function. This dual-control operation occurs only for function numbers 1, 2, 4, 5 and 9. The remaining functions only operate once during each cycle and therefore only have one set of START and STOP timers.

The input and output connections to the sequencer are contained in a 9-pin and a 25-pin rectangular connector, respectively. The pin designations are shown in Table 2. Both the positive and neutral power leads are switched through the relays in the sequencer. The output connections from the sequencer are then directed to the main control panel where distribution to the various functions occurs.

2.5 ELECTRICAL CONTROL PANEL

All of the electrically operated components of the monitor receive power from the electrical control panel, shown in Figures 8 and 9. The panel is essentially a switching and distribution point for both the

Table 2. SEQUENCER INPUT/OUTPUT CONNECTIONS

INPUT: 9-PIN CONNECTOR	
PIN No.	FUNCTION
1	Clock start (+24 VDC)
2	Clock reset (+24 VDC)
8	Sequencer power (+24 VDC)
9	24 VDC neutral
OUTPUT: 25-PIN CONNECTOR	
1	FUNCTION #1 (+24 VDC)
2	1 (neutral)
3	2 (+24 VDC)
4	2 (neutral)
5	3 (+24 VDC)
6	3 (neutral)
7	4 (+24 VDC)
8	4 (neutral)
9	5 (+24 VDC)
10	5 (neutral)
11	6 (+24 VDC)
12	6 (neutral)
13	7 (+24 VDC)
14	7 (neutral)
15	8 (+24 VDC)
16	8 (neutral)
17	9 (+24 VDC)
18	9 (neutral)
19	10 (+24 VDC)
20	10 (neutral)
21	11 (24 VDC)
22	11 (neutral)

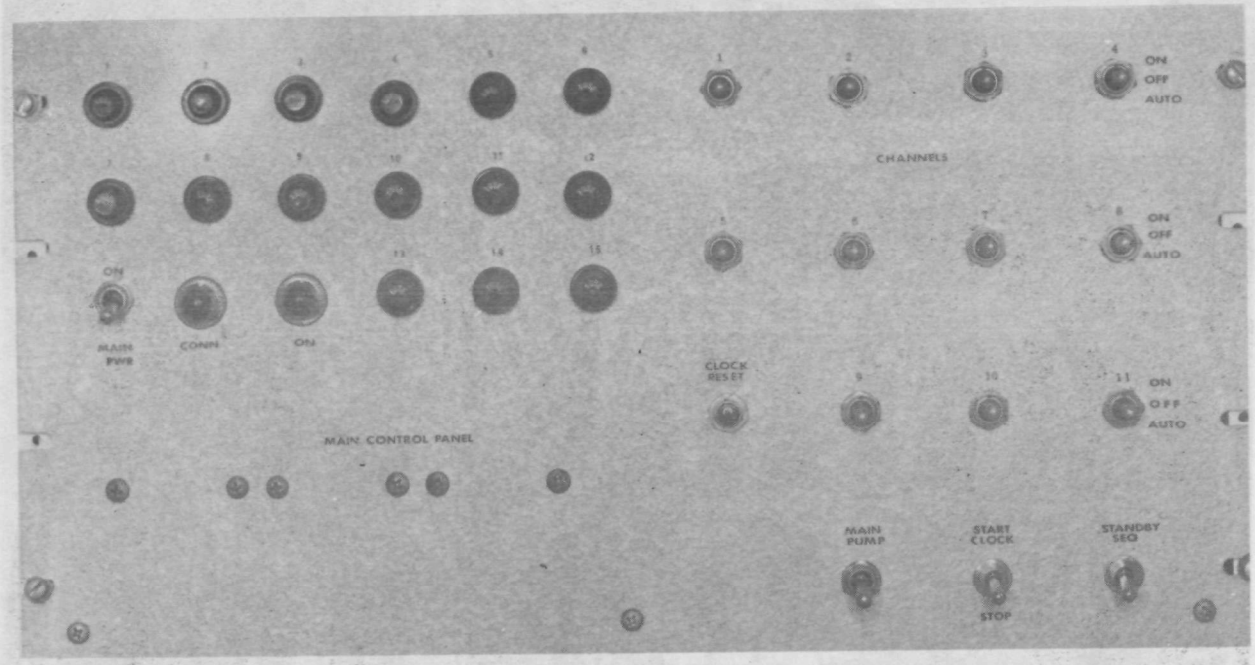


Figure 8. Electrical Control Panel

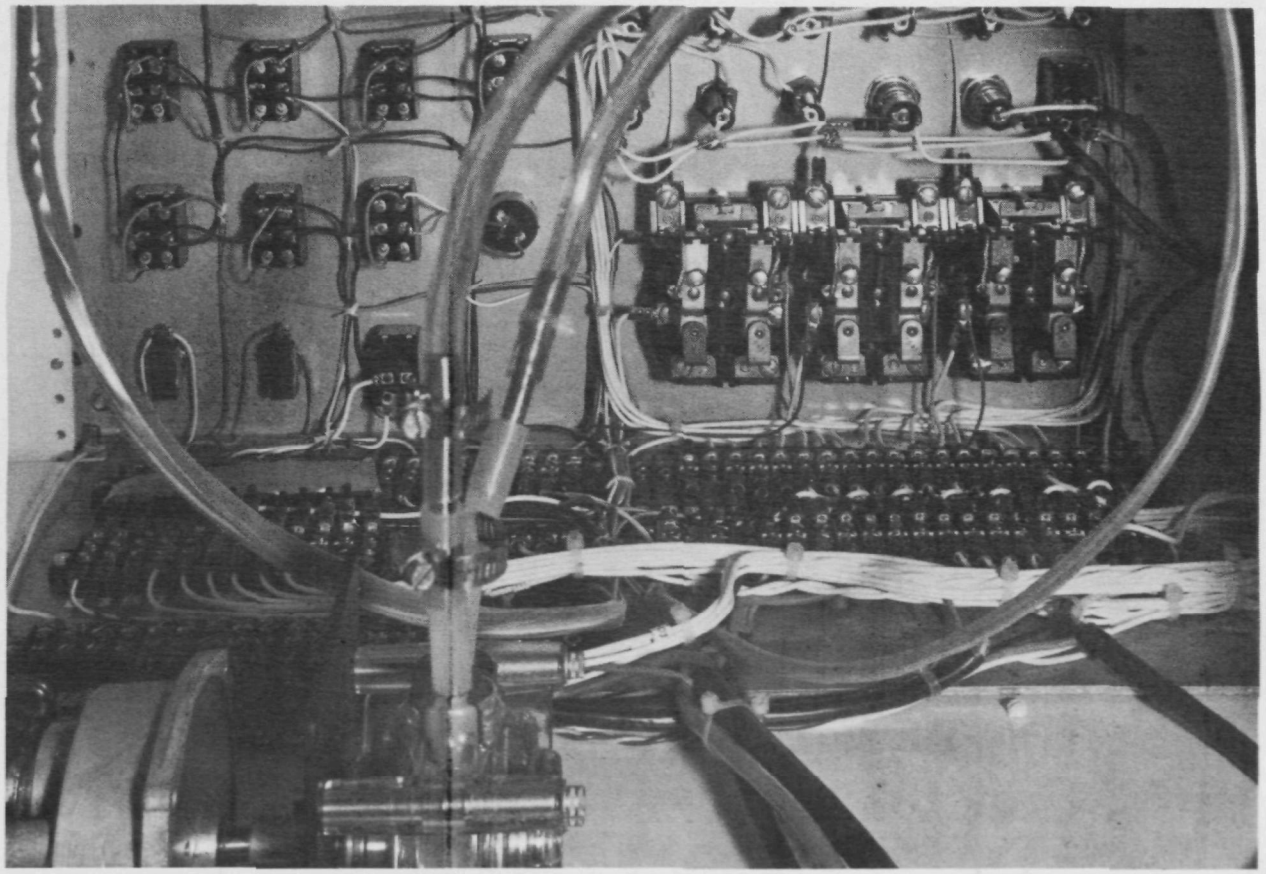


Figure 9. Terminal Strip Connections

115 VAC and 24 VDC power circuits. The front panel contains fuses for all the 115 VAC components, and switches to operate each of the 11 functions as described in Table 1 as well as operate the sequencer and the main sampling pump. Power is supplied to the unit through the main power switch, and indicator lights indicate whether the power is connected (unit plugged in), and if the power is turned on to the fuses. Figure 10 shows the general schematic of the 115 VAC circuit, and the fuse values and components controlled are listed also in Table 3.

The output from each of the sequencer channels is connected to the respective component through a 3-position toggle switch as shown in Figures 8 and 11. In the middle position, the component is isolated from power. In the "ON" position, 24 VDC power is supplied directly to the component, bypassing the sequencer. This option is convenient for checking various component operation without having to use the sequencer. In the "AUTO" position, the component is controlled by the sequencer.

The "Sequencer Standby" switch supplies power to the sequencer. No functions will operate in the AUTO mode unless the sequencer circuit is activated, as indicated by the "power on" indicator on the sequencer front panel. The "Clock start/stop" switch will supply power to the sequencer internal timer; activation of this circuit will be indicated at the "Clock Enable" light on the sequencer front panel. The clock reset button, a momentary pushbutton, will reset the timers as explained previously; activation of this circuit is also indicated on the sequencer front panel.

To facilitate connection of the components to the control panel, all connections are made via five terminal strips, illustrated in Figure 9. All the 115 VAC neutral terminals are connected together and are connected to one pole of the main power switch. All the 115 VAC ground terminals are jumpered together and are connected to the control unit enclosure, which is connected to the ground terminal of the input power lead. The "hot leads" from each fuse are also connected to a terminal strip. Each component requiring 115 VAC power is thus connected to 3 terminals; one for the "hot" lead, the second for the neutral lead, and the third to ground.

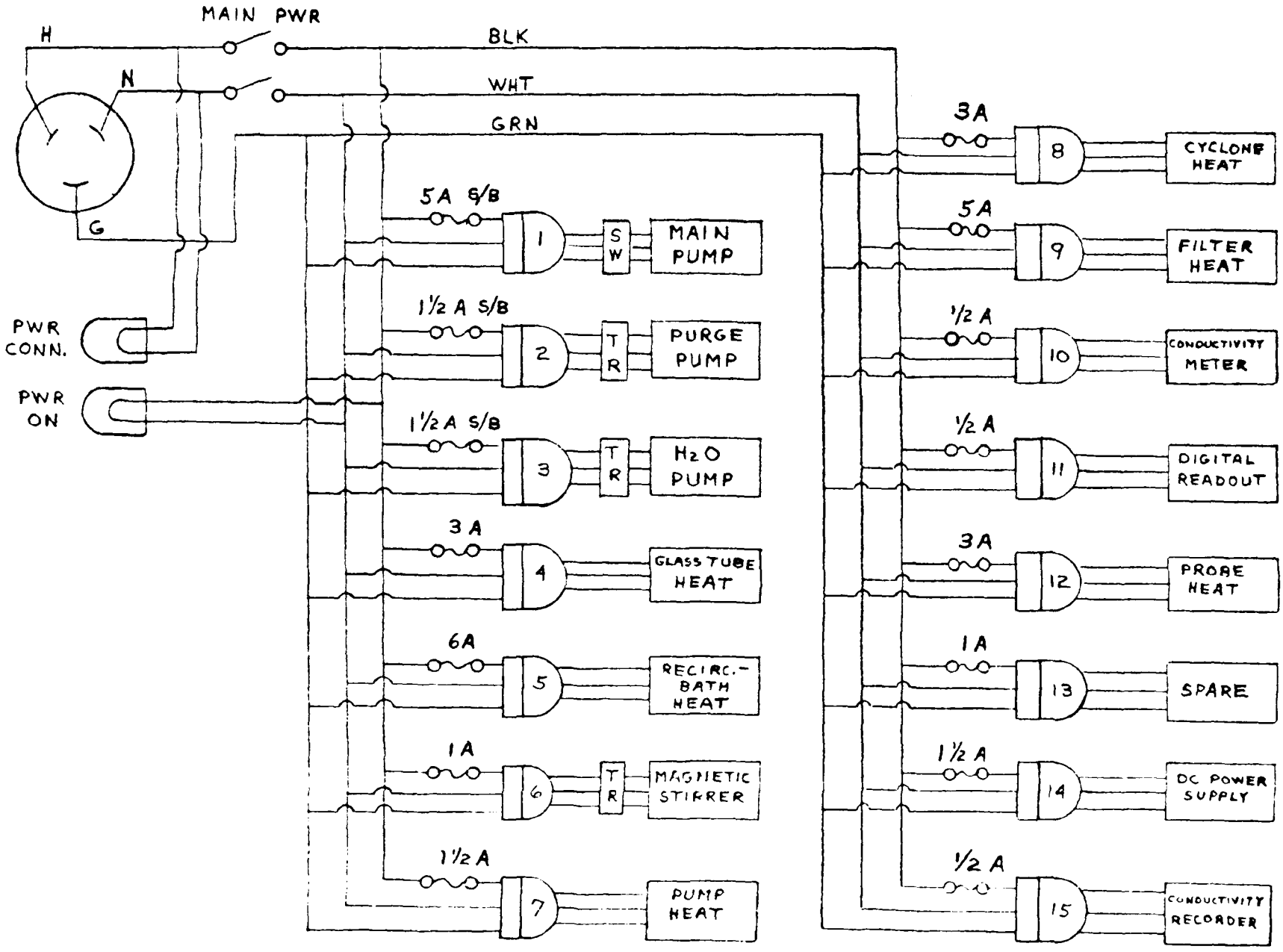


Figure 10. Electrical circuitry schematic.

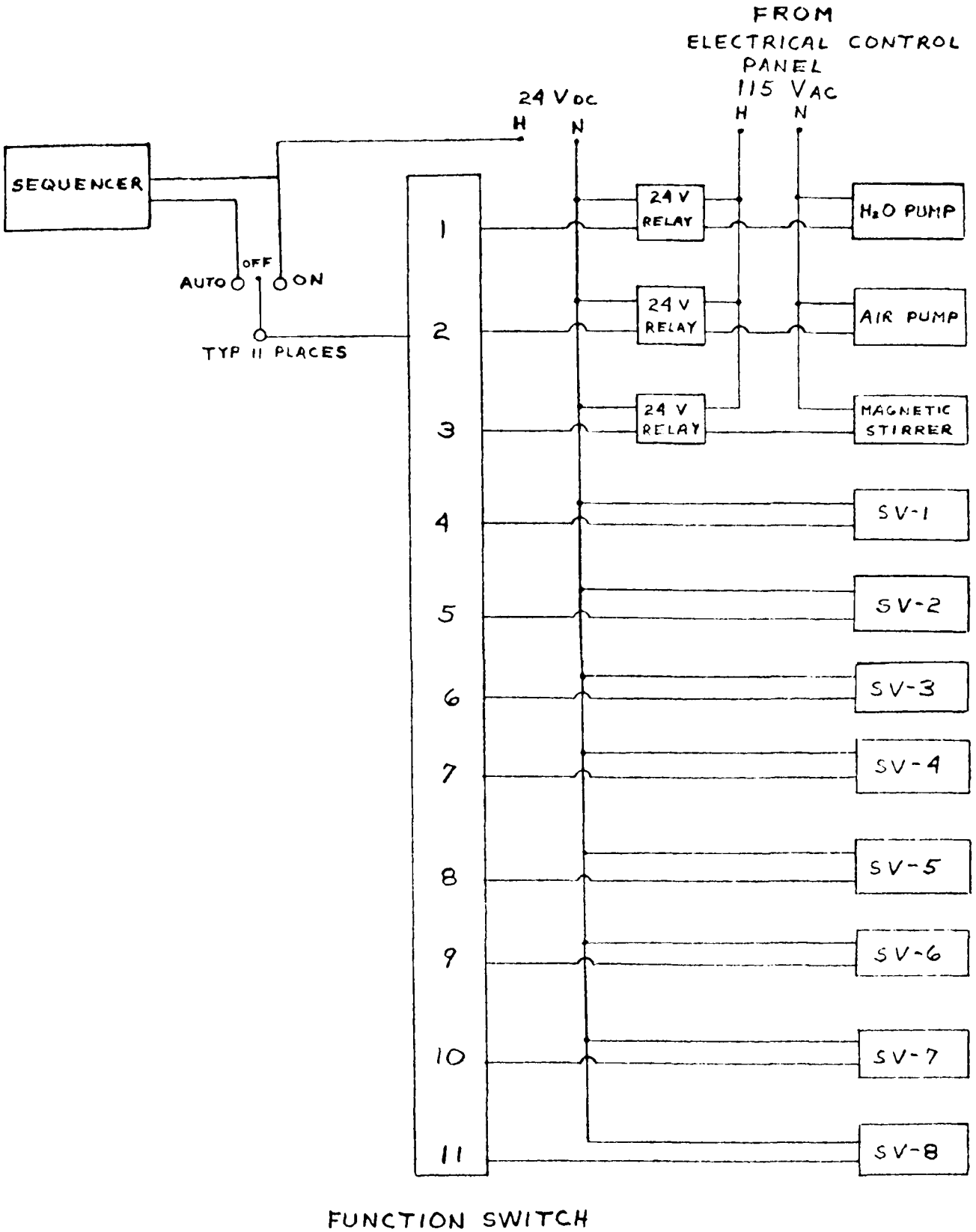


Figure 11. Function circuitry schematic.

Table 3. FUSE SIZES AND CIRCUITS

FUSE NO.	VALUE (A)	COMPONENT CONTROLLED
1	5	main sampling pump
2	1½	purge air pump
3	1½	peristaltic (H_2O) pump
4	3	glass tube heater
5	6	recirculator, heater
6	1	magnetic stirrer
7	1½	main pump heater
8	3	cyclone heater
9	5	filter heater
10	½	conductivity meter
11	½	digital temperature readout
12	3	probe heater
13	1	spare
14	1½	24 VDC power supply
15	½	conductivity recorder

The output of the sequencer is also connected through terminal strips. To facilitate troubleshooting, the components attached to each terminal are listed in the Operations and Maintenance Manual.

2.6 TEMPERATURE AND FLOW CONTROL

To prevent condensation of H_2SO_4 vapor in the sampling train prior to the condensation coil, the temperature of the components must be maintained at a temperature above 288°C. As described previously, the cyclone and filter are heated with heating mantles, and the probe, check valves, and orifice are heated with heating tapes which are controlled by a series of autotransformers, shown in Figure 12. Each autotransformer has a maximum output of 5 amperes at 115 VAC which is more than sufficient to operate the heaters.

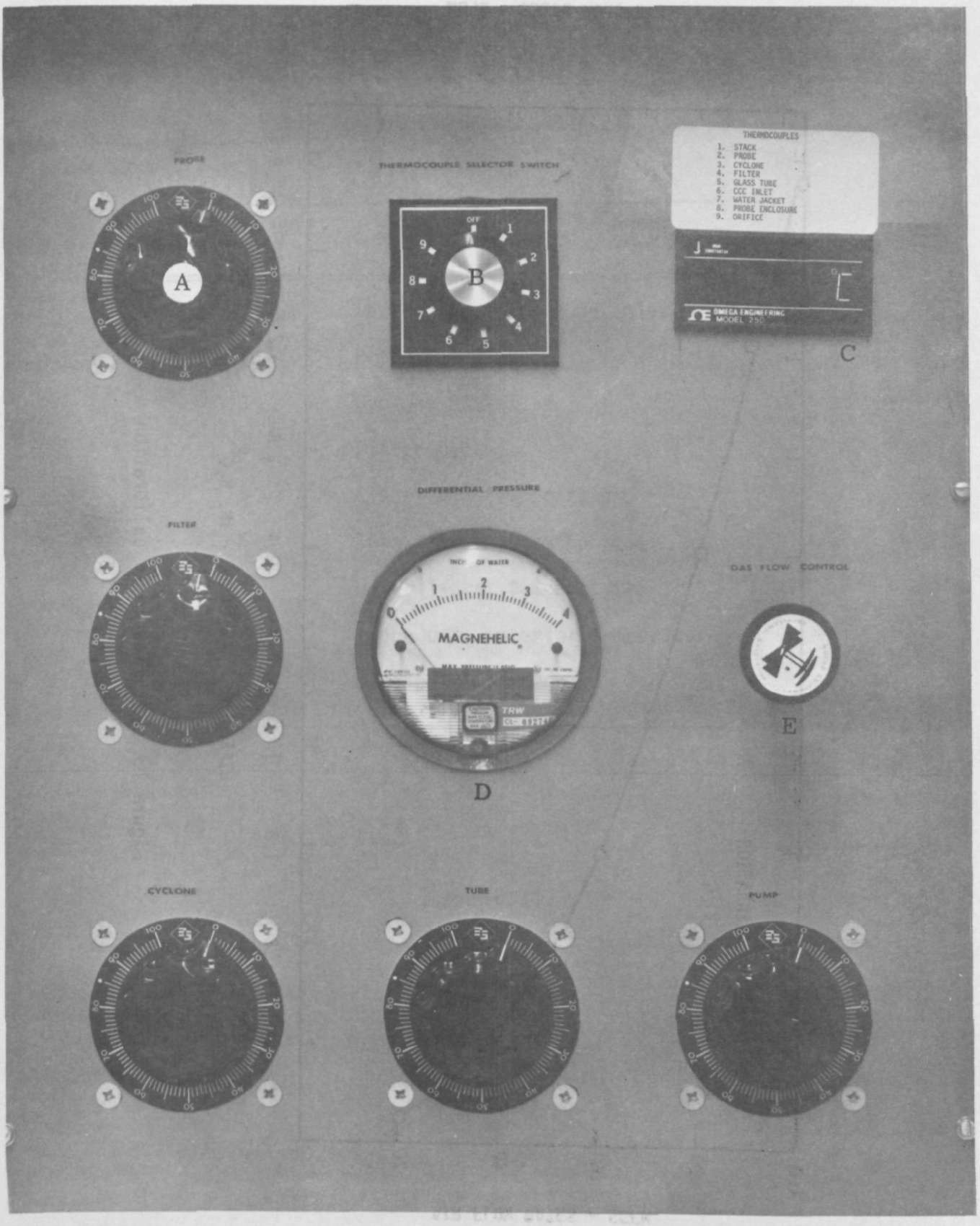
The temperature of the sampling train is monitored at 9 separate locations with Type J (Iron-Constantan) thermocouples. The thermocouple locations are listed in Table 4. A rotating switch connects these thermocouples to the digital readout, manufactured by Omega Engineering, Stanford Conn. (Model 250-J). No provision is made for recording of these temperatures; they are to be set prior to initiation of sampling and will be maintained by the power from the Variacs.

Since the measurement of sulfuric acid concentration requires an accurate measurement of the sampled gas volume, a calibrated orifice meter was manufactured and installed, shown in Figure 12. The differential pressure across the orifice is measured and displayed by a magnehelic gauge on a 0 to 4 in. H_2O scale. The orifice is of all stainless steel construction to reduce corrosion due to acid in the inlet gas. It is located within the control unit enclosure, immediately prior to the flow regulation valve. The orifice has been calibrated in SCFM, the results of which are shown in Figure 13. To reduce the error in meter indications due to temperature variation, the orifice is wrapped with a heating tape to maintain a gas inlet temperature of 60°C in cases where the unit is used in low ambient temperature. In this manner, the volume of sampled gas in standard conditions can be obtained from the differential pressure reading, and used to calculate sulfuric acid concentration as described in Section 4, once corrections for temperature and pressure are made.

Figure 12. Temperature and flow control panel

LEGEND:

- (A) HEATER CONTROL (AUTOTRANSFORMER)
- (B) THERMOCOUPLE SELECTOR SWITCH
- (C) DIGITAL TEMPERATURE READOUT
- (D) DIFFERENTIAL PRESSURE GAUGE
- (E) GAS FLOW CONTROL VALVE


PROBE
A
THERMOCOUPLE SELECTOR SWITCH
OFF
1
2
3
4
5
6
7
8
9
B
THERMOCOUPLES
1. STACK
2. PROBE
3. CYCLONE
4. FILTER
5. GLASS TUBE
6. CCC INLET
7. WATER JACKET
8. PROBE ENCLOSURE
9. ORIFICE
OMEGA ENGINEERING
MODEL 250
C
FILTER
DIFFERENTIAL PRESSURE
MAGNEHELIC
TRW
D
GAS FLOW CONTROL
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CYCLONE
TUBE
PUMP

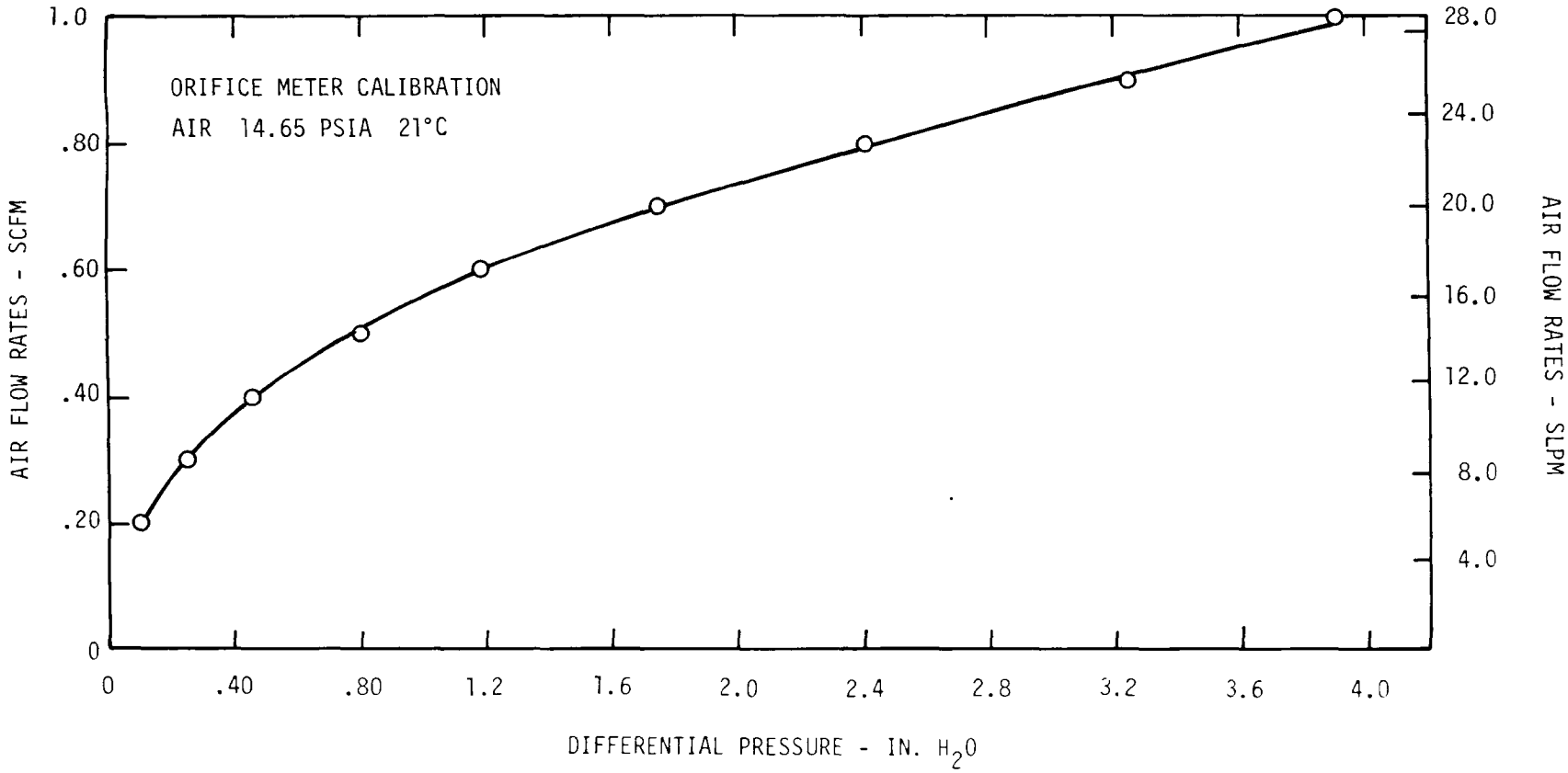


Figure 13. Air flow meter calibration

Table 4. THERMOCOUPLE LOCATIONS

THERMOCOUPLE NUMBER	LOCATION
1	Inside stack at probe inlet
2	Probe temperature
3	Cyclone Outlet
4	Filter Outlet
5	Glass tube temperature
6	Inlet to condensation coil
7	Water jacket temperature
8	Probe unit interior temperature
9	Orifice temperature

2.7 CONDUCTIVITY INSTRUMENTATION

The output of the monitor is in two forms; the first being differential pressure from an orifice meter, and the second being millivolt output from a conductivity meter. From calibration curves, these outputs can be used to determine the mass of sulfuric acid contained in the sample gas.

As outlined in Section 2.1, the basic operation of the monitor involves the condensation of sulfuric acid from the sample gas onto the walls of the condensation coil. This coil is then rinsed with deionized water and the solution directed into a conductivity cell (G in Figure 6). Here the electrical conductivity of the acid-rinse solution is measured with a conductivity bridge and recorded on a strip chart recorder. The conductivity bridge and recorder are shown in Figure 14. The output of the meter is then compared with calibration data of conductivity (micromhos/cm) versus mass of sulfuric acid as shown in Figures 15 and 16. Thus the mass of acid in the sampled gas can be obtained.

The conductivity cell contains a conductivity probe which houses two platimum-coated electrodes which are part of the conductivity bridge circuit. The conductivity probe maintains the electrodes at a fixed separation which is essential for accurate conductivity measurement. The conductivity probe is oriented at a 45° angle (see Figure 6) and is continually immersed in the rinse/wash solution. Vent holes in the probe tip allow for the escape of any trapped air so that the electrodes are completely immersed in the solution. The probe is manufactured by Beckman Instruments, Inc., number K-1 with a cell constant of 1.00/cm.

Since a wide range of acid concentrations can be expected to be encountered, the conductivity meter used has a dual range capacity. The meter operates on either a 0-500 micromhos/cm or a 0-5000 micromhos/cm scale. This is sufficient to cover the range of 0.5-40 ppm at a sampling rate of 12 Lpm for 7 minutes. A maximum concentration of 500 ppm can be sampled by reducing the sampling time to approximately 1 minute. The bridge is also manufactured by Beckman Instruments, Model RA5-X14-B-S8-T8.

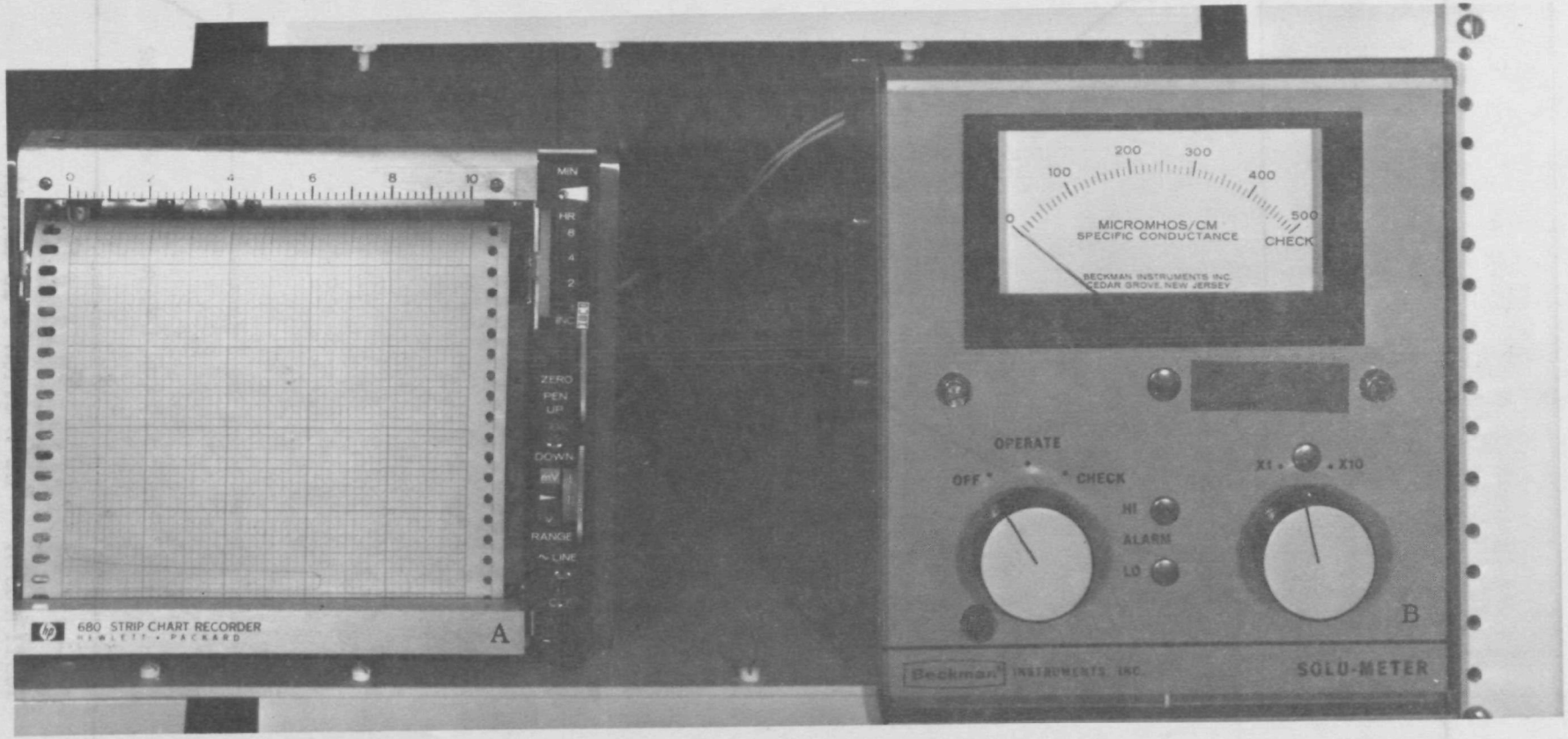


Figure 14. Conductivity Instrumentation

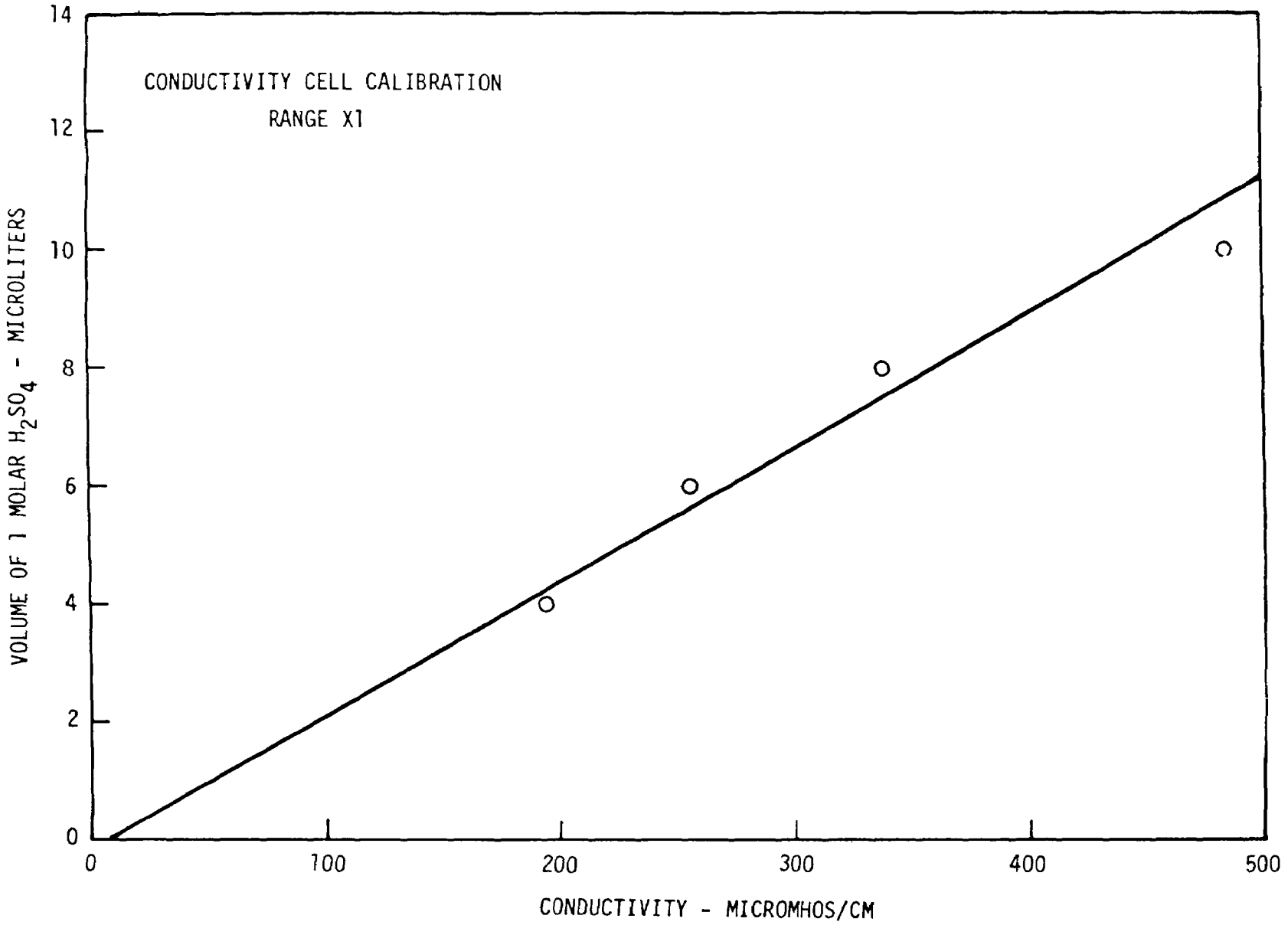


Figure 15. Conductivity cell calibration, X1 scale

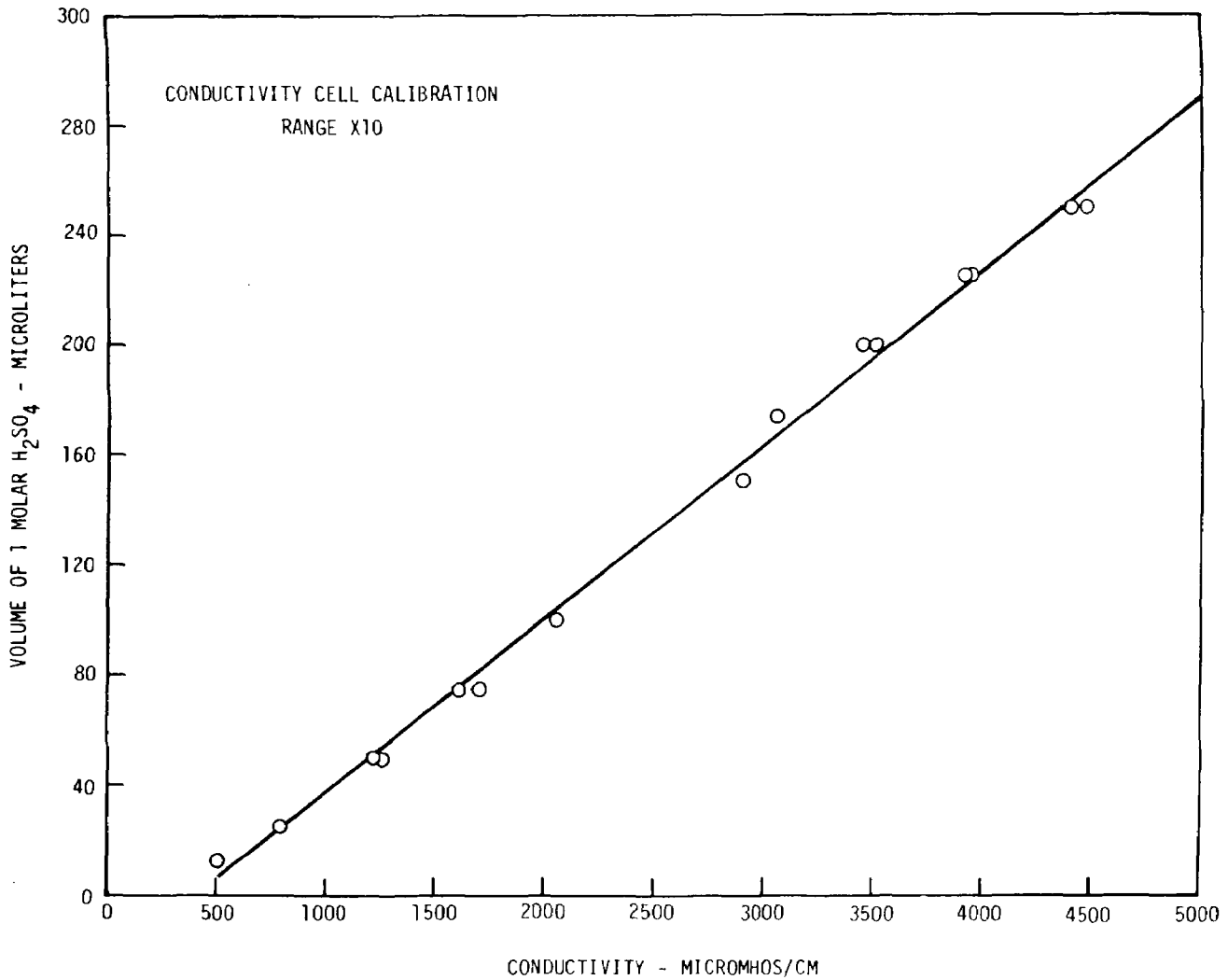


Figure 16. Conductivity cell calibration, X10 scale

To provide a continuous record of the conductivity meter output, a single-pen strip chart recorder is used. The conductivity meter output is 0-10 mV DC in the X1 range and 0-1 mV DC in the X10 range. This output is supplied to the recorder which then gives a continuous trace of the meter output. The recorder is a Hewlett-Packard model 680-015 with an electric writing option. It requires the use of electrosensitive paper (Hewlett-Packard number 9280-0136) which eliminates the problems associated with ink pens when operated at low speeds, i.e., clogging, leaking, etc. During normal automatic operation with a 15 minute total cycle duration, a chart speed of 8 in/hr (20.3 cm/hr) is used. However, for shorter cycle times, on the order of 1 or 2 minutes, a chart speed of 1 in/min (2.5 cm/min) is desirable to provide sufficient time resolution between cycles. The manufacturers manuals on these instruments are included in the Operations and Maintenance Manual.

2.8 ADDITIONAL EQUIPMENT

There are several other components in the monitor which serve to support the operation of the components discussed above. Most notable is the main sampling pump which is a 4-stage diaphragm type air pump. Manufactured by Air Dimensions, Inc., of Kulpsville, Pa., the model 299 used has a capacity of 28 Lpm at 458 mm of mercury vacuum when the 4 stages are connected in parallel. The heads are of 316 stainless and are Teflon coated; the diaphragms are of Teflon and neoprene. Replacement diaphragms are provided and can be easily interchanged in the field. The pump can be seen in Figure 17.

To transfer the deionized water from the reservoir to the sampling train, a peristaltic pump, shown in Figure 17, is used. A peristaltic pump is used because the water only comes in contact with the transfer tubing and not with any pump components, thereby preventing contamination. The pump is manufactured by The Barnant Corp, Barrington, Ill., and is their model 7541-80 with pump head number 7015-20. The pump operates at 80 rpm with a capacity of 134 ml/min.

Since the unit is to operate for extended periods unattended, provision is made for the recycling of the water used to wash the sampling train. A deionization column, shown in Figure 18 with the reservoir, is used to

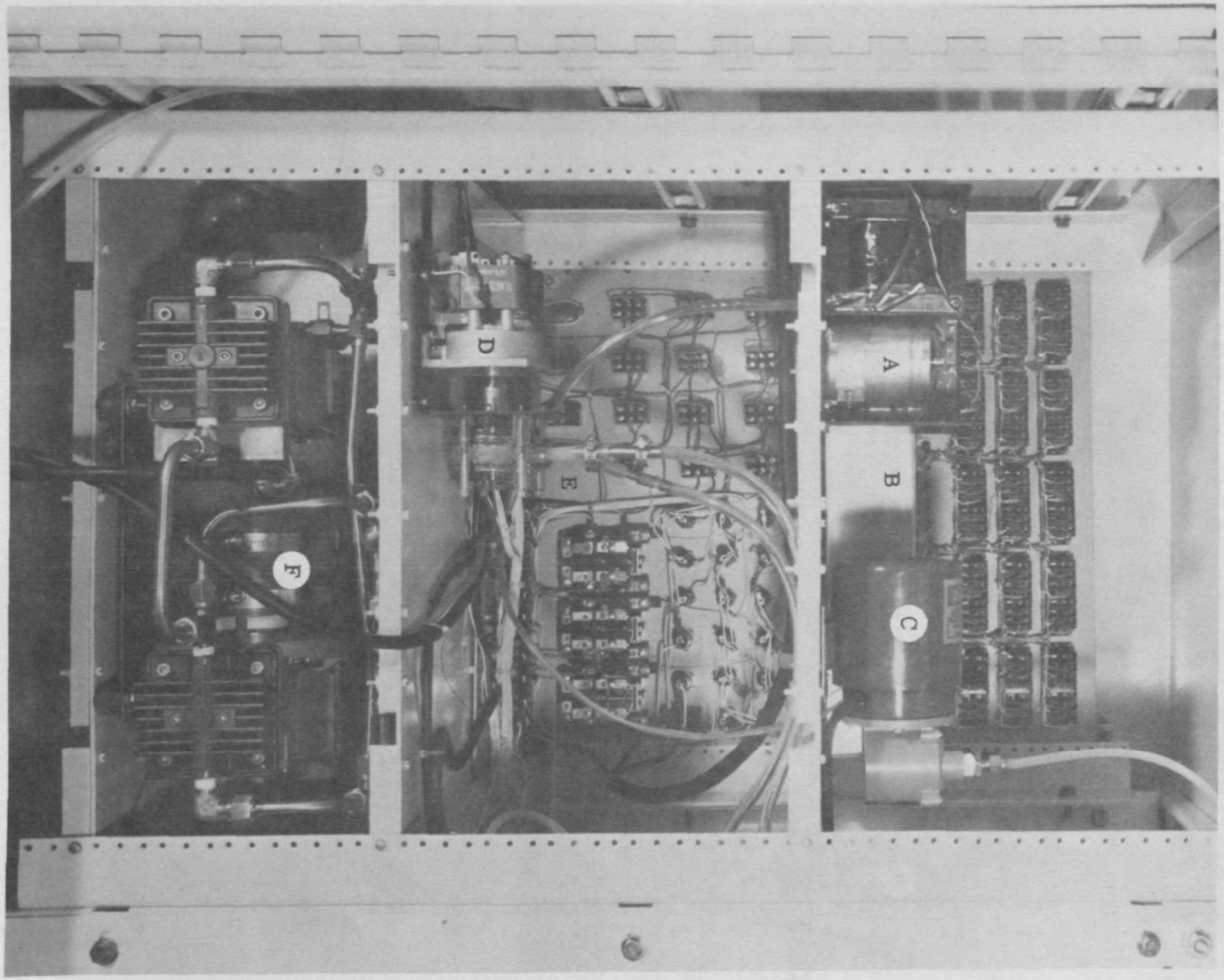
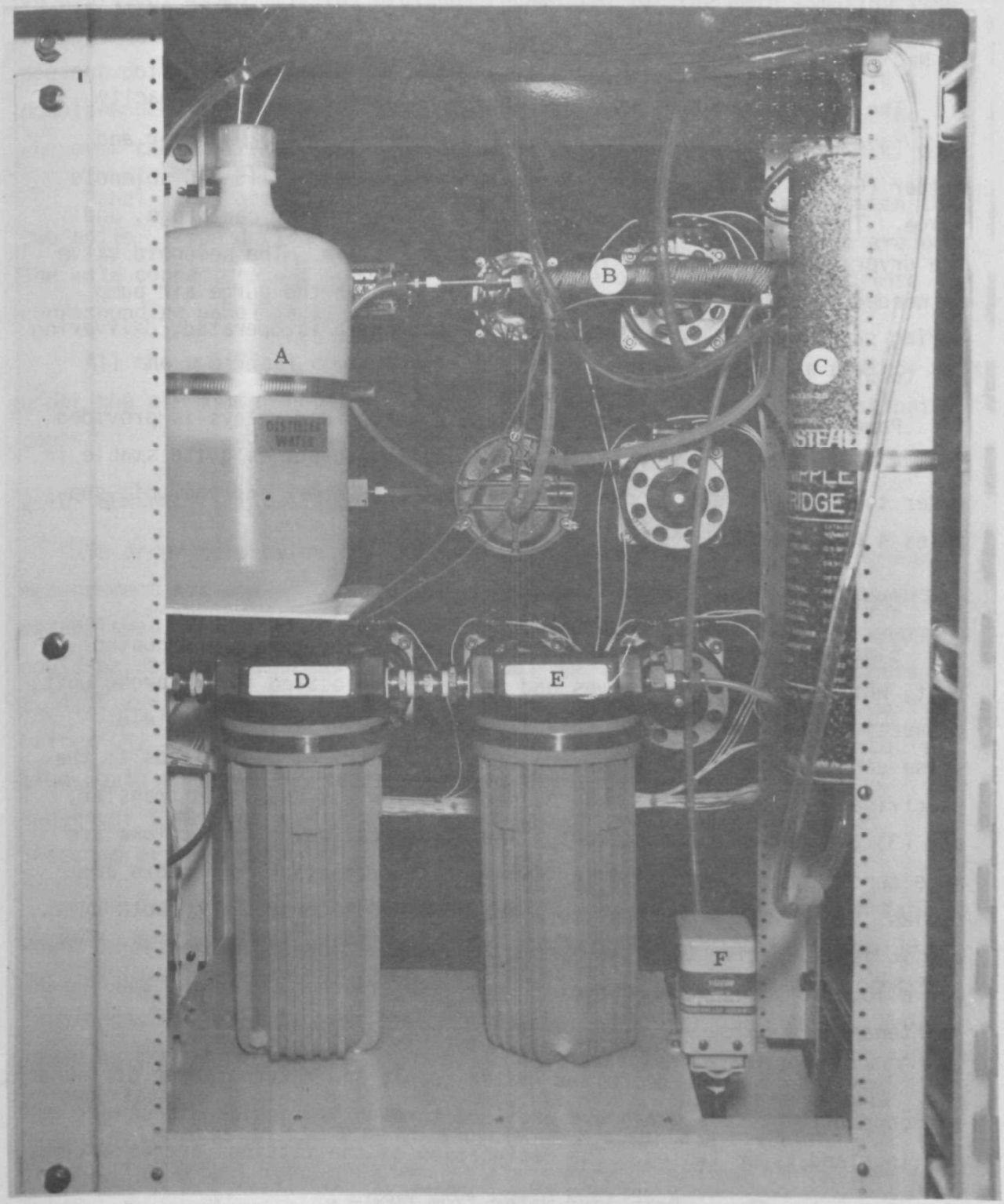


Figure 17. Control unit pump compartment: (A) VDC Power Supply, (B) Sequencher, (C) Purge Air Pump, (D) Peristaltic Pump, (E) Electrical Control Panel, and (F) Main Sampling Pump

Figure 18. Control unit filter compartment

LEGEND:

- (A) DISTILLED WATER RESERVOIR
- (B) CALIBRATED ORIFICE AND HEATER
- (C) DEIONIZATION COLUMN
- (D) PURGE AIR DRYER
- (E) PURGE AIR FILTER
- (F) PURGE AIR SOLENOID


A
B
C
D
E
F
DISTILLED WATER

purify the water from the rinse cycle. It is a Barnstead model D-8902 mixed resin cartridge with a total ion exchange capacity of 80 grams as NaCl.

The purge air system utilizes four components: a small capacity pump (#7530-40 from The Barnant Corp., Barrington, Ill.), a dryer and filter (Gelman Instrument Co., Ann Arbor, Mich.) and a 115 VAC solenoid valve. The filter housing contains a 0.2 micron filter cartridge, and the dryer housing contains type 13X molecular sieve. The solenoid valve is needed to prevent air from being pulled through the purge air pump during sampling. It opens whenever the purge pump is operated, delivering air to SV-1 (see Figure 6).

Power for the sequencer, the solenoid valves and relays is provided from a 24 VDC Elexon power supply. The voltage output is quite stable in order to provide a clean power input to the sequencer, and the unit supplies 4 A at 24 VDC.

2.9 UMBILICAL CONNECTIONS

Since all of the pumps and controllers are located in the control unit, while the solenoid valves and heaters are located in the probe unit, connections are provided for easy assembly and hook-up in the field. These connections are of three types: (1) electrical power leads to the electrical components, (2) tube connections for gas and fluid transfer, and (3) thermocouple connections. The electrical power connections are made through four 6-conductor environmentally resistant connectors and cables. The cables and connectors are numbered 1 through 4 on both units, and it is imperative that the numbers are matched during connection. The pin allocations for each connector are listed in the Operations and Maintenance Manual.

Provision for the deionized water supply and return, purge air supply, and conductivity cell drain are provided through 1/4" quick disconnect fittings and tygon tubing. The designation of the fittings are as follows:

Connector #1 — Deionized water from pump
Connector #2 — Air from purge air pump
Connector #3 — Water overflow from SV-3
Connector #4 — Conductivity cell drain

In addition, a 3/8" fitting provides connection for the main sampling line through which the gas sample is drawn. This line is of nylon tubing to prevent collapse under high vacuum levels. All of these fittings are double-ended shut-off types which prevent loss of fluid from the tubing whenever the umbilical is disconnected.

Panel jacks are provided for the thermocouple connections between the two units. Type J (Iron-Constantan) connectors and extension wire are used. The male connectors are numbered 1 through 8 and should be plugged into the corresponding panel jack.

All the umbilical connections and cables are stored in the control unit under the air filter housing. Access is gained through the rear cabinet doors.

2.10 GENERAL TIMING SEQUENCE

In order to provide for the automatic operation of the sampling and measurement systems of the monitor, a general sequence of operations was established. From this sequence, the operation of the 11 function channels could be determined which led to the dual operation of function numbers 1, 2, 4, 5 and 9 as described in Section 2.4. As part of the monitor design criterion, it was determined that all operations involved in data acquisition would occur in 999 seconds or less for a given cycle. Thus the sequencer timers were of 3-digit construction providing timing to a 1-second differential.

The general timing sequence for automatic sampling is shown in Table 5 which is keyed to the schematic of the monitor illustrated in Figure 19. This sequence is the maximum sequence length used under automatic control. Sample gas is drawn through the condensation coil for 400 seconds, followed by the operations of rinsing, data acquisition, washing, and drying as described in Section 2.3. The times listed in Table 5 are general approximations as to the time in a cycle when a certain operation will occur. The actual function timer settings were determined by laboratory tests. By examination of Table 5 and Figure 19, one can see how the systems operate during a sampling cycle to collect the sulfuric acid,

Table 5. TIMING SEQUENCE FOR SO_3 MONITOR - 400 SECOND SAMPLING TIME

t = 0 sec.	SV-5 in 1-2 position (off). All other valves off. Main pump begins to draw sample.	
300	SV-2 Open. SV-3 Open.	Peristaltic pump on; measuring vessel filled.
320	SV-2 Closed. SV-3 Closed.	Peristaltic pump off.
400	SV-5 switched to 1-3 position (on). SV-1 in 1-3 position (off). SV-4 in 2-3 position (off). SV-8 switched to 2-3 position (on).	Purge air pump on; low volume SO_2 purge.
410	SV-1 switched to 1-2 position (on). SV-4 " " 1-2 " (on). SV-8 " " 1-3 " (off). SV-6 Open.	D.I. H_2O rinse of coil.
430	SV-1 switched to 1-3 position (off). SV-6 Closed.	Purge air pump off. Magnetic stir on; conductivity measurement taken.
500	SV-2 Open. SV-7 Open.	Peristaltic pump on. Magnetic stir off; coil and cell rinsed.
700	SV-1 switched to 1-2 position (on) SV-6 Open. SV-7 Closed. SV-2 Closed.	Peristaltic pump off. Purge air pump on; coil and cell dried.
990	SV-1 switched to 1-3 position (off). SV-4 " " 2-3 " (off). SV-5 " " 1-2 " (off). SV-6 Closed.	Purge air pump off. Main pump begins to draw sample.

Timer resets to 0; cycle repeats

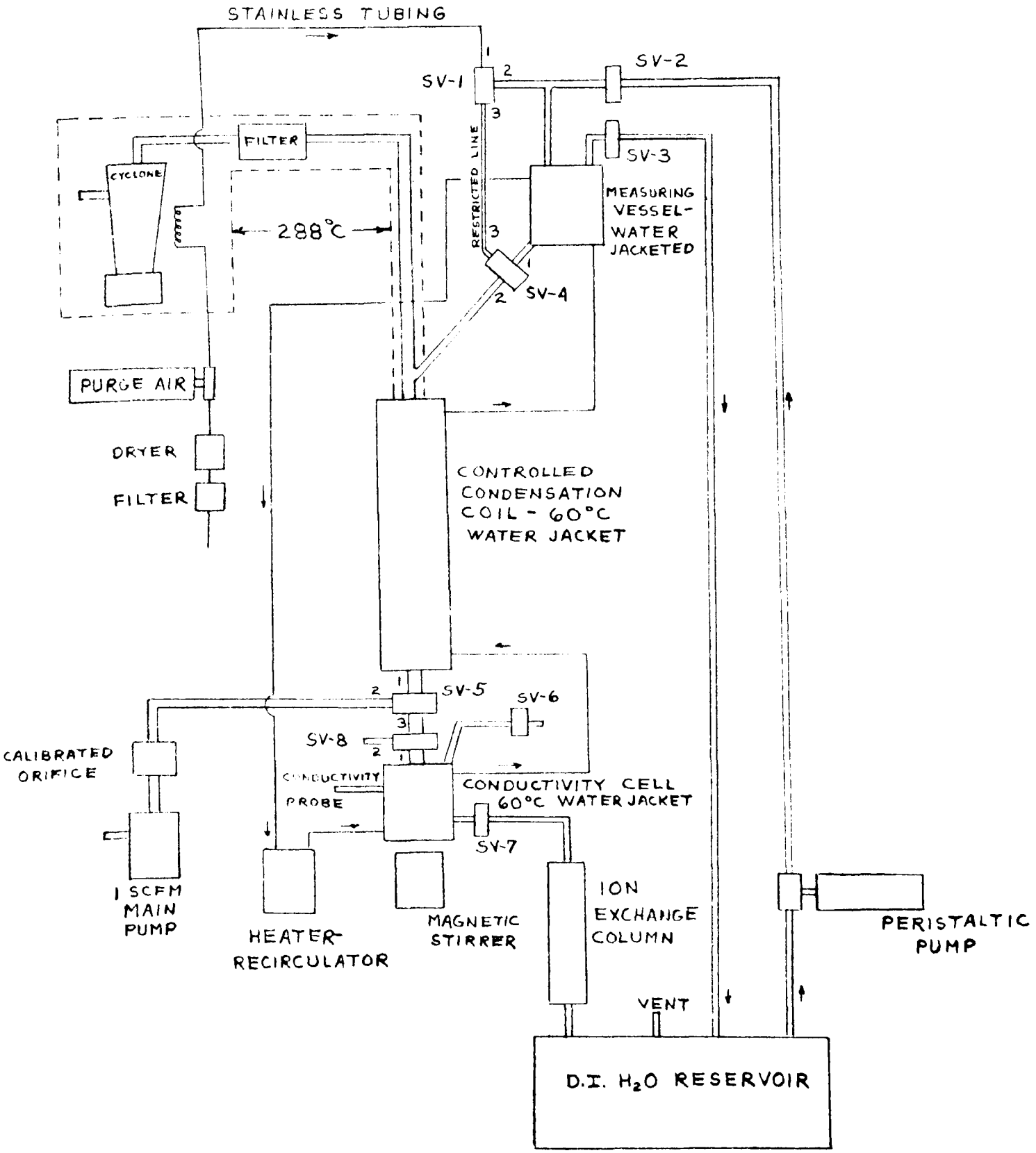


Figure 19. Schematic of Sulfuric Acid Monitor

measure the acid content, and prepare the system for the next sampling cycle. The solenoid valves are primarily responsible for isolating the rinsing and drying systems from the main sampling system, and then allowing the rinse solution or dry air to pass through the appropriate components during the appropriate time in the cycle.

SECTION 3

LABORATORY TESTS

Once the monitor construction was complete, an extensive series of laboratory tests were performed to characterize the performance of the systems and to calibrate the output of the instrumentation. The purpose of these tests was to determine the system accuracy and to identify any problem areas before performing an actual field test of the unit.

3.1 SEQUENCER TIMER SETTINGS

The timing sequence outlined in Table 5 is a general sequence only; it does not provide for the overlap required in the operation of the 11 functions to account for component response times. Here the versatility of the 3-digit set point timers becomes most apparent, for the adjustment of the START or STOP time of a component can be performed by rotating the proper digit to the desired setting to allow a component to operate at precisely the right moment in a cycle.

Using manual operation of the 11 functions, it was determined by observation of the condensation coil and fritted disk within the coil that a drying time of 280 seconds would ensure that all moisture in the sampling system would be removed following a wash cycle. Next, by placing a 1 molar sulfuric acid solution in the conductivity cell in a sufficient volume to obtain a reading of 5000 micromhos/cm (the maximum concentration readable with the conductivity meter), the time necessary to wash out the sampling system was obtained. A wash cycle of 200 seconds was found to be sufficient to wash out the highest acid concentration expected. Thus 480 seconds of a cycle must be devoted to washing and drying the sampling system.

A period of 85 seconds was allotted for taking the conductivity measurement, a time which allowed for complete mixing of the H_2O-H_2SO_4 solution in the conductivity cell. Of the 999 seconds in a cycle time, approximately 400 seconds were available for actual sampling of the gas. This figure was used as the basis for setting the function timers for the maximum sampling time permissible. By observing the operation of each of the components, the START and STOP times on each function channel were adjusted until the monitor operated satisfactorily under automatic control.

As an example, the timer settings for a 400 second sampling time (999 second cycle time) are shown in Table 6. It must be noted that the time allocated for reading the solution conductivity, washing the system, and drying the system, are fixed. However, the sampling time can be reduced from 400 seconds to 60 seconds depending upon the concentration of acid in the sample gas stream. At a high concentration (300-500 ppm) a short sampling time is used to keep the conductivity meter reading within range. At a low concentration (0.5-40 ppm) the maximum sampling time is used to ensure accurate readings of conductivity. The Operation and Maintenance Manual contains a table of suggested sampling times and sample gas flow rates for various acid concentrations. The timer settings are all reduced the same number of seconds according to the sampling time variation from the standard 400 seconds. Thus, if a sample time of 300 seconds is desired, all the timer settings are reduced 100 seconds from those shown in Table 6.

3.2 CALIBRATION OF CONDUCTIVITY CELL

The key component of the monitor is the conductivity cell; here is where the determination of the mass of sulfuric acid collected is made. Because of its importance, considerable care was taken in calibration of the cell. A 1.000 molar solution of H_2SO_4 was prepared and a precision glass syringe obtained. The conductivity cell and other glassware were maintained at 60°C, and various volumes of the H_2SO_4 solution were injected directly into the cell via the cell vent (outlet to SV-6 in Figure 6). At each time when an acid solution volume was added, the measuring vessel was filled and the deionized water was blown through the condensation coil into the conductivity cell. After 85 seconds, the reading was taken with the stirrer operating. It was noted that the operation of the stirrer did not affect the reading; however, the meter needle deflected whenever the stirrer was first turned ON or OFF. The conductivity instrumentation therefore only responded to the transient magnetic field created during startup or shutdown of the stirrer.

In this manner the conductivity cell was calibrated under conditions exactly duplicating those encountered during normal operation of the monitor. The water volume in the cell, the cell temperature, and the

Table 6. SEQUENCER TIMER SETTINGS

400 SECOND SAMPLING TIME; 990 SECOND CYCLE DURATION			
Function Number		Time On	Time Off
1	H_2O pump	300 500	320 700
2	purge air pump	406 710	435 990
3	magnetic stirrer	415	655
4	SV-1	415 705	436 990
5	SV-2	300 500	330 700
6	SV-3	300	330
7	SV-4	415	990
8	SV-5	400	990
9	SV-6	415 730	436 990
10	SV-7	499	732
11	SV-8	405	415

stirrer operation were identical to that of a normal operating condition. Calibration curves were generated for the two conductivity meter ranges, taking 3 sets of measurements at different times for each volume of sulfuric acid solution injected. These results are shown in Figures 15 and 16. It can be seen that the relationship between the volume of sulfuric acid injected into the conductivity cell to the conductivity meter output is linear. From these calibration curves, the mass of acid collected during a test can be obtained because the mass of sulfuric acid in a 1.000 molar solution is fixed. A representative calculation is shown in Section 4.3.

3.3 COIL RINSE EFFICIENCY

The operation of data acquisition involves the rinsing of a fixed volume of the deionized water through the condensation coil, thereby washing the sulfuric acid which has condensed on the walls of the coils into the conductivity cell. The efficiency of the rinse was examined in the following manner.

Sulfuric acid (150 μl of 1.000 molar solution) was injected into the conductivity cell and 1 measuring vessel volume of deionized water was added. The conductivity meter reading was recorded. This process was repeated with 2 and then 3 measuring vessel volumes of water added to the conductivity cell. This established a base line for the rinse efficiency check.

The same volume of 1.000 molar H_2SO_4 was then injected at the inlet to the condensation coil and the measuring vessel emptied through the coils into the conductivity cell. The conductivity meter reading agreed with the base line reading within ± 0.7%. The process was repeated with 2 and 3 measuring vessel volumes of water rinsing through the coils. These readings agreed with the baseline readings within ± 1.1%. Three sets of readings were taken at each test which provided repeatability to the tests. From these results it was concluded that the present rinse volume was sufficient to rinse the coils completely.

3.4 ACID INJECTION TESTS

A sulfuric acid aerosol generator consisting of a calibrated syringe pump, a heated quartz injection manifold, a precision compound gauge, five flowmeters, and three thermocouples was prepared for further testing of the monitor. The injection manifold was attached to the probe inlet connection of the cyclone, so that the manifold simulated the probe inserted in a sulfuric acid ladden gas stream for the tests. Oxygen, nitrogen, and SO_2 supply bottles were connected to the flowmeters and the meters calibrated. These gases would represent a typical stack gas composition for the tests. The compound gauge was used to monitor the manifold pressure, and the main pump adjusted so that a slight negative pressure (25 mm Hg vacuum) existed at a flow rate of 8 Lpm through the system.

The heaters and mantles were checked for operation and proved to work quite well. The glassware prior to the condensation coil was heated to 300°C by using only 50% of the capacity of the autotransformers. With the probe unit door closed, the internal temperature of the unit reached 45°C after 8 hours and stabilized at that point.

The system was then leak checked prior to each sampling test; if any flow registered on the flowmeters with the injection manifold sealed, the system was dismantled until the leak was found. No unusual difficulty was encountered in achieving a leak-free system.

Gas consisting of 8% O_2 and 92% N_2 was sampled at 8 Lpm through the system. The entire sampling system prior to the condensation coil, including the acid injection manifold, was maintained at 290-300°C, and the manifold pressure was maintained at 25 mm Hg vacuum. A total of 49 tests were performed using the system under automatic control.

For each test, the syringe pump was operated for a 3.75 minute period, injecting a 1.000 molar H_2SO_4 solution into the injection manifold at rates varying from 0.0042 mL/min to 0.059 mL/min, depending upon the concentration of sulfuric acid desired for the test. The conductivity meter reading was recorded on the conductivity recorder. These tests covered the range from 1 to 100 ppm, and were repeated 7 times. The results are summarized in Section 3.7.

As a further check of the system operation, several tests were performed with the acid being injected for 3.75 minutes but the gas being sampled for 16.6 minutes, an additional 12.8 minutes of sampling after the acid injection stopped. This was to determine if acid was being held up in the system during the normal 400 second sampling time, and if this acid could be recovered by additional gas sampling. The measurements showed that almost no difference occurred with these readings over those taken with a 400 second sampling time; the readings agreed within ± 2%.

From these tests the operating limits of the monitor could be established. At the sampling rate of 12 Lpm, an acid concentration of 0.5 ppm will provide a conductivity reading which will be 20% of full scale in the low range of the conductivity meter. This is the recommended limit of system operation; readings lower than this may be too erratic due to instrumentation limits. Converesely, by sampling for only 60 seconds at a rate of 8 Lpm, a concentration of 500 ppm can be accommodated by the upper range of the instrumentation.

3.5 SO_2 TESTS

At the reduced temperatures encountered in the condensation coil, the presence of water vapor in the gas stream can cause the SO_2 product to be oxidized to SO_3. The critical factor in preventing this is maintaining the temperature above 60°C. In order to ensure that any SO_2 present in the gas sampled does not affect the SO_3 measurement, several tests were performed to determine the SO_2 effects upon the system.

The syringe pump was filled with distilled water and operated in the same manner as in the acid injection tests described above. An SO_2 concentration of 4000 ppm in the inlet gas was used with an oxygen flow rate of 0.64 Lpm (8% O_2), a nitrogen flow rate of 6.75 Lpm, (82% N_2) and a water flow rate of 0.48 Lpm (6% H_2O). The SO_2 flow rate was 0.125 Lpm. After performing 9 tests using the water injection system at 4000 ppm SO_2 concentration, it was demonstrated that the SO_2 effect could barely be detected at the most sensitive range of the conductivity meter. Readings on the order of 6 to 8 micromhos/cm were obtained.

3.6 SYSTEM COLLECTION EFFICIENCY

Finally, the collection efficiency of the glass sampling system was investigated. The syringe pump used had a very steady feed rate; the conductivity readings were fairly constant between tests at a given syringe injection rate. However, the absolute value of the feed rate was not necessarily that as advertised by the manufacturer. To calibrate the pump, a 1.000 molar H_2SO_4 solution was pumped into sample bottles using feed rates ranging from 0.0042 mL/min to 0.059 mL/min for a period of 3.75 minutes. This duplicated the conditions used in the acid injection tests.

The sample bottles were then titrated to determine the volume of 1.000 molar H_2SO_4 each contained. As an example, the pump operating for 3.75 minutes at a feed rate of 0.059 mL/min pumped 201.3 μL. By using this accurate volume of acid with the results of the acid injection tests, it was found that 92% of the acid injected at the probe inlet was recovered at the conductivity cell.

3.7 ENDURANCE TEST

Since the monitor is to operate for at least 24 hours on a continuous basis, an endurance test was performed demonstrating that capability. The system was operated under automatic control with the glassware heated for a 24 hour period. Every four hours, a specific quantity of 1.000 molar H_2SO_4 was added at the top of the condensation coil, and the reading taken after the coil was rinsed and the solution added to the conductivity cell. These readings were compared with the conductivity cell calibration curve. During the entire period, no degradation in the system performance could be detected. It was shown that the length of operation of the monitor on a continuous basis will be determined primarily by the particulate loading in the gas stream and its effect upon the filter.

3.8 RESULTS OF LABORATORY TESTS

From the outcome of the laboratory tests, it was demonstrated that the monitor was capable of automatic operation to detect sulfuric acid

concentrations in the range of 0.5 ppm to 500 ppm. It was also demonstrated that the system was unaffected by 4000 ppm SO_2 in a gas stream containing 6% H_2O,

The response of the system to H_2SO_4 concentration has been shown to be linear, with an overall system accuracy of ± 9% at 0.5 ppm acid concentration, and ± 7% at 10 ppm acid concentration. The system collection efficiency was shown to be 92%.

Setup and operation of the monitor was shown to be quite easy. Adjustment of sampling times was a simple task, facilitated by the thumbwheel units used in the sequencer construction. Manipulation of the probe unit was not difficult with two operators, and so the present design was deemed quite satisfactory to continue in the test program.

SECTION 4

FIELD TEST

Upon demonstration of the monitor's performance in the laboratory, it was desired to demonstrate its performance in an actual field environment. In particular, the performance of the system's filtration system needed to be tested as well as the duration cycle of the monitor under field conditions. Hence, the monitor was prepared in its final deliverable condition with all components securely mounted in the two enclosures, and a field test scheduled at the Shawnee Steam Plant in Paducah, Kentucky.

4.1 THE TEST FACILITY

Located 29 miles west of Paducah, the Shawnee Steam Plant is part of the Tennessee Valley Authority's system of power plants. The unit houses 10 generators with a total maximum power output of 1000 megawatts. Associated with the power plant is a pilot scale scrubber operation being managed by Bechtel Corporation. This venturi-type scrubber is being used to reduce the SO_2 levels of the effluent gas of 1 out of the 10 coal-fired boilers of the facility.

The automatic SO_3 monitor was transported to the Shawnee Power Plant and the unit was hoisted to the third story level of the wet scrubber facility by the use of a small hoist. This level contained the sampling ports located at the inlet to the scrubber. The ports were 7.6 cm (3 in.) in diameter, located at 90° intervals along the outer diameter of the 102 cm (40 in.) I.D. scrubber inlet. Two inlets were located at the same level corresponding to two separate scrubbers, only one of which operated at a given time. Both were tied into the same duct leading from the same boiler.

4.2 TEST DESCRIPTION

4.2.1 Equipment Set-up

The glassware components which were shipped separately from the main units were inspected upon arrival. Following the procedure as outlined in the Operations and Maintenance Manual, the glass sampling train was

assembled into the probe unit. The umbilical connections between the two enclosures were made and the operation of the system components were checked.

The sampling probe and its replacement, however, were severely damaged during shipment. The probe was dismantled and a Teflon Swagelok union used to repair the fractured vycor inner element of the probe. Replacement vycor tubes were manufactured at TRW and sent to the test site. In the interim, the test program was continued using the repaired probe.

The probe unit was suspended on a rail at the sampling port at the scrubber inlet. A set of turnbuckles held the unit and provided a height adjustment for the probe. The enclosure was free to move along the rail since the turnbuckles were held by a series of rollers. Because of space limitations, it was not possible to mount the probe into the unit before inserting the probe into the duct. Consequently, the probe was inserted to the centerline of the duct (68.6 cm from the port flange face) and the probe unit rolled into position so that the probe joint seated into the cyclone inlet. Figures 20 and 21 show the probe unit in position at the scrubber inlet prior to initiation of a test. Manipulation of the probe unit proved to be fairly easy because of its relative light weight and through the use of the roller suspension unit provided at the sampling port.

4.2.2 Initial Testing

To ensure that the calibration of the conductivity probe had not been altered during shipment, the conductivity cell and probe were recalibrated. A 0.996 molar solution of H_2SO_4 was prepared and injected directly into the conductivity cell via the outlet to SV-6. The results of this calibration provided conductivity readings nearly identical to those obtained in the laboratory calibrations. It was determined that the calibration curves obtained initially were valid and the unit was readied for sampling.

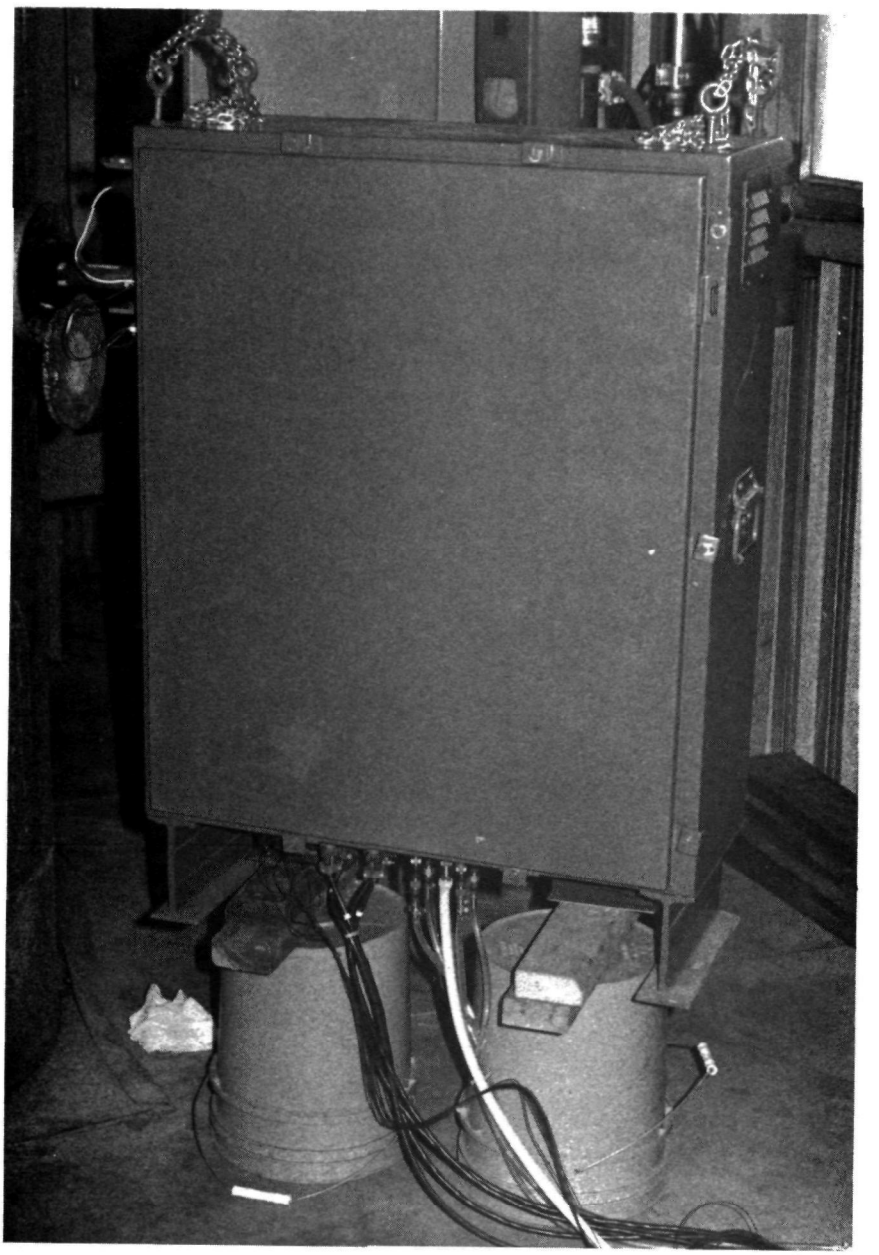


Figure 20. Probe unit at scrubber inlet

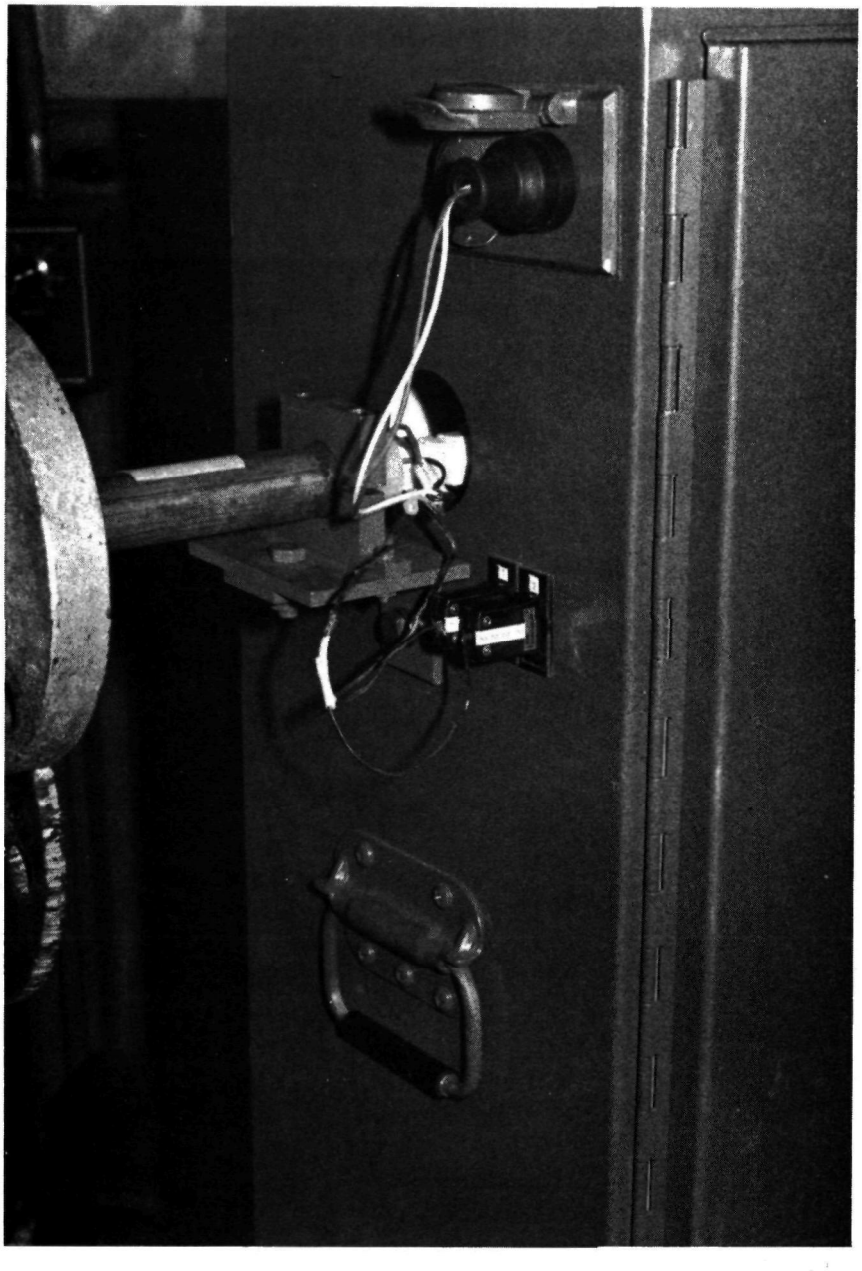


Figure 21. Probe connections at sampling port

With the probe inserted in the duct with the nozzle facing downstream the components were slowly heated to their prescribed temperatures. Because the duct gas temperature was 150°C, a lower power setting on the probe heater was required to heat the probe to 300°C.

Automatic sampling was initiated and the system performed exactly as prescribed using the repaired probe. After one hour of sampling, the manual Goksoyr-Ross system was prepared and the probe inserted 53.4 cm into the duct from a port located 90° from the automatic system. A manual sample was taken for a 20 minute period, and the readings recorded from the automatic system. The results are discussed in Section 4.3.

After 2 hours of sampling, it appeared that water vapor from the sampled gas was condensing in the vacuum lines and in particular in the magnehelic gauge. A water trap and absorber were prepared and, during the data acquisition and washing part of a cycle, were added to the vacuum line prior to the magnehelic gauge. A rotameter and dry test meter were also added to provide back-up data on the gas flow; it was not known what effect the condensed water would have on the magnehelic gauge.

At 3 hours and 45 minutes after initiation of automatic sampling, the flow rate through the system began to drop off rapidly. Examination of the medium frit in the condensation coil showed a covering of a dark brown residue of unknown constitution. The system was shut down and the probe removed from the sampling port.

The condensation coil was removed and cleaned for 2 hours in hot chromic acid to remove the substance trapped in the frit. The filter was removed and photographed, as shown in Figure 22. The Tissuequartz filter pad was impregnated with a very fine brown dust. The filter was weighed and it was determined that 0.26 grams of material had been collected in the 3.75 hour period sampling at 4.16 Lpm (standard conditions).

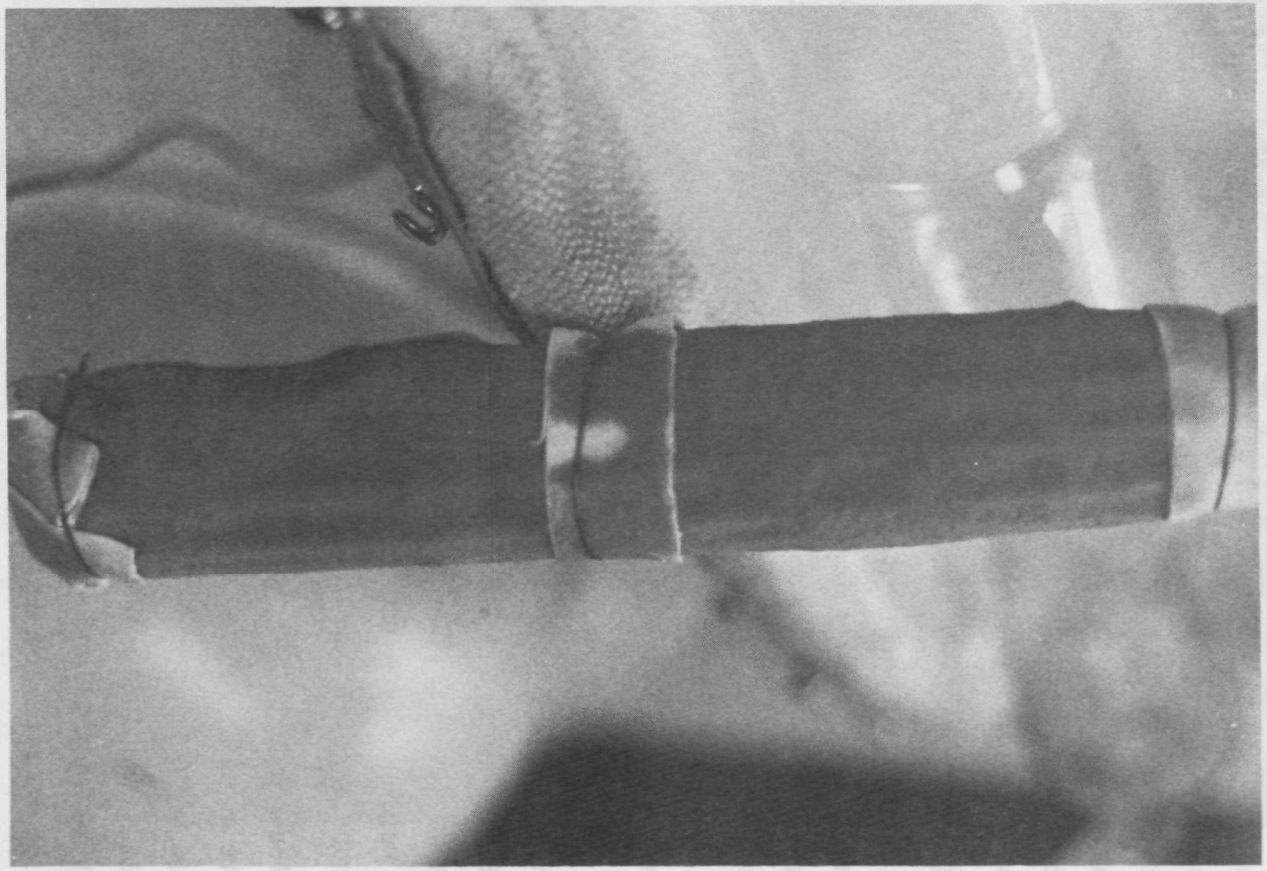


Figure 22. Filter element after test

4.2.3 Endurance Test

Upon receipt of the replacement probe core, a new probe was constructed to replace the repaired probe used in the initial phase of testing. A new filter element was placed in the filter holder and the now clean condensation coil was placed into the probe unit.

Officials at the power plant indicated that at approximately 2.5 hours into the initial testing run, the first scrubber shut down momentarily, causing a large volume of particulates to be vibrated from the walls of the duct. The momentary shutdown was caused by equipment failure so a decision was made to stop operation of that scrubber. Because of this, the monitor had to be moved to the second scrubber inlet and the probe unit set up for testing once again.

The system was leak checked and the joints tightened until no flow registered on the rotameter at 625 mm Hg vacuum. The glassware was then heated to 300°C with the probe outside of the duct. Table 7 shows the thermocouple readings before and during a test, and the corresponding autotransformer settings. With the pump turned ON and the flow adjusted for 5.58 Lpm (standard conditions), the probe unit was rolled into position with the probe inserted to the centerline of the second duct (68.6 cm from the flange face).

Approximately 1.5 and 6 hours after initiation of automatic sampling, a sample was again taken with the manual Goksoyr-Ross system with the probe inserted 53.4 cm into a port located 90° from the automatic system. The results are discussed in Section 4.3.

Nine hours after initiation of the endurance test, it became apparent that a brown oily substance was being collected on the frit in the condensation coil. The air flow rate through the system was fairly unaffected, but the pressure drop through the system had risen from 227 mm Hg to 375 mm Hg. Problems arose during the rinse cycle of sampling. The substance on the frit seemed to impede the flow of water throught the coil. At first, the conductivity readings began to decrease, indicating that not all of the acid in the coils was being washed into the conductivity cell.

Table 7. TEMPERATURE CONTROL DATA — TYPICAL DATA RUN

THERMOCOUPLE NUMBER	LOCATION	TEMPERATURE °C		VARIAC SETTING
		BEFORE TEST	DURING TEST FLOW = 6.1 lpm	
1	Inside Stack	152	152	-
2	Probe	316	300	82
3	Cyclone Outlet	336	310	53
4	Filter Outlet	310	308	48
5	Glass Tube	310	304	78
6	Condensation Coil Inlet	40	159	-
7	Water Jacket	60	60	-
8	Probe Unit Interior	40	48	-
9	Orifice	30	33	0

Then the water used in the wash cycle began to back up the coils and into the purge air line (between SV-1 and SV-2). Because the water took longer to be blown out of the system, the timing of SV-6 and SV-7 was invalidated. The water level begain to rise in the conductivity cell and so the test was halted.

A second condensation coil was installed and the system leak checked. The glassware was then heated to 300°C again with the same filter element in the filter holder. With the probe reinserted into the scrubber inlet and an identical flow rate used, the pressure drop through the system returned to its original 227 mm Hg level.

The system operated for 2.5 more hours until the same problem occurred with the second frit. Water flow through the frit was again restricted. During the time when the measuring vessel was rinsed through the coils, the water appeared to bead up on the firt rather than pass smoothly through it, as was the case in the laboratory tests. Because the timing of SV-6 and SV-7 could not be adjusted long enough to accommodate the erratic water flow, the test was stopped. The probe was removed from the duct and the monitor turned off.

The filter was weighed after it had cooled and it was determined that 0.46 grams of particulates had been collected during the 11.5 hours of testing. No particulates could be seen in the region downstream from the filter, indicating that the filter seal had been effective.

4.3 TEST RESULTS AND CONCLUSIONS

A total of 53 tests were performed during the field demonstration covering a one week period. The sulfuric acid concentration ranged from 7 ppm to 20 ppm at the inlet to the scrubbers, with each scrubber receiving a fairly constant concentration of acid with respect to time.

The conductivity recorder maintained a constant record of the conductivity meter output. A typical trace of conductivity output is shown in Figure 23. It can be seen that the system output, and hence the sulfuric acid concentration, remained fairly constant between tests.

Figure 23. Conductivity recorder output

The trace for each test can be seen to remain at a steady baseline during the sampling phase of the test cycle. This corresponds to the conductivity of the wash-cycle water in the conductivity cell which is maintained at the height of SV-7. With the addition of the acid contained in the rinse solution from the measuring vessel, the conductivity meter output can be seen to rise suddenly to a new level, determined by the conductivity meter range and the recorder span. With the meter range in the X1 position and the recorder span at 10 mV DC, full scale on the recorder (100%) corresponds to a conductivity of 500 micromhos/cm. With the meter range in the X10 position and the recorder span at 5 mV DC, a scale reading of 20% on the recorder corresponds to a conductivity of 5000 micromhos/cm. The response of the system to conductivity is linear, so that intermediate readings correspond to a fixed percentage of the maximum scale reading.

The recorder trace can be seen to remain at the new level for approximately 1.5 minutes at which point the trace begins to decay exponentially to the baseline level during the washing phase of the cycle. The baseline measurement will continue through the drying phase of the cycle and the sampling phase of the next cycle.

By observing the baseline for the curves, the condition of the wash water and hence the deionization column can be monitored. A steady climb of the baseline between successive measurements indicates that the column is not deionizing the water sufficiently and should be replaced. This is covered in the Operations and Maintenance Manual.

During the three periods when a sample with the manual Goksoyr-Ross system was being taken, the dry test meter readings were recorded. The total volume of gas sampled during each cycle was recorded along with the meter gas temperature and pressure. The gas flow through the system was not steady; an initial period of high mass flow occurred at the beginning of a cycle, lasting for several seconds. This was due to the fact that during the washing and drying periods the sampling train is valved-off from the vacuum pump by SV-5, while the vacuum pump remained running evacuating the lines and meters betwen the probe unit and the control unit. Whenever SV-5 opened again, the pressure difference in the system resulted in a high flow condition until steady state was reached.

The gas volume sampled in each case was converted to standard conditions using the following relationship:

$$G.V.\ (SCF) = \left[M.V.\right]\left[\frac{530}{T_M + 460}\right]\left[\frac{P_{BAR} - P_M}{29.92}\right] \qquad (1)$$

where

M.V. = meter gas volume reading

T_M = meter gas temperature (°F)

P_{BAR} = ambient barometric pressure (inches Hg)

P_M = meter gas vacuum (inches Hg)

To calibrate the ppm concentration of sulfuric acid on a volumetric basis, the acid volume recovered was converted to a gaseous volume at standard conditions. Following the procedure as outlined in the Operations and Maintenance Manual, the steps necessary were to

1. Obtain the volume of 1 molar H_2SO_4 collected using the conductivity meter output and the calibration curves presented in Figures 15 and 16.
2. Obtain the mass of H_2SO_4 in milligrams by using
   AM = [volume of acid in microliters] [0.09808 mg/μl]
3. Using the ideal gas law, obtain the volume of gaseous H_2SO_4 at 294°K and 1 atmosphere pressure. The volume should be in milliliters, obtained by using

$$A.V. = [\text{mass of acid in milligrams}]\ [0.24610\ \text{ml/mg}] \qquad (2)$$

Since 1 ppm on a volumetric basis corresponds to 1 mL of acid per cubic meter of sampled gas, the gas volume sampled was converted to cubic meters. It was further assumed that the sample gas contained 9% H_2O by volume which was added to the dry gas meter readings to obtain a total gas volume. The acid concentration was then

$$C = A.V/G.V. \qquad (3)$$

Table 8 shows the comparative results of the automatic system versus the manual system. The samples were taken at nearly identical locations and times. It can be seen that the first measurement with the automatic system using a repaired probe gave a reading 7% lower than the manual system. Since the Teflon union used to repair the probe was unheated, it is probable that sulfuric acid was condensing on the relatively cool surface and therefore was not recovered.

Subsequent readings with the new probe provided much better agreement between the systems, with a standard deviation of 4.9%. It can be seen that the readings with the automatic system were consistently below that of the manual system. This may be due to the transient behavior of the gas flow through the gas meter, resulting in a higher gas volume reading than what was actually sampled.

To provide reference information on the conditions encountered at the scrubber inlet, an analysis of the coal fired during the testing program was obtained. Table 9 shows the analysis of the coal as received and as fired. In addition, samples were taken at the inlet to the second scrubber using an Aerotherm High Volume Stack Sampler to determine particulate loadings and particle size distribution. These samples were taken at the same level as the sulfuric acid monitor probe, so that an accurate measurement of the particle sizes encountered by the monitor were obtained. Table 10 shows the analysis of the particle size samples.

Examination of these results indicate that the monitor can be expected to operate for periods greater than 12 hours in length in areas where the particle concentrations are less than those encountered in the field test. Because the particles were of such small size, a very small mass was collected in the cyclone collection flask. Particles greater than 10μ would be collected at the cyclone in streams where particles of this size were encountered. In streams with a low grain loading (5 g/m^3) of particles less than 10μ in diameter, the monitor can be expected to operate for periods much longer than 24 hours in length. In regions downstream of a scrubber, where particle loadings and organic compounds are minimal, the monitor could operate for quite extensive periods, possibly several days in duration.

Table 8. FIELD TEST RESULTS

TEST NUMBER	LOCATION	PROBE USED	SAMPLE AIR FLOW (lpm)	ACID CONCENTRATION - ppm	
				MANUAL SYSTEM	AUTOMATIC SYSTEM
5	North Scrubber Inlet	Repaired	5.8	19.51	17.07
18	South Scrubber Inlet	New	6.1	7.39	6.79
51	South Scrubber Inlet	New	9.9	8.82	8.75

Table 9. SHAWNEE FACILITY NUMBER 10 BOILER COAL ANALYSES

Sample date: 8/2/78

ANALYSIS PERFORMED	PERCENT BY WEIGHT					HEATING VALUE J/KG	WEIGHT PER MONTH KG
	MOISTURE	VOLATILE MATTER	FIXED CARBON	ASH	SULFUR		
AS RECEIVED	12.6	38.6	43.8	17.6	3.5	2.689×10^7	
AS BURNED	12.6	33.7	38.3	15.4	3.2	2.475×10^7	39,100

Table 10. SHAWNEE PARTICULATE LOADINGS

Date: July 24, 1978 Location: Wet Scrubber

MASS LOADING

	INLET	OUTLET
GRAIN LOADING	12.104	0.0854 G/SCM (DRY)
% MOISTURE	8.83	14.13
% ISOKINETIC	1.45	11.30

BRINK SIZE DISTRIBUTION

	D 50	STG WT MG	STG WT %	STG CUMUL %
CYCLONE		47.96	82.0	18.0
STAGE 1	4.60	6.33	10.8	7.2
STAGE 2	2.76	2.77	4.7	2.4
STAGE 3	1.92	0.87	1.5	1.0
STAGE 4	1.05	0.31	0.5	0.4
STAGE 5	0.70	0.06	0.1	0.3
FILTER		0.19	0.3	

% ISOKINETIC	7.43	STACK TEMP C	125
GRAIN LOADING G/SCM	5.1758	STACK PRESS ABS	738.9 mm
IMPACTOR FLOW RATE (Q)	0.0019	DEL PC mm HG	38.35
VOL SAMPLED CM	0.015		

MRI SIZE DISTRIBUTION

	D 50	STG WT MG	STG WT %	STG CUMUL %
STAGE 1	36.11	16.99	34.1	65.9
STAGE 2	17.40	0.72	1.4	64.5
STAGE 3	6.53	1.11	2.2	62.3
STAGE 4	2.89	6.15	12.3	49.9
STAGE 5	1.61	12.21	24.5	25.4
STAGE 6	0.70	4.99	10.0	15.4
STAGE 7	0.45	2.21	4.4	11.0
FILTER		5.48	11.0	

% ISOKINETIC	0.35	STACK PRESS	721.1
GRAIN LOADING	0.100	VOL METER	0.537
METER TEMP DEG C	31.4		

SECTION 5

RECOMMENDATIONS

As a result of the intensive laboratory and field test program, it is felt that the present prototype performed satisfactorily, providing reasonably accurate measurements of sulfuric acid concentration on a semi-continuous basis. However, several suggestions can be offered for the improvement of the unit for future development.

5.1 SIZE REDUCTION

Since the present unit was a prototype, size and weight considerations were not primary; development of a workable accurate system was the goal. Now that the design has been proven, steps should be made to reduce the size and weight to make a more field-worthy unit.

The control unit enclosure could be reduced to one-half its present size by repositioning the components. By using solid-state triacs instead of variacs, considerable size and weight savings could be made in the temperature control panel. Constructing the cabinet of aluminum would further reduce the weight so that a control unit weight of approximately 150 pounds might be attained.

Through redesign of the filtration system, the probe unit could be reduced in size by 20%. Constructing the outer case out of aluminum would result in a substantial weight savings.

5.2 IMPINGER SYSTEM

The field test demonstrated that water from the sampled gas will condense in the vacuum lines causing problems with the flow measurement devices. A water trap and absorber should be added to the sampling system to eliminate this problem.

5.3 GAS FLOW MEASUREMENT

Since the measurement of the gas volume sampled is critical, the use of a dry test meter is advised. This type of meter would provide the total volume of gas sampled during a test cycle, accounting for

variations in flow which may occur during initiation of the sampling. A thermocouple and vacuum gauge should be used in conjunction with the meter to correct the flow readings to standard conditions.

If it is desired that a magnehelic differential pressure meter be used, a series of calibration curves at various pressures and temperatures should be developed. The advantage of the orifice meter is one of weight; however it can only provide gas flow readings at a steady-state condition.

5.4 ORGANIC REMOVAL

In situations where the monitor will be sampling gas streams containing heavy organic compounds, it appears as a result of the field tests that provision must be made for the removal of these compounds. Otherwise, depending upon the condensation temperature of the compounds, they may condense in the condensation coil and present problems with the operation of the system. Operation in gas streams free of these organics present no problems; however for universal use the problem must be resolved.

5.5 FILTER REDESIGN

Although the filter designed and used in the prototype performed well, handling of the component proved difficult. Care had to be taken when wrapping the filter element with the Tissuequartz filter pad. Sealing the pad against the filter support proved to be a tenuous process — applying too much pressure to the sealing surface would tear the pad whereas applying too little pressure would not result in a proper seal. Additionally, because of the filter size the probe unit enclosure was necessarily large.

It is suggested that a small program be initiated to evaluate filter designs and develop a new filter. By reducing the filter housing size, the probe unit may be made smaller and, additionally the S-shaped tube housing the check-valves (D in Figure 6) might be eliminated.

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT The report describes the development, construction, and testing of a prototype automatic H2SO4 vapor and aerosol monitor. The device was based on the controlled condensation (Goksoyr/Ross) approach to H2SO4 measurement. In this approach, H2SO4 is condensed out of a filtered gas stream (at 250 C) using a water-jacketed coil maintained at a temperature (62 C) below the dewpoint of H2SO4. The H2SO4 collected in the coil is recovered automatically and its electrical conductivity is correlated with H2SO4 concentrations. The monitor is capable of continuous unattended operation for a 24-hour period in streams of moderate (5 g/cu m) particulate loadings. Readings of solution conductivity are recorded continuously, and new samples of the gas stream for analysis are obtained every 10 minutes. H2SO4 concentration can be determined from the instrument and associated calibration curves within 5 minutes of sample acquisition; determination requires only reading recorder output and sample gas volume, obtaining values from calibration curves, and inserting these values into expressions for ppm concentration in the gas stream. The prototype can detect H2SO4 concentrations in the range of 0.5 to 500 ppm, at temperatures up to 300 C, with 3000 ppm SO2, 8-16% H2O, and up to 9 g/cu m of particulate matter in the gas stream.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Automation	Pollution Control	13B	13H
Sulfuric Acid	Condensing	Stationary Sources	07B	
Sulfur Trioxide		Goksoyr/Ross Method		
Vapors			07D	
Aerosols				
Monitors			14B	

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