MONOSORB®   SURFACE AREA ANALYZER

Quantachrome Coporation reserves the right to make instrument design changes and/or improve performance without notice

QUANTA CHROME Corporation

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INSTALLATION

Six feet of copper tubing with a "Swagelok" fitting on one end
is provided with the MONOSORB. The "Swagelok" fitting should
be attached to the input receptacle located on the lower right
side of the MONOSORB. An extra "Swagelok" nut and ferrules are
in the packing and should be used to attach the other end of the
tubing to the gas regulator of a tank containing 30 mole per cent
adsorbate in Helium. If the pressure regulator does not have
the proper fitting, then the standard hose fitting can be used.
The 1/8" copper tubing can be soft soldered (acid core) into
the hose connection orifice. If necessary, drill or bore out
the I.D. of the hose connector.

As shown in Figure I, insert a sample cell into a cell holder
and insert the holder into the receptacle on the front panel
labelled "SAMPLE". It will be necessary to push on the cell
holder while holding the back of the MONOSORB.

Place a sample cell in the cold trap station located on the
right side of the MONOSORB. The cell installation is similar
to the method of insertion in the cell holder.

Open the toggle valve located on the lower right side
of the MONOSORB. Using the needle valve located under the
flow meter on the upper front panel, adjust the flow until
the float is centered on or near the 6 cm mark. A regulator
pressure in the range of 10-50 PSIG will enable easy adjust-
ment of the float position. Do not exceed 50 PSIG.

The MONOSORB will be purged of all air in 5-10 munutes. After this time, the power switch, located on the left side of the lower front panel, may be turned on. Allow 20 - 30 minutes for complete electronic warm up and cessation of all electronic drift.

CAUTION: Turning on the power switch causes current to flow through the thermal conductivity filaments. They operate at elevated temperature and can gradually oxidize in air. Therefore, always allow a few minutes of purge time before turning on the power. Be certain that a cell is inserted in the "SAMPLE" and cold trap position for flow continuity throughout the flow circuit. (See Figure II).

Place the powder to be analyzed in a sample tube, leaving some room above the powder for the unimpeded flow of gas. Insert the cell into a cell holder (Fig. I) and place the holder in its receptacle labelled "OUTGAS". As shown in Fig. III, clamp the heating mantle around the cell. Plug the mantle's power line into its receptacle on the upper panel. Also plug the thermocouple lead into the "Jack" located next to the thermocouple gauge. Set the thumbwheel switch located on the upper panel, to the desired temperature in ^{o}C.

NOTE: The temperature meter indicates full scale if the thermocouple is not connected.

CAUTION - Glass heating mantles should not be used above 300° C. For temperatures over 300° C up to 400° C quartz mantles and sample cells are available.

The temperature and time for proper sample decontamination varies with the nature of the sample and is determined best by experimentation. For outgassing of three samples simultaneously, Quantachrome manufactures the "QUANTECTOR" and "MONOTECTOR" outgassing instruments which both outgas samples and indicate when the samples are ready for analysis.

SAMPLE PREPARATION

Generally, because of the small sample size used in the MONOSORB, about 15 minutes is adequate for outgassing.

If samples cannot be heated, the method of repetitive cycling can be used. This method involves repetitively adsorbing and desorbing the adsorbate from the powder surface. With each desorption, the adsorbate will carry some of the contaminants from the surface. Usually three to six cycles is adequate.

The difference in the weight of an empty and full sample cell is the weight of sample. It is recommended that the weight of the full cell be obtained after analysis in order to avoid weighing impurities removed during outgassing of the sample.

II   MEASUREMENT OF SURFACE AREA

Remove the cell holder from the outgassing station by pulling on both knurled rings. The cell is automatically sealed as the holder is removed and can not be contaminated. Place the sample cell holder into the receptacle on the front panel labelled "SAMPLE". Fill a Dewar Flask with liquid nitrogen (or other coolant if nitrogen is not used as the adsorbate). Clamp the Dewar onto the chrome plated bar on the right edge of the cabinet. See Figure IV.

Push the polarity toggle switch toward the rear of the instrument. Using the fine and coarse zero adjustments position the signal meter to indicate zero. Then raise the Dewar Flask until the liquid nitrogen is one-half to one inch from the top of the arms of the cell. After about a one-minute delay, the meter will show a signal and the integrator will start accumulating counts. This is the adsorption signal which normally is not used for surface area measurements but can be used to find the correct attenuator setting for the subsequent desorption signal. When the meter returns to zero, reverse the polarity switch, re-zero the meter using the fine and coarse controls and clear the counter by pressing the button on the panel below the digital counter.

Remove the bath from the sample cell. In approximately one minute, the desorption signal will reach the detector. When the desorption is completed, the meter will return to zero and the integrator will display a number. Multiply the number appearing on the counter by the attenuator setting to calculate the surface area of the sample. Dividing by the sample weight gives the specific surface area of the sample.

For the maximum accuracy, it is best to weigh the sample after outgassing and analysis in order to avoid weighing the impurities. Simply weigh the empty sample cell and reweigh after completing the analysis.

If samples are not properly outgassed, the meter may not return to the base line. This can occur because the bridge is balanced prior to desorption with the sample immersed in the coolant. As the cell warms up contamination can enter the flow stream resulting in a slight positive or negative signal. Should this occur, place the sample in the outgassing station for continued outgassing.

NOTE: FILAMENTS SHOULD NOT BE LEFT ON WITH THE SAMPLE

CELL REMOVED OR WITH NO FLOW THROUGH THE SYSTEM.

During the adsorption and desorption processes, the flow will be altered. This is due to the contraction and expansion of the gases as the cell is cooled and warmed. This behavior is normal and will not effect the results as long as the ball is on the 6 cm mark before the desorption signal is started. If the signal is generated before the float returns to the 6 cm mark, some error can occur. Should this happen, immerse the cell in a beaker of water to hasten the rate at which the cell returns to ambient temperature.

The MONOSORB contains two flow paths. The valve on top of the cabinet, when turned 90°, permits the flow to traverse the long flow path. When facing the front of the cabinet the valve directs the flow through a short flow path. For very high surface area samples the long flow path will have to be used in order for the ball to return to the mark on the rotameter tube before the

desorption signal commences. FOR MAXIMUM SPEED AND ACCURACY
THE SHORT FLOW PATH SHOULD BE USED WHENEVER POSSIBLE, by re-
ducing the sample volume. However, if the sample surface area
is very large or if larger quantities of sample are required such
that the ball does not return to the mark prior to the start of
signal, then the long flow path should be used. The maximum
surface area in the sample cell should not exceed 150 square
meters. In order to reduce the total analysis time on high surface
area samples, it is suggested that adsorption be performed using
the short path and desorption signals be monitored using the
long path. If this procedure does not suffice, then reduce the
sample quantity.

For best results all signals should have their peak above 50% of
full scale. The MONOSORB will give a signal linear to volume
desorbed only if the signal is above 50% of full scale. If
signals are over 100% of full scale, on the highest attenuator
setting, reduce the amount of sample. Signals less than 50% of
full scale on the lowest attenuator setting will correspond to less
than $0.12m^2$ of area.

Always use attenuator values that gives the largest signal height.
Signals slightly over 100% of full scale are preferable to those
slightly over 50%.

To insure maximum gas purity a cold trap is provided. A Dewar
flask filled with coolant is clamped in place on the chrome
plated bar on the right side of the instrument. When shutting
down the MONOSORB, be certain to remove and clean the cold trap
to prevent impurities from diffusing into the system.

When transferring a sample from the "OUTGASSING" station to
the "SAMPLE" station, a signal peak will be seen, with the
polarity switch toward the front of the instrument. This peak
is due to a small amount of air that is trapped on the vent side
of the sample as the holder is inserted. The adsorption-desorption
sequence should not be started until this signal is completed.
This small quantity of air will do no damage to the filaments.
The input side of the sample cell does not have any air con-
tamination because there is a continuous outflow of gas as the
cell holder is inserted. The sample therefore, remains uncon-
taminated when transferred from the "OUTGASSING" station to the
"SAMPLE" station.

The MONOSORB operates by measuring the quantity of adsorbate gas adsorbed on a solid surface by sensing the change in thermal conductivity of a flowing mixture of adsorbate and an inert carrier gas. Usually the adsorbate is nitrogen and the inert carrier gas is helium. The recommended concentration is 30 mole percent nitrogen. For operation with other gases see page 21.

The theoretical basis upon which the MONOSORB operates is the B.E.T. [1] equation. The derivation, limitation and assumptions of the B. E. T. theory are discussed in many modern texts on surface chemistry. [2]

The B. E. T. equation is:

$$\frac{1}{X\left(\frac{Po}{P}-1\right)} = \frac{1}{XmC} + \frac{C-1}{XmC}\frac{P}{Po} \tag{1}$$

Where;

$P =$ adsorbate vapor pressure

$Po =$ adsorbate saturation vapor pressure at the temperature of the coolant bath.

$X =$ weight of adsorbate adsorbed on a surface when in equilibrium with a given relative pressure, P/Po.

$Xm =$ weight of adsorbate required to cover the surface with one molecular layer.

$C =$ a constant which is a function of the adsorbate-adsorbent interaction energy.

A plot of $\dfrac{1}{X\left(\frac{Po}{P}-1\right)}$ versus $\dfrac{P}{Po}$ yields a straight line with a slope of $\dfrac{C-1}{XmC}$ and an intercept of $\dfrac{1}{XmC}$.

The weight of adsorbate on the surface at one monolayer of coverage, Xm, is given by equation (2).

$$Xm = \frac{1}{slope + intercept} \tag{2}$$

Where;

Slope of B.E.T. plot $= \dfrac{C-1}{XmC}$

Intercept of B.E.T. plot $= \dfrac{1}{XmC}$

Experimentally, most surfaces give B.E.T. plots with intercept values only a few percent of the value of the corresponding slope. If the intercept is considered negligible compared to the slope and made to vanish then equation (1) becomes

$$\frac{1}{X\left(\frac{Po}{P}-1\right)} = \frac{C-1}{XmC}\frac{P}{Po} \tag{3}$$

Expanding the right hand side of equation (3) gives

$$\frac{C-1}{XmC}\frac{P}{Po} = \frac{1}{Xm}\frac{P}{Po} - \frac{1}{XmC}\frac{P}{Po} \tag{4}$$

Since $\dfrac{1}{XmC}$ is the intercept, which is assumed to be zero, equation (3) becomes

$$\frac{1}{X\left(\frac{Po}{P}-1\right)} = \frac{1}{Xm}\frac{P}{Po} \tag{5}$$

and

$$Xm = X\left(1 - \frac{P}{Po}\right) \tag{6}$$

From the ideal gas equation

$$X = \frac{\overline{P}VM}{RT} \tag{7}$$

Where;

$\overline{P}$ = ambient pressure

V = volume of adsorbate adsorbed and subsequently desorbed.

M = adsorbate molecular weight

R = universal gas constant

T = ambient temperature

Substituting for X in equation (6) yields

$$X_m = \frac{\overline{P}VM}{RT}\left(1 - \frac{P}{Po}\right) \tag{8}$$

The total surface area of a sample can be determined once X_m is known.

$$S_t = \frac{X_m \, N \, A_{c.s.}}{M} \text{ square meters } (m^2) \tag{9}$$

Where:

S_t = total area of all the adsorbate molecules in one adsorbed monolayer or the total sample surface.

N = Avogadro's number

M = adsorbate molecular weight

$A_{c.s.}$ = adsorbates's cross sectional area

Substituting equation (8) into equation (9) and rearranging terms gives

$$S_t = \frac{\overline{P}VN \, A_{c.s.}}{RT}\left(1 - \frac{P}{Po}\right) \tag{10}$$

Table 1 gives some commonly accepted values of adsorbate
cross sectional areas, Ac.s.

<center>TABLE 1</center>

Adsorbate	Ac.s. ($M^2 \times 10^{-20}$)	Reference
Nitrogen	16.2	3
Krypton	19.5	4
Argon	14.2	5
Xenon	25.0	6
Oxygen	14.0	7
Ethane	20.5	8
Butane	46.9	9

Using nitrogen as the adsorbate and at $295^{\circ}K$ ($22^{\circ}C$) and 1.0
atmosphere ambient pressure equation (10) becomes

$$S_t = V \left(1 - \frac{P}{Po}\right) 4.03 \tag{11}$$

The MONOSORB is used with a tank supplying adsorbate with a
fractional pressure of 0.3. The saturated vapor pressure is
then $0.3 \, \overline{P}$, ($\overline{P}$ = ambient pressure). The saturated vapor pressure
for the pure adsorbate Po will, in the case of nitrogen, be
slightly higher than ambient pressure because of impurities
dissolved in the coolant bath. Values of Po are always found
to be 10 - 20 mm. Hg. above ambient.

Using a mean value of 15 mm. and assuming 1.0 atmosphere, as
previously used for ambient pressure

$$P/_{Po} = \frac{0.3 \, (760)}{775} = 0.294 \tag{12}$$

Equation (11) becomes

$$S_t = 2.84 \ (V) \ m^2 \qquad (13)$$

thus, the sample has 2.84 m^2 of area for each cm^3 of gas adsorbed.

The MONOSORB is designed to accurately and reproducibily give an integrator count of 2.84 for each cm^3 of gas desorbed from the sample surface when the cell is removed from the bath. If adsorbates other than nitrogen are used, the number on the integrator, although reproducible, will not accurately represent the true surface area. If other adsorbates are used, consult the section on "Other Adsorbates", (Section VI).

THE ONE POINT METHOD

In the derivation of equation (13) some assumptions made were;

   a) $T = 295^{\circ}K$

   b) $\bar{P} = 760$ mm

For ambient temperatures other than $295^{\circ}K$ multiply the integrator reading by $\dfrac{295}{T \text{ ambient}}$.

For ambient pressures other than 760 mm multiply the integrator reading by $\dfrac{P \text{ ambient.}}{760}$

For input gas concentrations differing slightly from fractional adsorbate pressures of 0.3 multiply the integrator reading by $\dfrac{1 - \dfrac{P}{Po}}{0.706}$.

Each of the above corrections are generally small and can be neglected.

The extent of the error implicit in the one point method can be calculated as follows:

   Solving equation (1) for Xm gives

$$Xm = X \left(\frac{Po}{P} - 1 \right) \left(\frac{1}{C} + \frac{C-1}{C} \frac{P}{Po} \right) \tag{14}$$

The assumption of the one point method is that the intercept of a B.E.T. plot, $\dfrac{1}{XmC}$ (c.f. eq. 5) is zero.

The equivalent statement is that C is assumed to be infinity. With this assumption equation (14) becomes

$$Xm = X \left(\frac{Po}{P} - 1 \right) \frac{P}{Po} \tag{15}$$

The relative error inherent in the one point method is then

$$\frac{Xm - Xm}{Xm} = \frac{1 - \frac{P}{Po}}{1 + (C-1)\frac{P}{Po}} \qquad (16)$$

The table below shows the relative errors as a function of P/Po and C in the range of relative pressures from 0.1 to 0.3, the usual range of applicability of the B.E.T. equation.

TABLE II

	P/Po = .1	P/Po = .2	P/Po = .3	
C = 1	0.90	0.80	0.70	
C - 10	0.47	0.29	0.19	
C = 50	0.17	0.07	0.04	$\frac{Xm - Xm}{Xm}$
C = 100	0.08	0.04	0.02	
C = 1000	0.009	0.004	0.002	
C = ∞	0.0	0.0	0.0	

The error in Xm and therefore S_t, the surface area, will be less than 5% for almost all measurements at relative pressures of 0.3. By far, the great majority of C values is greater than 50.

If an estimate of the value of C can be made most of the error intrinsic to the one point method can be eliminated. Quantachrome Corporation will carefully measure the value of C for any sample for a nominal fee.

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V   CALIBRATION

From equation (13) it is seen that 1.0 cm^3 of desorbed nitrogen corresponds to 2.84 m^2 of surface. It is necessary therefore, that the thermal conductivity detector and digital integrator be calibrated to give a reading of 2.84 for 1. 0 cm^3 of nitrogen.

To calibrate the MONOSORB for nitrogen, follow the instructions outlined below after a 10-15 minute warm up period.

With the rotameter float centered on the 6 cm mark, purge the MONOSORB of all contaminants. A steady reading on the meter on the lowest attenuator setting will indicate a clean system. Place the attenuator in the "1" position and the Polarity Switch toward the front of the instrument. Then zero the meter and clear the count.

Using the precision gas sampling syringe provided, inject 1.0cc of air into the septum on the front panel with the gas mixture flowing, (air has essentially the same thermal conductivity as nitrogen and can be used in its place). Observe the peak of the signal, it should be between 95 and 100% of full scale. If it is not, adjust the "sensitivity" knob located on the left side of the instrument. If the "sensitivity" adjustment is not sufficient, place the sensitivity control to mid-position, then open the rear of the MONOSORB and adjust the voltage output by turning the screw on the 9-15V power supply clockwise to increase the signal. Use caution when making this adjustment since 110V leads come into the power supply. It is advisable to remove the power line from the wall outlet when making this adjustment.

Repeat the injection of 1.0 cc of air to confirm that the signal peak is between 95 and 100% of full scale. With the 1.0cc injection the integrator should give 284 counts. If it does not turn the "Count Rate" adjustment knob located on the left lower side of the MONOSORB until a lcc injection gives a count of 284. Several injections may be necessary for this step. Typically, the syringe with the use of the "Channey Adaptor" is reproducible to better than 1%. Therefore, the integrator can be considered calibrated if several injections produce readings in the range 284 ± 3 Counts.

If the "Count Rate" adjustment knob does not offer sufficient range to give the required number of counts then the coarse count rate adjustment should be used. If this becomes necessary center the "Count Rate" adjustment knob (5 turns from either end) and then open the integrator housing. This is the gold colored box accessable by opening the rear of the MONOSORB. Four small hold down screws are removed and the cover will slide out. Adjust the pot labelled "Count Rate" until a lcc injection gives about 284 counts. The final adjustment can be made, after closing the integrator box, using the external "Count Rate" control.

NOTE:

Once the correct sensitivity has been established it should not be necessary to further adjust this control. Occasionally, syringe needles can be plugged and the lcc volume required for calibration may not be completely introduced. Therefore, make sure that the syringe needle is not plugged prior to readjusting the sensitivity. A good way of testing the syringe and needle is to dip the tip of the needle into a beaker of water while depressing the plunger.

A continuous stream of bubbles will indicate that the needle is clear. Do not suck water into the needle when making this test and be certain to dry the needle before using again.

Also located on the left lower side are two holes through which a Phillips screwdriver can be inserted to adjust the integrator's zero and threshold settings. The zero adjustment controls the integrator zero which is properly set when the meter reads zero with the attenuator on infinity. The threshold adjustment controls the .percent of full scale at which the integrator commences counting. To set the threshold, place the meter at 1-2% of full scale using the coarse or fine controls. Adjust the threshold until the integrator just starts counting, a count approximately every 10 seconds. Confirm that no counts occur when the meter is put back on zero.

The zero and threshold controls are factory set and normally do not have to be adjusted. The user may find it necessary to adjust these controls from time to time particularly if the MONOSORB is exposed to extreme temperature variations. A coarse zero adjustment is located on the Integrator P.C. Board next to the "Count Rate" pot.

If the integrator count rate is excessive it will stop counting. This "Latch Up" condition can be corrected by adjusting the zero controls to place the meter on scale above zero and then cycling the polarity switch.

The MONOSORB has an electronic linearization network which provides that all signals will be linearly counted if the 1.0 cc count is correct.

The MONOSORB will hold its calibration as long as the flow rate remains unchanged. The rotameter ball may indicate slight flow rate variations due to hysteresis or electrostatic charge build up on the glass float and walls. However, ignore these fluctuations as long as the calibration gives 284 counts. Flow rates are controlled by a mechanical feedback needle valve sensitive to upstream pressure variations. This flow controller will hold the flow constant to 0.3% for several pounds of up-stream pressure change.

Once calibrated do not vary the flow control setting. When stopping flow through the MONOSORB, use the toggle valve on the right side of the instrument. When flow is resumed the flow control valve may equilibrate at a slightly different setting. Therefore, it is advisable to check the calibration after each start up. If the count is greater than 284, increase the flow slightly and decrease the flow if the count is less than 284. When making this adjustment, turn the flow control knob only a few degrees. It may be necessary to adjust the flow by an amount less than that to which the rotameter ball can respond.

The "Count Rate" control should be adjusted only for the first calibration after receipt on the MONOSORB. Thereafter, all calibrations should be performed by slightly adjusting the flow rates.

If the adsorbate is changed to a gas other than N_2, use the method described in Section VI for calibration. The "Count Rate" control is used to help set up the initial calibration for any adsorbate.

Thereafter, the MONOSORB calibration is maintained by making only very slight flow adjustments. So long as the flow remains undisturbed, the MONOSORB calibration will not vary.

ALTERNATE CALIBRATION PROCEDURE

An alternate method of calibration relieves the user of the need to position the rotameter float on the 6 cm mark and the need to adjust the count rate control.

With the rotameter float and the count rate adjustment both located near the center of their ranges, allow adsorption and then desorption to occur. Assume for example that the count is 358 with the attenuator on "8". The surface area will not be 8 x 3.58 = (28.64M^2) because both the flow and the count rate adjustment are incorrectly set. However, a calibration factor can be easily determined by injection 1 cm^3 of air on an attenuation of "1". For example, if a 1 cm^3 injection on unit attenuation gives 242 counts, then the surface area corresponding to 358 counts on an attenuation setting of "8" would be 3.58 x 8 x $\frac{284}{242}$ = 33.59M^2.

VI   OTHER ADSORBATES

Rewriting equation (10) and assuming;

$\bar{P} = 1$ atm

$P/P_o = 0.3$

$T = 295°K$

one obtains

$$St = 1.74 \times 10^{19} \text{ Ac.s.V} \tag{17}$$

the value of Ac.s. for the adsorbate can be obtained from Table I or another source. When Ac.s. is expressed in square meters and multiplied by 1.74×10^{19}, equation (17) becomes

$$S_t = KV, \text{ m}^2 \tag{18}$$

Where;

$K = 1.74 \times 10^{19}$ Ac.s. and V is in cm^3.

The MONOSORB can now be made to read surface area directly by following the calibration procedure outlined in the previous section.

As an example consider butane as the adsorbate. (Butane is convenient to use since its normal liquefaction temperature is close to 0°C and it completely desorbs from most surfaces at 150°C. Therefore, an ice water slurry and heating mantle are all that is required for using butane as the adsorbate). Equation (18) rewritten for butane becomes

$$S_t = 8.16 \text{ V}, \text{ m}^2 \tag{19}$$

It is therefore necessary to cause the integrator to give 816 counts for a 1.0 cc injection of butane when on an attenuation factor of "1".

Since the conductivity signal of butane is greater than that
of nitrogen (or air), the meter reading will be off scale,
over 100%, for a 1.0 cc injection. As discussed in the section
on Calibration, turn down the voltage until the peak height for
1.0 cc butane injection is 95-100% of full scale on unit
attenuation.

The digital integrator cannot be speeded up to give 816
counts for 1.0 cc of butane as required by equation (19).
Therefore, the following equation should be used.

$$S_t = \frac{I_s}{I_1} \times 8.16 \times Att. \tag{20}$$

Where;

I_s = The integrator reading for the sample analyzed.

I_1 = The integrator reading for a 1.0cc injection of
pure butane on attenuator setting of unity.

Att = Attenuator Setting.

In general, for any adsorbate, the total sample surface area
can be calculated from equation (21)..

$$S_t = \frac{PNAc.s}{RT} \quad 1 - P/P_o \cdots \times \frac{I_s}{I_1} \times Att. \tag{21}$$

For a relative pressure of 0.3, ambient pressure of 1.0
atm and ambient temperature of 295°K, equation (21) becomes

$$S_t = 1.74 \times 10^{19} Ac.s. \times \frac{I_s}{I_1} \quad Att. \tag{22}$$

Equation (22) will hold for any attenuator setting as long
as a 1.0 cc injection of pure adsorbate into the flowing
mixture gives a signal of 95-100% of full scale with the
rotameter float centered on the 6 cm mark.

In its most general form, equation (22) can be written as

$$S_t = \frac{PNA_c.s.}{RT} \left(1 - \frac{P}{Po}\right) \frac{Is}{I_1} \ Att. \tag{23}$$

Where, as before,

S_t = Total sample surface area.

P = Ambient pressure.

N = Avogadro's number (6.023×10^{23}).

Po = Saturation vapor pressure of the adsorbate.

P = Partial pressure of the adsorbate.

R = Universal gas constant ($82.1 \ cm^3$ atm. degK^{-1} mole $^{-1}$).

T = Temperature, ^oK.

Is = Integrator reading for the sample analyzed.

I_1 = Integrator reading for 1.0 cc injection of pure adsorbate on attenuator setting of unity.

Att = Attenuator Setting.
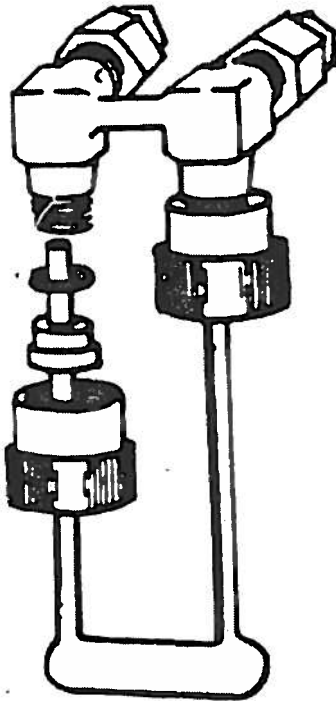
FIG. I

SAMPLE CELL AND CELL HOLDER
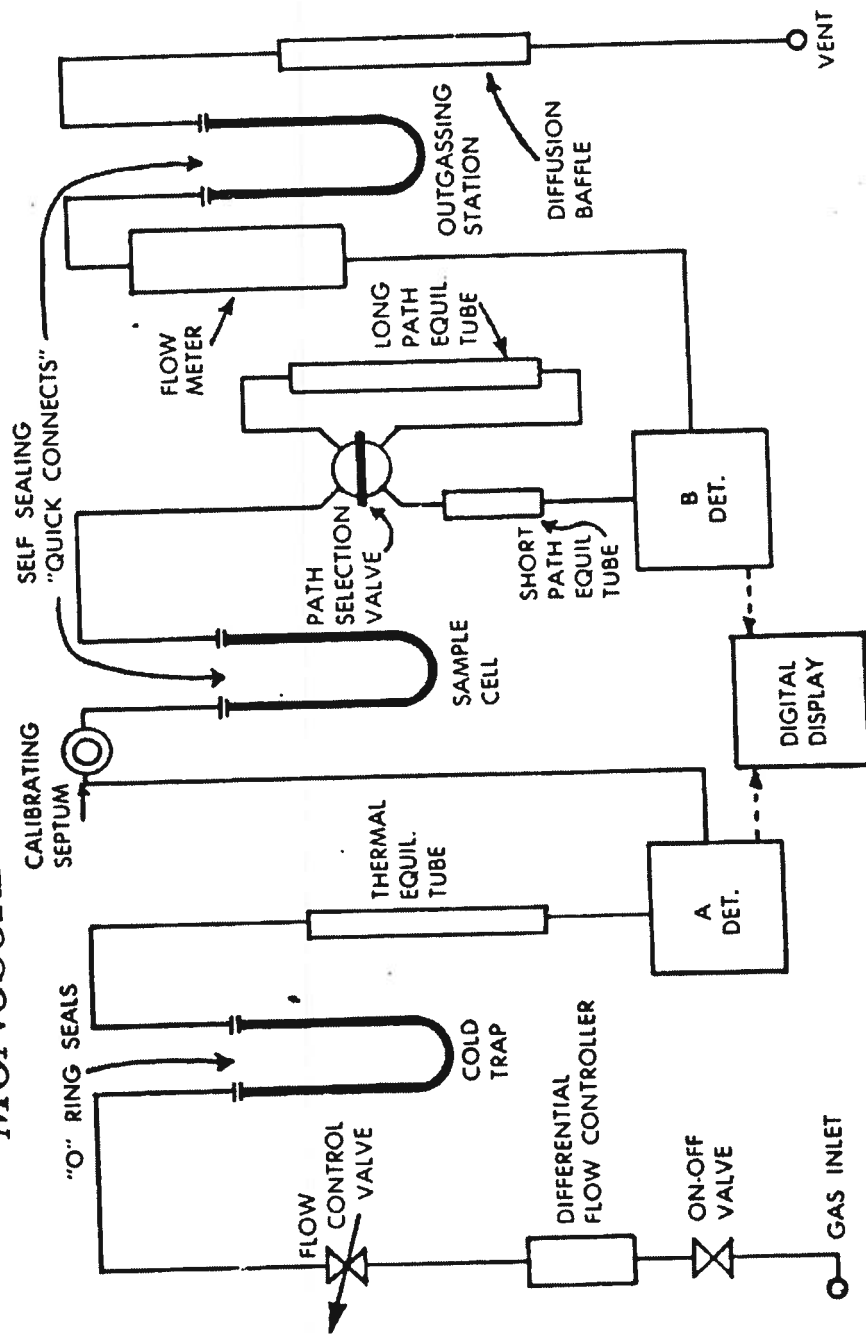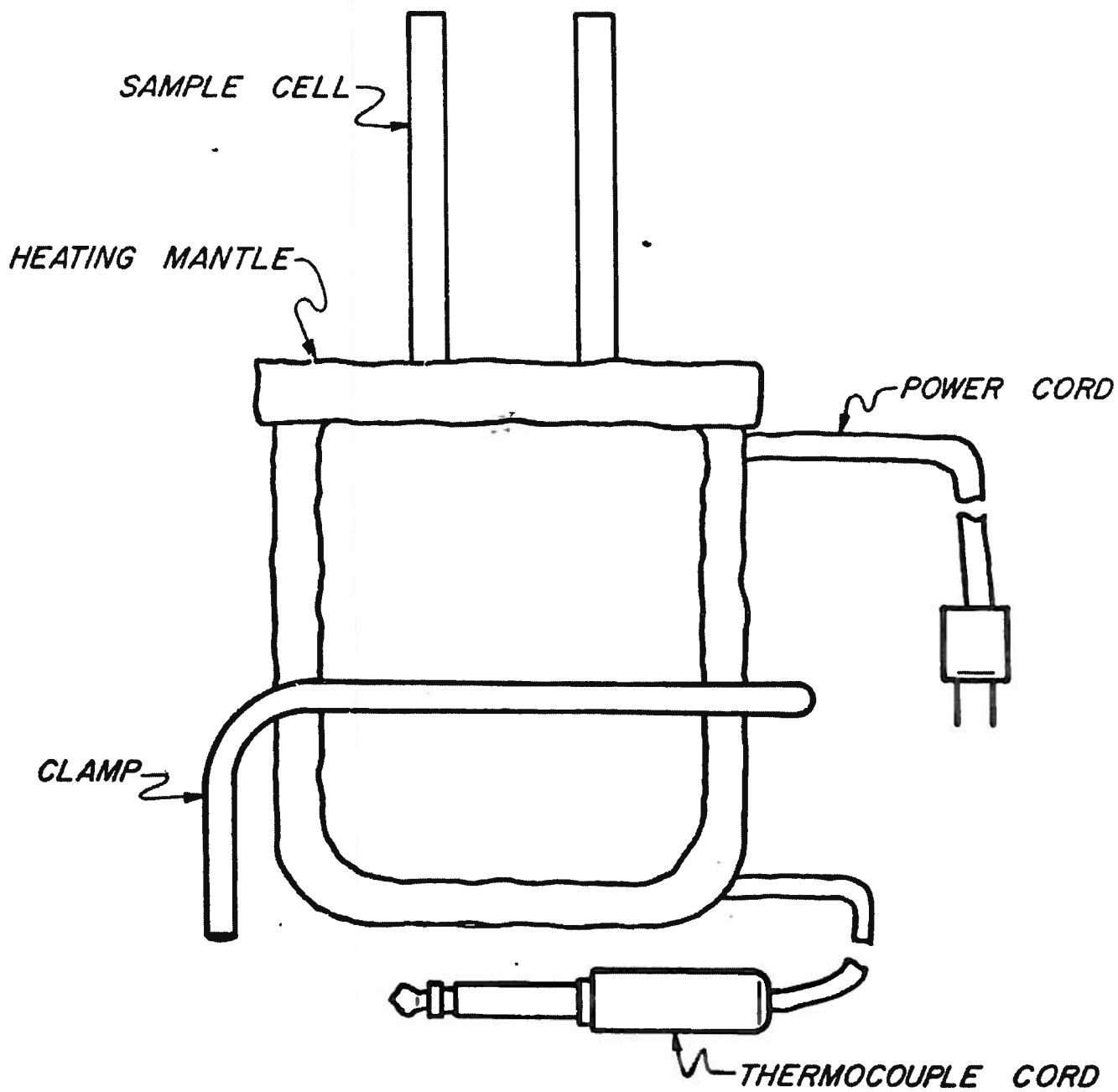
FIGURE II

MONOSORB GAS FLOW SCHEMATIC

SELF SEALING
"QUICK CONNECTS"

"O" RING SEALS

CALIBRATING SEPTUM

FLOW METER

PATH SELECTION VALVE

SAMPLE CELL

LONG PATH EQUIL. TUBE

SHORT PATH EQUIL. TUBE

OUTGASSING STATION

DIFFUSION BAFFLE

VENT

B DET.

DIGITAL DISPLAY

A DET.

THERMAL EQUIL. TUBE

COLD TRAP

FLOW CONTROL VALVE

DIFFERENTIAL FLOW CONTROLLER

ON-OFF VALVE

GAS INLET

FIGURE III

DEWAR ASSEMBLY

FIG. IV
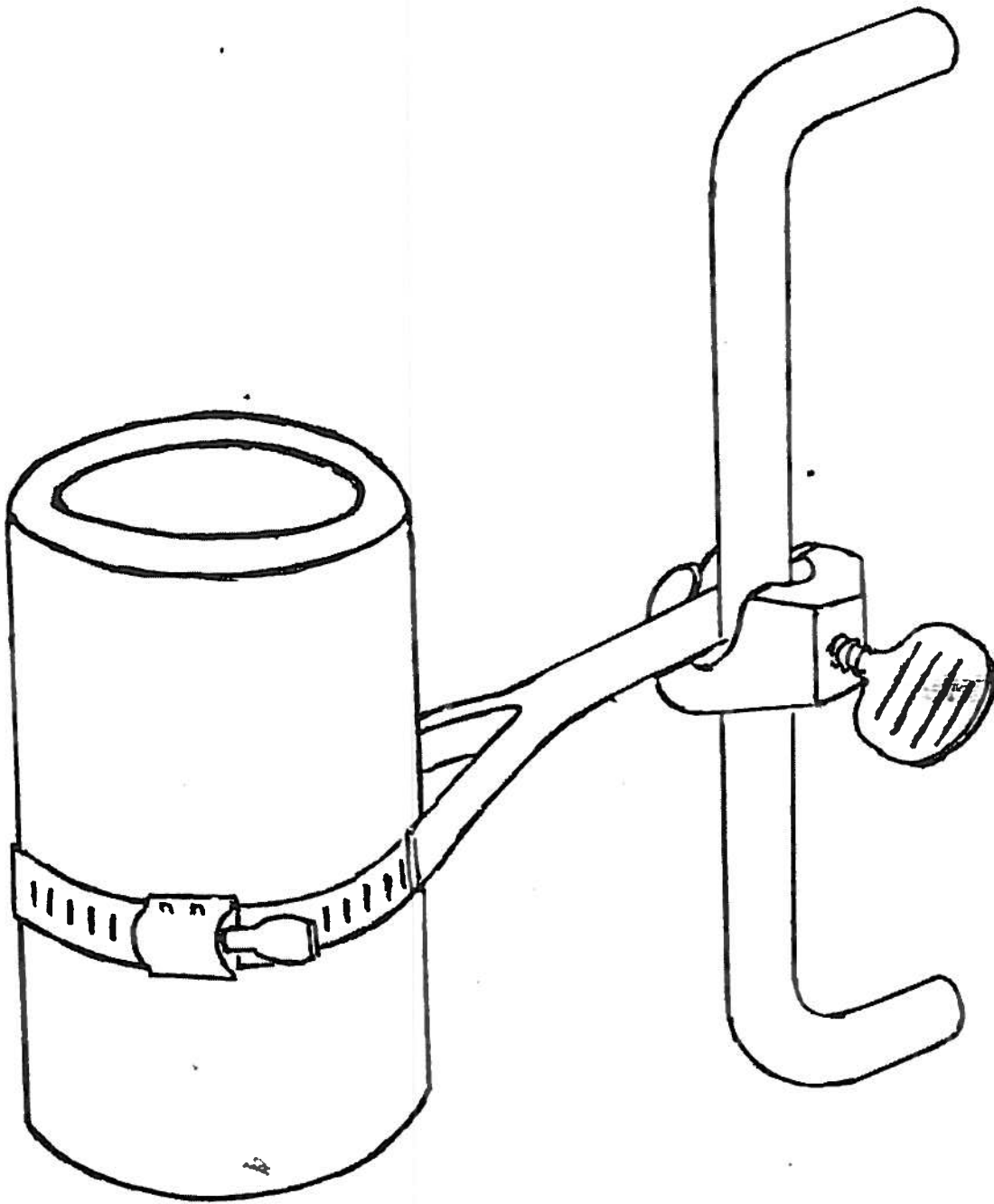
FIGURE V

EXTERNAL RECORDER (LOCATED ON REAR PANEL)
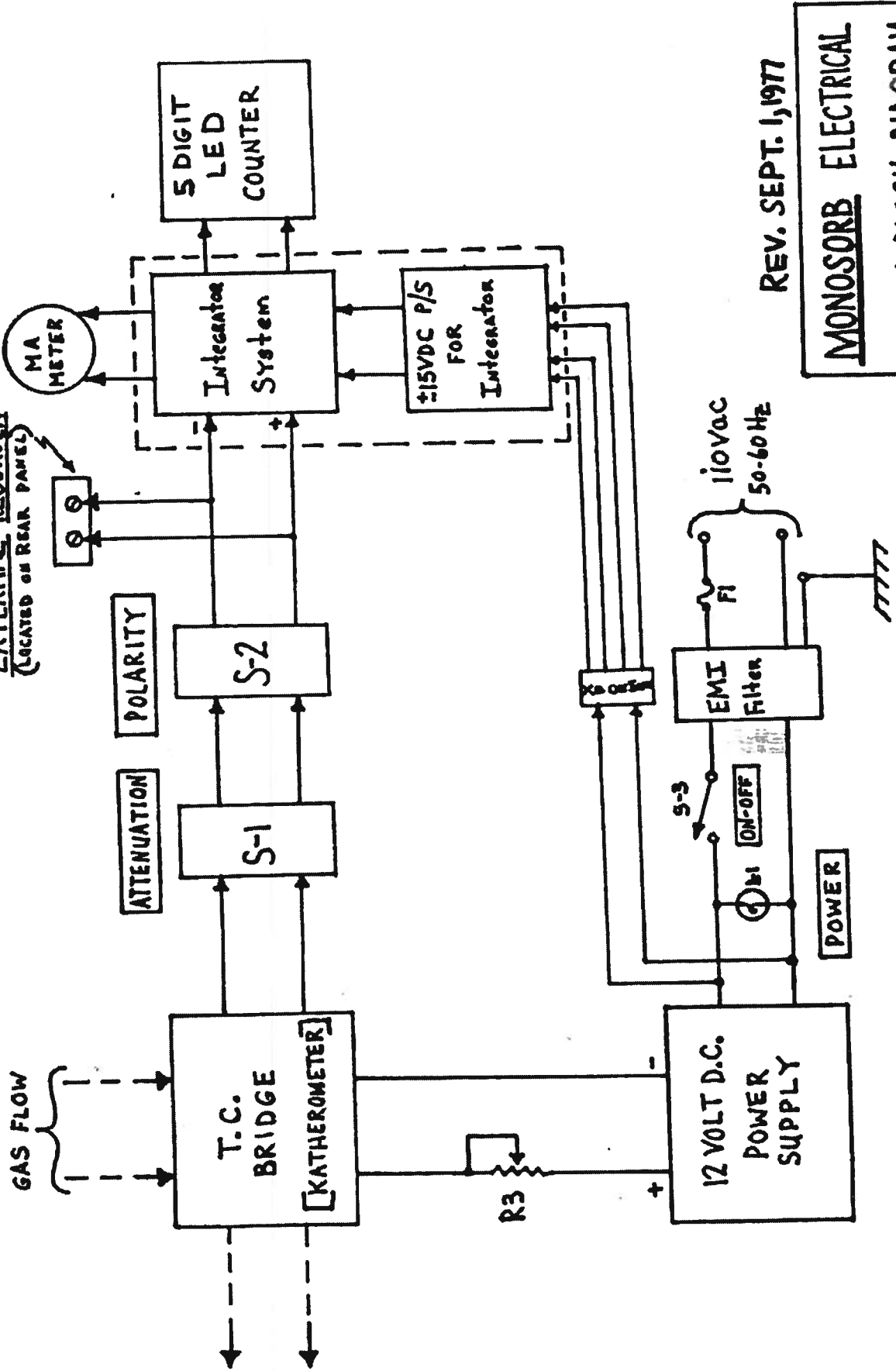
MONOSORB ELECTRICAL SYSTEM BLOCK DIAGRAM

REV. SEPT. 1, 1977

FIGURE VI

INTEGRATOR 60274-3C MS

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FIGURE VII
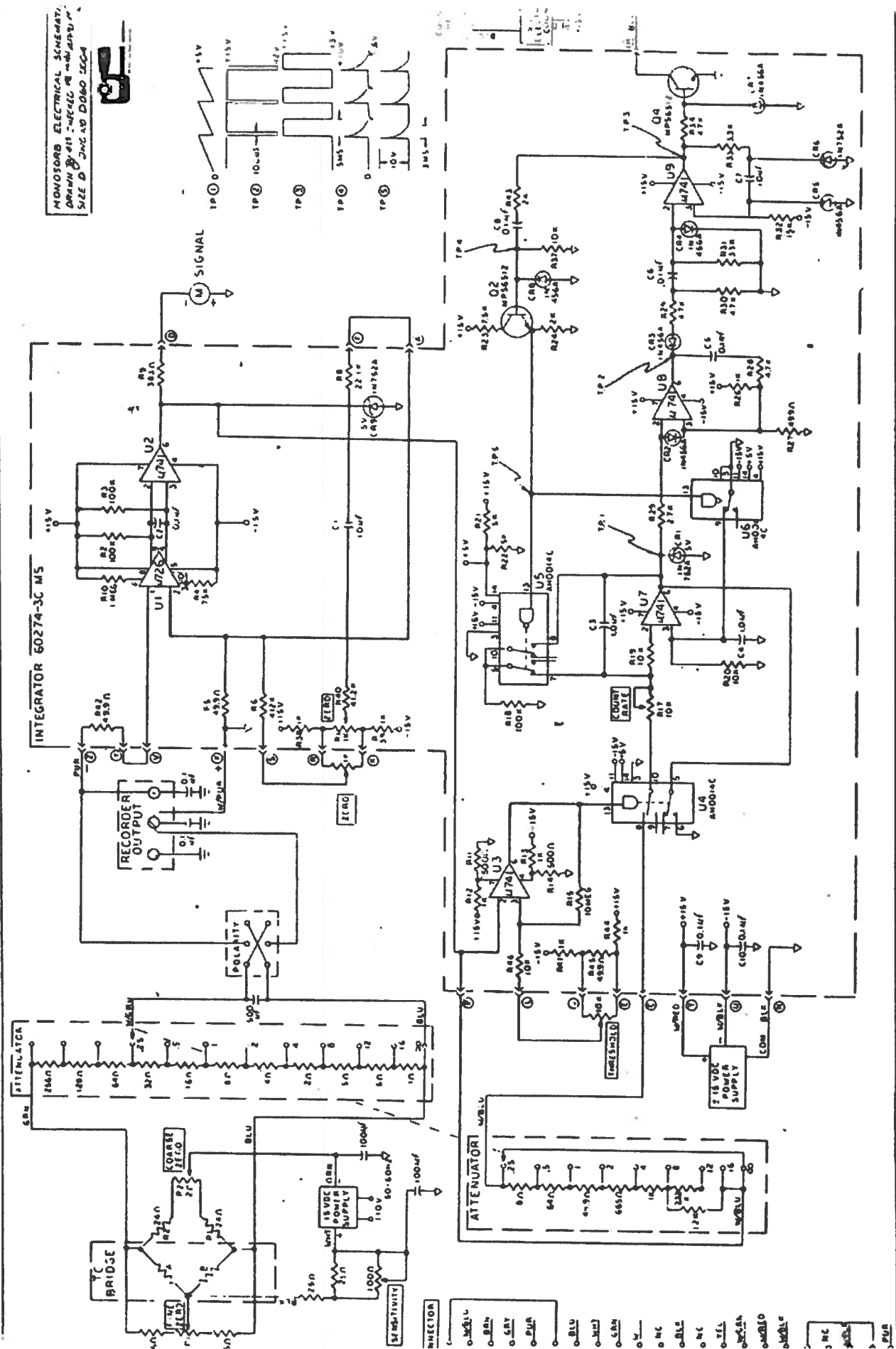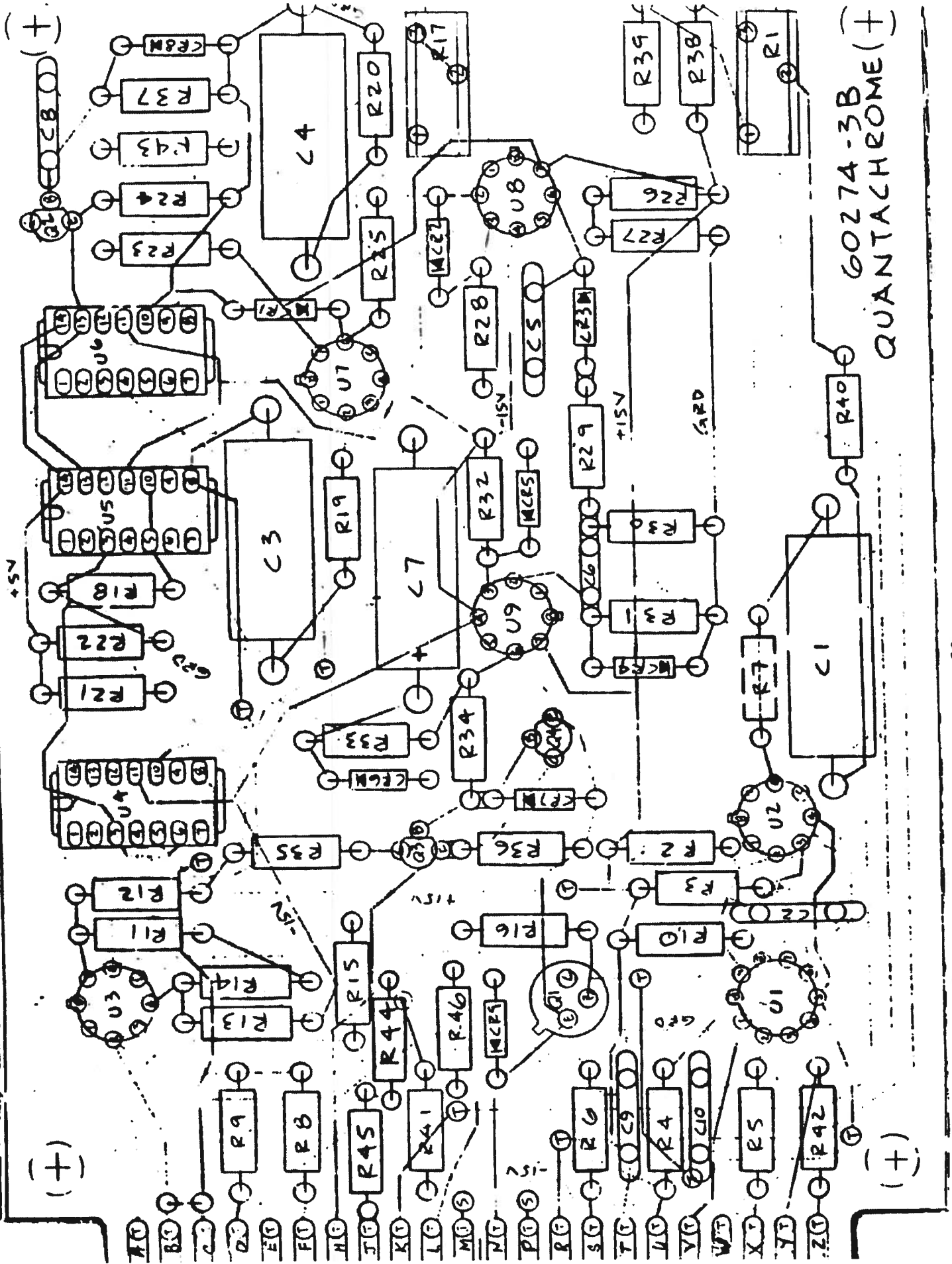

60274-3B
QUANTACHROME

FIGURE VIII

VIII   APPENDIX I - INTEGRATOR CALIBRATION PROCEDURE

ZERO ADJUSTMENTS:

The Integrator is provided with two zero adjustments. The "Coarse zero" is factory set so that the side mounted "ZERO ADJUST" is at midrange for meter zero. In the advent of a major shift in system operating parameters due to component aging, the coarse adjust pot (R1 of Figure VII) can be re-adjusted to bring the side mounted ZERO pot within its operating range with the attenuator front panel switch in the infinity (∞) position.

If the panel meter is pinned in either the full scale or down scale position and all power supply voltages are correct, the input op amp (726 HC) (U1 Figure VII) is probably defective. This unit is provided with a ten-pin plug-in socket. Replace this unit. When this unit is replaced it is necessary to readjust the "Coarse Zero" pot.

NITROGEN SURFACE AREA OF CARBON BLACK

MONOSORB METHOD

1.   <u>SCOPE</u>

   1.1   This method covers the determination of the surface of carbon black, using a nitrogen-helium gas mixture.

2.   <u>APPARATUS</u>

   2.1   MONOSORB SURFACE AREA ANALYZER complete with the following:[1] :

   2.1.1   HEATING MANTLE,

   2.1.2   DEWAR FLASKS, 2

   2.1.3   SAMPLE CELLS, 5

   2.1.4   SAMPLE CELL HOLDERS, 4

   2.1.5   CALIBRATION SYRINGE

   2.1.6   COPPER INPUT LINE for connecting gas supply.

   2.2   ANALYTICAL BALANCE, 0.1 mg sensitivity.

   2.3   GAS CYLINDER with Pressure Regulator.

   2.4   SMALL FUNNEL.

   2.5   BEAKER, 500 ml.

3.   <u>REAGENTS</u>

   3.1   NITROGEN-HELIUM MIXTURE - Thirty mole percent nitrogen ±2% premixed with helium. This mixture must be dry.

   3.2   LIQUID NITROGEN

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[1] Available from the Quantachrome Corp.

4.   INITIAL INSTALLATION

4.1   Follow the instruction manual supplied with the instrument for proper Installation.

5.   PROCEDURE

5.1   Fill the Dewar flask with liquid nitrogen and immerse the cold trap sample tube in the flask.

NOTE-1-: The liquid nitrogen level should be kept within 1/2" to 1" of the sample tube holder during all tests. The flask should be covered (sheet styrofoam works well for this) to prevent excessive loss of the liquid nitrogen.

5.2   Open the toggle valve allowing the gas mixture to begin purging the apparatus for a minimum of 5 minutes.

NOTE 2 - This step must be performed before turning on the electronics, or the sensing elements will be damaged.

5.3   Plug the heating mantle power line and the thermocouple lead into their respective receptacles. Set the temp control to bring heating mantle to $300 \pm 10^{\circ}$ C while the electronics are allowed to warm up.

5.4   After purging the apparatus for 5 minutes, turn on the power switch and allow the electronics to warm up for 30 minutes minimum.

5.5   Check that the rotameter float is centered on the 6 cm mark. Adjust the flow control valve if necessary.

5.6   With the attenuator in the " 1 " position, and the polarity switch towards the front of the instrument, zero the meter and clear the counter.

5.7   Pump the calibration syringe two to three times and then inject 1.0 cc of air into the septum on the front panel. The counter should begin operating in about 2 minutes.

5.8   Observe that the meter goes from zero to a peak of 95 to 100% of full scale and then back to zero for a complete count of 2.84 $\pm$0.03. Adjust the counter if the count is outside this specified range and repeat 5.7.

NOTE 3 - Use the "sensitivity" control knob to adjust the 95 - 100% signal peak.

NOTE 4 - Use the "counter" control knob to adjust count, or very small adjustments of the counter may be made by use of the flow control valve. If the count is greater than 2.84, increase the flow slightly; if less, then decrease the flow.

NOTE 5 - Counter must cease to count when meter is on zero or "threshold" must be adjusted. See instruction manual.

5.9   Instrument shall be considered calibrated when two consecutive counts are within 0.02 counts of each other.

5.10   Weigh to 0.0001 g, a clean, dry, empty sample tube and record weight.

5.11   Roughly weigh sample as follows:

Grade of Black	Weight Range, g
N100 Series	0.18 - 0.20
N200	0.20 - 0.22
N300	0.27 - 0.29
N500	0.24 - 0.26
N600	0.27 - 0.29
N700	0.31 - 0.33

5.12   Pour test sample into sample tube. Use a pipe cleaner to remove any dust that remains on side walls of the tube.

NOTE 6 - A "V" shaped spatula works well for pouring sample into tube if a small funnel is not available.

, 5.13   Insert sample tube into tube holder, and insert tube holder into "outgas" station.

NOTE 7 - Hold onto the back of the MONOSORB unit with one hand while inserting the tube holder into the receptacle with the other.

5.14   Place the heating mantle around the sample tube, and apply the heating mantle clamp.

NOTE 8 - Mantle temperature will drop below 300° C, but will normally recover in a few minutes to $300 \pm 10^{\circ}$ C.

5.15   Outgas samples of tread grade blacks for $15 \, {}^{+5}_{-0}$ minutes and carcass blacks $10 \, {}^{+5}_{-0}$ minutes.

5.16   Remove the outgassed sample from the "OUTGAS" station.

5.17   Remove the tube and tube holder from the "SAMPLE" station.

5.18   Insert outgassed sample into the "SAMPLE" station.

NOTE 9 - Within a few seconds, the counter will begin, and a peak reading will occur on the meter; this peak is due to a small amount of air that is trapped on the vent side of the sample as the holder is inserted. Step 5.20 should not be started untill this signal is complete.

5.19   If another sample is to be tested, insert it into the "OUTGAS" station and place heating mantle in position to begin outgassing.

5.20   The attenuator settings for the weights given in 5.11 are usually as follow:

N110 series blacks	Set attenuator to 8	
N200	8	
N300	8	
N500	4	
N600	4	
N700	4	

5.21   Push the polarity switch towards the rear of the instrument.

5.22   Adjust the signal meter to zero, using the fine and coarse zero adjustment knobs.

5.23   Raise the Dewar flask until the liquid nitrogen is 1/2 to 1" from the sample tube holder.

5.24   After a minute or so, the meter will show a signal and the counter will start.

NOTE 10 - This is the adsorption signal which is not used for the surface area measurement but can be used for checking on the correct attenuator setting. The correct attenuator setting is the highest setting which will have the signal peak occur below 50% of the meter scale.

5.25   When the meter returns to zero and no counts, pull the polarity switch towards the front of the instrument.

5.26   Rezero the signal meter and clear the counter by pressing the counter button.

5.27   Remove the Dewar flask and immediately immerse the sample cell in the beaker of room temperature water until the rotameter ball returns to the 6 cm mark.

NOTE 11 - It is important that the rotameter ball return to the 6 cm mark before the counter starts. The immediate immersion in water accomplishes this.

5.28   In a minute or so, the meter will begin showing a signal and the counter will start.

5.29   Dry the sample tube.

5.30   Observe the peak of this desorption signal. It must occur in the 50 - 100% range of the meter for an acceptable test.

NOTE 12 - If peak occurs below 50%, or above 100%, begin the test again at 5.21 using the next higher, or lower, attenuator setting, whichever is appropriate.

5.31   After the meter returns to zero, record the counter reading and the attenuator setting.

NOTE 13 - To repeat a test on the same sample, just repeat steps 5.21 through 5.31.

5.32   Remove the sample tube and holder from "SAMPLE" station.

5.33   If another sample has been outgassed while testing this sample, then proceed to step 5.16 and begin another test.

5.34   Remove the sample tube from the sample holder and weigh the sample and sample tube. Record as total weight.

NOTE 14 - Do not remove the sample tube from the tube holder until ready to weigh. The quick-disconnect assembly of the tube holder is air tight and prevents water, or other contaminants, from being absorbed by the sample.

6. CALCULATIONS

6.1 Calculate the nitrogen surface area as follows:

$$NSA = \frac{Attenuator \quad x \quad Counter}{Total\ weight - Tare\ weight}$$

where: NSA = nitrogen surface area, $10^3 m^2/kg$,

Attenuator = attenuator setting,

Counter = counter reading, 0.00 m^2,

Total weight = weight of the sample and

tube, g, and

Tare weight = weight of the sample tube, g.

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