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WM Project 10,11,16
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Dr. J. W. Bradbury
Geotechnical Branch
Office of Nuclear Material
Safety and Safeguards
U.S. Nuclear Regulatory Commission
Room 623-SS
Washington, D.C. 20555

Dear John:

Enclosed is the progress report for the month of December 1984 for B0290, "Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques and Procedures." Also enclosed is the description of the BET surface area that you requested.

Sincerely,

Susan

Susan K. Whatley, Manager
Repository Licensing Analysis
and Support
Chemical Technology Division

SKW:kk
Enclosures
cc: Office of the Director, NMSS (Attn: Program Support Branch)
Division Director, NMSS Division of Waste Management (2)
M. R. Knapp, Chief, Geotechnical Branch
R. J. Starmer, Geotechnical Branch
D. J. Brooks, Geotechnical Branch
Branch Chief, Waste Management Branch, RES
G. F. Birchard, Waste Management Branch, RES
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G. K. Jacobs
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Laboratory Evaluation of DOE Radionuclide Solubility Data & Selected Retardation Parameters Experimental Strategies, Laboratory Techniques, and Procedures - Report for Dec.1984

4. AUTHORS *(If more than three, name first author followed by "and others")*

A. D. Kelmers, et al.

5. NAME OF CONTRACTOR	MAILING ADDRESS *(Number and street, city, state and zip code)*	TELEPHONE NO.
S. K. Whatley Oak Ridge National Laboratory	P. O. Box X Oak Ridge, TN 37831	624-6135

6. DATE MANUSCRIPT COMPLETED	7. NRC PROGRAM SPONSOR/TECHNICAL MONITOR	TELEPHONE NO.
January 1985	J. W. Bradbury	427-4055

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SKW
01/08/84

MONTHLY PROGRESS REPORT FOR DECEMBER 1984

PROJECT TITLE: Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques, and Procedures

PROJECT MANAGER: S. K. Whatley

TASK LEADER: A. D. Kelmers

SCIENTIFIC STAFF: W. D. Arnold, G. K. Jacobs, S. Y. Lee, R. E. Meyer, and F. G. Seeley

ACTIVITY NUMBER: ORNL #41 37 54 92 6 (FIN No. B0290)
NRC #50 19 03 1

PROGRESS HIGHLIGHTS

Technetium Studies:

A 50-day sorption isotherm was completed for pertechnetate in synthetic groundwater GR-4 with Cohassett basalt under anoxic conditions at 60°C. As in previous experiments, little sorption was measured when the initial technetium concentration was as high as 10^{-3} to 10^{-4} mol/L; it is assumed that these concentrations exceeded the reducing capacity of the basalt surface. At initial technetium concentrations of 10^{-6} to 1.6 x 10^{-12} mol/L, sorption ratios of 12 to 18 L/kg were obtained. These values are slightly higher than the Rs values of 9 to 17 L/kg which we reported for a parallel 14-day experiment [September Monthly Progress Report]. Pertechnetate sorption by basalt continues to show a slow continued sorption with time, i.e., a steady-state condition is not reached in laboratory tests lasting only 1 to 2 months.

Uranium Studies:

The white precipitate observed in blank tests (no basalt present) with uranium(VI) in synthetic groundwater GR-2 at 60°C has been identified by x-ray diffraction techniques as sodium boltwoodite, $Na(H_3O)UO_2(SiO_4)\cdot nH_2O$. This compound is not included in the data bases for PHREEQE, MINTEQ, or EQ3/EQ6. We previously reported [NUREG/CR-3851, Vol. 3] that we are observing apparent concentration limits for uranium under oxic conditions that are lower than those given in the Site Characterization Report [SCR 1982]. Our new results suggest that this is likely due to the fact that boltwoodite was not considered in that calculation of the uranium solubility limit. Our results show the importance of identifying the solid phase present in experimental measurements and the limitations of the existing data bases for uranium.

Neptunium Studies:

The 1.0 mCi of ^{237}Np needed for the neptunium isotherms was received from ORNL Isotope Distribution as solid NpO_2 which had been sintered at a high temperature. The solid is quite refractory and we are developing a quantitative dissolution method for preparation of concentrated solutions to allow extending the neptunium sorption isotherms to the apparent concentration limit. The ^{235}Np which is used to trace the ^{237}Np solutions has not been received from Argonne National Laboratory; we are checking on the delivery date.

Chromatographic Studies:

No progress to report.

Sample Acquisition:

No new samples received.

Geochemical Calculations:

No progress to report.

General Aspects:

None

MEETINGS AND TRIPS

A. D. Kelmers and R. E. Meyer attended the US-Federal Republic of Germany Workshop on Geochemistry of Radionuclide Migration held in Oak Ridge on December 6 and 7. The following paper was presented: A. D. Kelmers, F. G. Seeley, W. D. Arnold, R. E. Meyer, F. J. Smith, and G. K. Jacobs, Evaluation of Radionuclide Geochemical Information for Department of Energy Candidate High-Level Waste Repositories. The paper will be published in the workshop proceedings.

REPORTS AND PUBLICATIONS

The progress report for the period April-June 1984 was completed on mats and forwarded to the NRC Project Manager for issuance as NUREG/CR-3851, Vol. 3.

Preparation of the annual report for October 1983-September 1984 continued.

PROBLEM AREAS

None

COST/BUDGET REPORT

Expenditures were $37.2K for the month of December and $138.2K for the fiscal year to date. A detailed cost/budget report will be sent under separate cover.

1.1 BET NITROGEN SURFACE AREA

System No. 1

1. Method

The amount of nitrogen adsorbed at liquid nitrogen temperature on the surface of a material is measured at several equilibrium pressures. These data are used with the Brunauer, Emmett, and Teller equation to calculate the specific surface area of the sample. It is assumed that one cubic centimeter of nitrogen gas forms a monolayer on 4.37 square meters of surface. The amount of nitrogen required to form a monolayer is determined and multiplied by 4.37 square meters per cubic centimeter to obtain the total surface area of the sample.

2. Range and Sensitivity

The sample should have at least 2 square meters of surface and preferably not more than 25. The method can be used for samples with specific surface areas in the approximate range of 0.1 to several hundred square meters per gram.

3. Precision

The precision is ±3.0% at the 95% confidence level on a control sample of about 77 square meters per gram.

4. Apparatus and Reagents

4.1 Pyrex glass sample container fitted with a Dewar bottom seal, a high vacuum stopcock, and a standard taper ground glass fitting.

4.2 Sample pretreatment apparatus capable of attaining 10^{-3} millimeters of mercury pressure, and a furnace for baking the samples (Figure 1).

4.3 Apiezon Type N high vacuum lubricant.

4.4 Helium, spectrometrically pure (> 99.9%).

4.5 Nitrogen, spectrometrically pure (>99.9%).

4.6 Surface area measurement system (Figure 2).

4.7 Dewar flask.

4.8 Liquid nitrogen

4.9 Mercury barometer

4.10 Liquid nitrogen vapor pressure manometer.

5. Safety

Reasonable care should be exercised when working with and around glass systems, especially when attaching and detaching the sample to the receiving arm of the test system.

Leather gloves are worn during breaking of the glass tubing for encapsulation of the sample. Didymium eye glasses are provided for eye protection from the sodium flame and are worn during the glass-blowing operations.

SAFETY GLASSES ARE REQUIRED AT ALL TIMES IN THE LABORATORY

6. Preparation of Sample

6.1 Seal the bottom of the sample tube. (This is usually done ahead of time on a large quantity of tubes by the glass shop.)

6.2 Obtain the sample tube tare weight. Be sure the balance zero has been verified at the beginning of the shift.

6.3 Transfer an appropriate amount of sample to the tared sample tube and obtain the total weight.

6.4 Obtain the sample weight by subtracting the tare weight from the total weight.

6.5 Insert a glass wool plug into the sample tube and mark the sample identification on the tube. Also mark a reference line just above the glass wool.

6.6 Attach a tapered ground glass joint fitted with a stopcock to the sample tube by means of a CAJUN coupling.

6.7 Determination of Moisture Content

6.7.1 Weigh a glass sample bottle which has been cleaned with soap and water and dried at 230°F ± 5°F for at least 1 hour.

6.7.2 Place approximately 1 gram of sample in the bottle.

6.7.3 Weigh sample and bottle.

6.7.4 Place in furnace designated for this purpose and leave for 2 hours. The furnace is maintained at 150°F with a low flow air bleed passing through at all times.

6.7.5 Remove from furnace and cap immediately.

6.7.6 Let cool to room temperature.

6.7.7 Remove cap and reweigh.

6.7.8 Percent moisture is calculated with the surface area on the HP9821A desk computer.

6.7.9 Empty sample into discard container provided.

6.7.10 CLEAN AND DRY BOTTLES AT ONCE.

7. Pre-treatment of samples (See Procedure 1.10)

Be sure to note in logbook at end of shift the status of any treatment in progress.

8. Pre-Operational Procedure for Measurement System (Figures 2 and 3)

8.1 Power switch 2 in ON position.

8.2 Vacuum block switch 8 in ON position.

8.3 Toggle switch 3 in ON position for vacuum.

8.4 Heater current meter 11 for thermocouple vacuum gauge 12 set at 31 milliamperes using heater current adjust knob.

8.5 Vacuum meter 12 should read 10 microns or less. If appropriate vacuum cannot be reached, the following need to be investigated.

8.5.1 Check Welch pump and Diffusion pump for operational integrity.

8.5.2 Check system stopcock for leak around ground glass joint.

8.5.3 Check to determine if the other system also shows a backpressure.

8.5.4 Notify supervisor for assistance if high pressure still exists.

8.6 Internal system temperature should read between 28-30°C.

9. Testing Procedure

9.1 Remove the sample container from the pre-treatment apparatus and attach it to the surface area measurement system (Figure 2). DO NOT PLACE IN LIQUID NITROGEN AT THIS POINT.

9.2 Open by-pass valve 9, vacuum block 8, and vacuum 3. Open system stopcock 13 and evacuate the system to 10^{-3} mm. Hg.

9.3 Open the sample container stopcock 14 and evacuate the system and sample to 10^{-3} millimeters mercury pressure. Close system stopcock 13. If pressure is observed when sample is opened, check for leaks in stopcock or sample. Retreat or prepare a new sample if needed.

9.4 Close by-pass valve 9, and lower mercury from top two bulbs of the gas burette 15 to the index mark below the second bulb. Close vacuum valve 3.

9.5 Admit helium to the system with helium button 5 to a pressure reading between 250-300 output on the Digitec 16.

NOTE: All Digitec readings should be divided by 1.66667 before using in calculations. This converts the output to millimeters of mercury pressure. Example - Digitec reading 250. 250 ÷ 1.66667 = 150 mm. Hg.

9.6 Record the equilibrium pressure of helium and the cabinet temperature. Then raise the mercury level in the gas burette 15 to the index mark below the top bulb. Record the helium pressure.

9.7 Hand calculate the helium volume (STP) (See calculation section) of the system for each of the recorded pressures. These volumes should agree within 0.1%, otherwise determine cause for disagreement before proceeding with test.

9.8 Using a Dewar flask containing liquid nitrogen, immerse the sample container to the reference mark located on the capillary portion of the sample container. Allow sample to reach liquid nitrogen temperature. ALWAYS MAINTAIN LIQUID NITROGEN LEVEL EVEN WITH THE MARK.
The Dewar flask must be emptied at beginning of each shift in order to remove collected ice which will affect the nitrogen temperature.

9.9 Open system stopcock 13 and admit helium into the sample container. Using regulator 10 and button 7, adjust the mercury level to the mark just below the top bulb of the burette. After equilibrium is reached, record the helium pressure.

9.10 Raise the mercury level in the gas burette to the top index mark by using regulator 10 and button 7. After equilibrium is reached, record the helium pressure.

9.11 Hand calculate the helium factor (See calculations). Average of two helium factors should agree within 0.1% as in 9.7.

9.12 Open valves 9 and 3 to evacuate helium from the system and the sample container. Evacuate to 10^{-3} mm. Hg.

9.13 Close system stopcock 13, by pass valve 9, and vacuum valve 3.

9.14 Lower mercury level in the gas burette emptying two or three bulbs to the appropriate index mark by using regulator 10 and button 7.

9.15 With nitrogen button 6 admit nitrogen to the system to 150-200 mm. Hg. pressure which is a reading between 250-333 on the Digitec 16. Adjust mercury level to the index mark and record the pressure.

9.16 Raise the mercury level in the gas burette one bulb to the appropriate index mark using regulator 10 and button 7. After equilibrium is reached, record the nitrogen pressure.

9.17 Hand calculate the nitrogen volume (STP) (see calculation section) of the system at each of the pressures recorded. These volumes should check within 0.1%, otherwise determine cause for disagreement before proceeding with test.

9.18 Replenish the liquid nitrogen in the Dewar flask until the level is at the mark on the sample container. Maintain this level throughout the test. Open system stopcock 13.

9.19 Raise the mercury in the gas burette to the index mark that will give maximum pressure in the system of about 180 mm. Hg. Record the equilibrium pressure, remembering 180 mm. Hg. = 300 on Digitec. Surface area measurements will usually be made in the range of 0.05 to 0.25 relative pressure depending upon the material being tested. Sometimes it may be necessary to work with half-bulb measurements so that the pressures will be within this range. This is accomplished in the following manner.

9.19.1 Raise or lower the bulbs to the desired pressure.

9.19.2 Allow pressure equilibrium to be attained.

9.19.3 Record pressure and close stop cock 13 to system.

9.19.4 Raise or lower mercury to nearest bulb line.

9.19.5 Record pressure and bulb number. Half-bulb readings may be taken initially or as the last point whichever is convenient.

9.20 Lower the mercury level in the gas burette one bulb to the index mark below this bulb. Record the equilibrium pressure.

9.21 Repeat step 9.20.

9.22 Repeat step 9.20.

9.23 Record the barometric pressure and the vapor pressure of nitrogen at liquid nitrogen temperature. The latter is obtained from a nitrogen vapor pressure manometer with a side arm of the manometer immersed in liquid nitrogen and is located between systems 1 and 2. This determination must be made using the same liquid nitrogen source as is being used in the test and with a clean ice-free Dewar flask. Add the observed pressure difference to barometric pressure. This gives the vapor pressure of the nitrogen.

9.24 Calculate the surface area of the sample on 9821A computer using "BET" Tape file 1.

9.25 Open bypass valve 9 and vacuum valve 3, remove the liquid nitrogen from around the sample container and let the sample warm to room temperature. Then close system stopcock 13 and remove the sample container from the system.

CAUTION

Do not open system to atmosphere until the bypass valve 9 is open, the vacuum block valve 8 is closed and the vacuum 3 is closed.

9.26 Wipe off excess grease from stopcocks so as to prevent buildup in opening as they are reused.

9.27 Empty used powder samples into the discard container provided.

9.28 Record data on form UCN-1951 (13 2-67).

10. Calculations

Although all calculations are made on the HP9821A desk computer, it is desirable to hand calculate the helium volume, helium factor and nitrogen volume. Hand calculation of these parameters assures that the analyst will know the data is adequate.

Pc = Pressure ÷ 1.66667

BF = Bulb Factor

T = Temperature Kelvin

V_b = Vol. of Helium or Nitrogen

V_t = Total cc of Nitrogen or Helium

γ = Helium Factor

$$V_b = \frac{Pc \times BF}{T}$$

P_o = Nitrogen Vapor Pressure

$$\gamma = \frac{V_t - V_b}{Pc}$$

Calculation for the HP9821A calculator is on next page.

BET

```
Memory Erase
Install Tape "BET"
LDF   1    For BET    No. 1
LDF   2    For BET    No. 2
EXECUTE
END        RUN PROGRAM
```

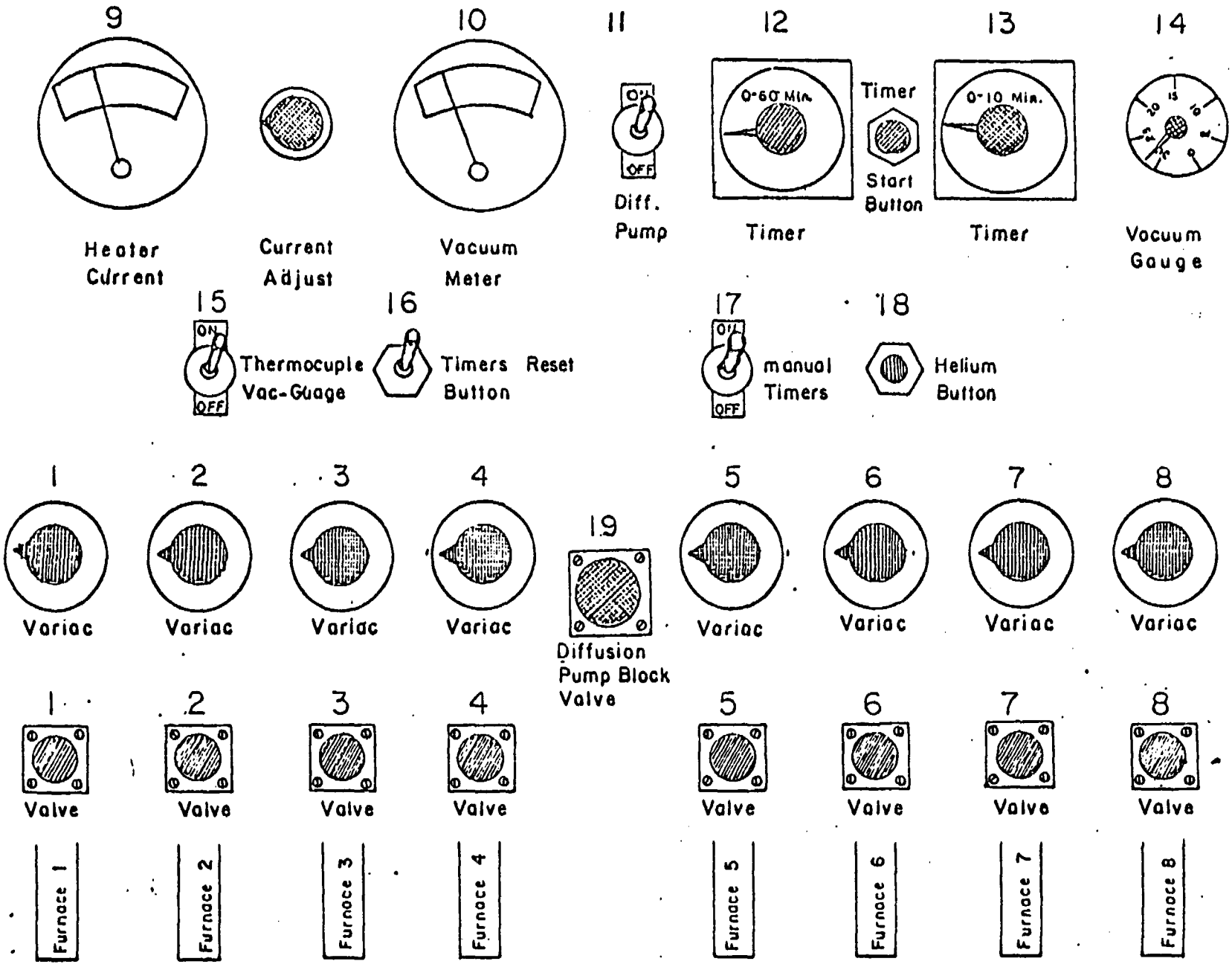
Enter T, °K	RUN PROGRAM		
Enter P_o Pres. mm Hg	RUN PROGRAM	PRINTS	Vapor Pres.
Enter He Pres.	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	He Vol.
Enter He Pres.	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	He Vol; Avg. He Vol.
Enter He Pres	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	He Factor
Enter He Pres.	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	He Factor; Avg. He Factor
Enter N_2 Pres.	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	N_2 Vol.
Enter N_2 Pres.	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	N_2 Vol; Avg. N_2 Vol.

Enter "0" if half bulb
    Enter half bulb pres.
    Enter N_2 pres.
    Enter Bulb No.

Enter "1" if changing gas volume	RUN PROGRAM		
Enter Pres. stopcock closed	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	Volume in Sample Area
Enter "0" if no other volume change	RUN PROGRAM		
Enter as for Regular Points			
Enter "1" if adding gas	RUN PROGRAM		
Enter Pres.	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	N_2 Vol.
Enter Pres.	RUN PROGRAM		
Enter Bulb No.	RUN PROGRAM	PRINTS	N_2 Vol.
		PRINTS	new total N_2 Vol.

For Regular Point

Enter N_2 Pres.	RUN PROGRAM	
Enter Bulb No.	RUN PROGRAM	PRINTS X = Pc/Po.
		PRINTS $Y = \frac{X}{Va\ (1-X)}$
Repeat for each point		
After last point	RUN PROGRAM	PRINT Intercept
		PRINT Slope
		PRINT Observed Y
		PRINT Calculated Y
Enter moisture bottle wt.		
if none, Enter A "1"	RUN PROGRAM	
Enter moisture bottle with sample wt.		
if none, Enter A "2"	RUN PROGRAM	
Enter dry weight		
if none, Enter A "2"	RUN PROGRAM	PRINTS Bottle and sample wt.
		PRINTS Bottle weight
		PRINTS Dried Sample
		PRINTS % moisture
Enter sample tube wt.		
if none, Enter A "0"	RUN PROGRAM	
Enter sample and tube wt.		
or just sample wt., if		
no tube wt.	RUN PROGRAM	PRINTS weights
		PRINTS Corrected wt.
		PRINTS Volume of monolayer
		PRINTS Surface Area
		PRINTS "C"
		PRINTS System Number
Enter sample No.		PRINTS Sample No.
STOP END		RUN PROGRAM



Pretreatment System Panel, Figure 1

Nitrogen Surface Area System No. I

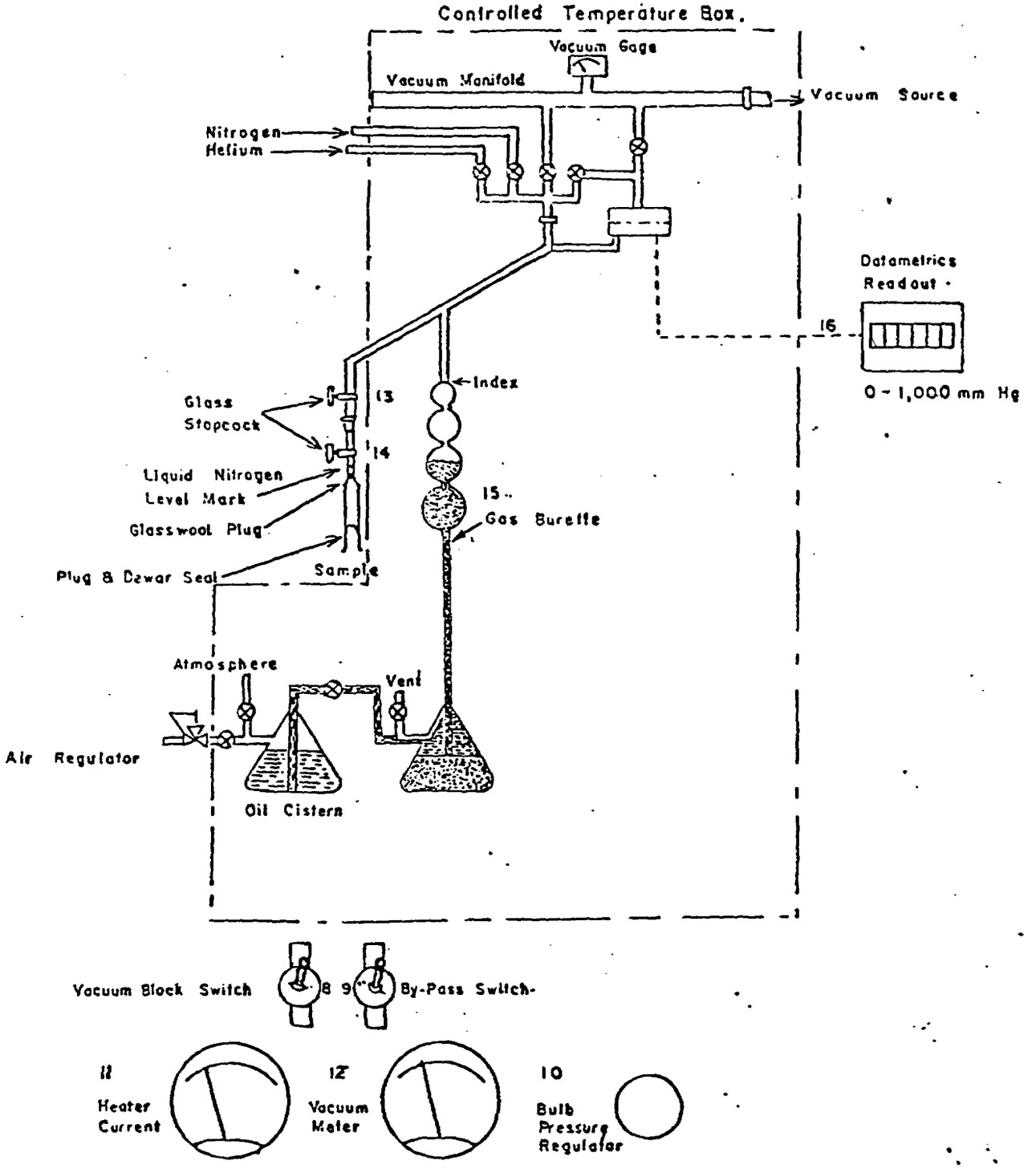
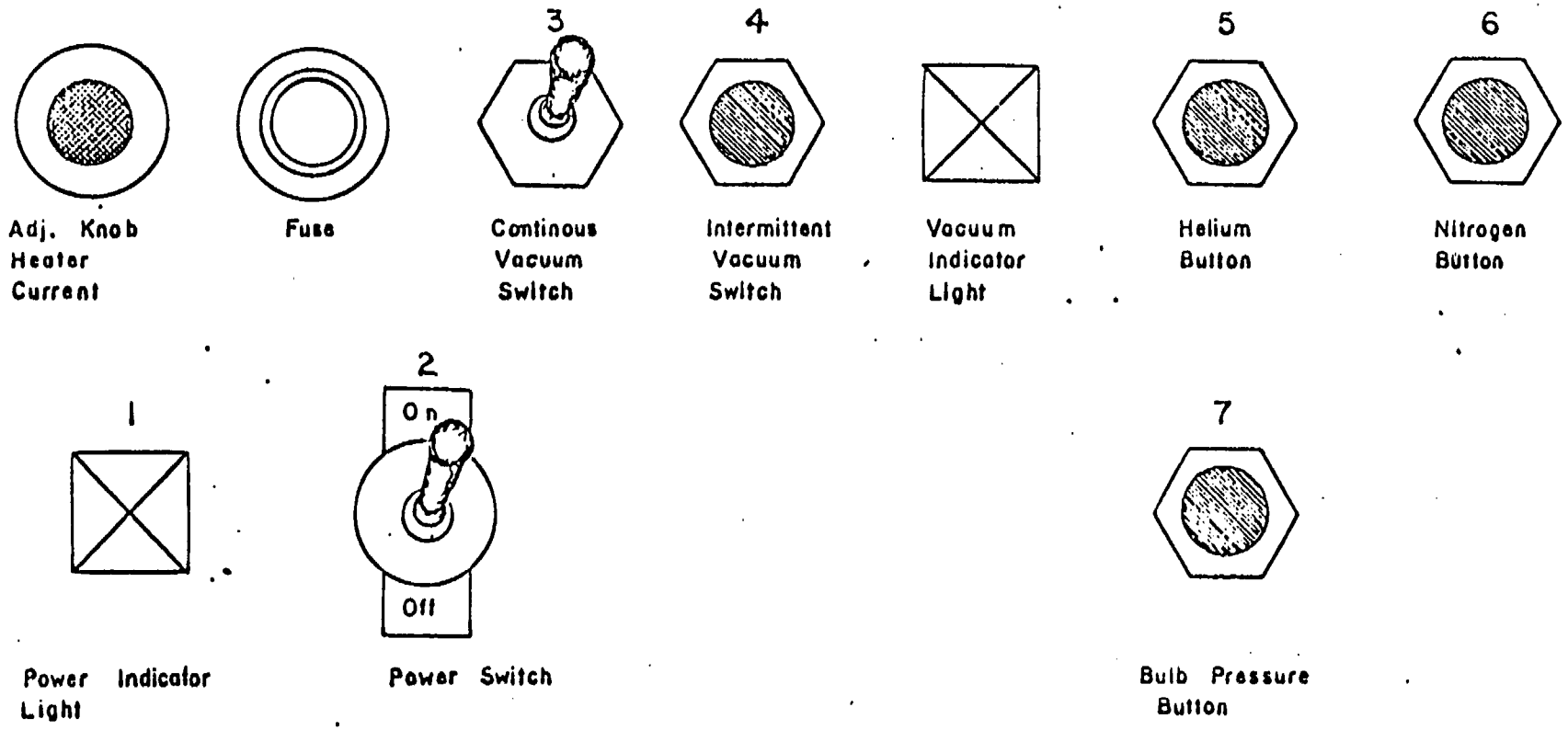


Figure 2



Top View Control Panel, System I

Figure 3

SURFACE AREA DATA

SAMPLE NO. OR CODE	WEIGHT	TREATMENT	DATE	OPERATOR

DESCRIPTION

REQUISITION NO.

Time or Line No.	B	G	S	T_o	T_i	T_c	P_o	P	P_c	I	V_u	V_s	Gamma	V_t	V_a	X	$V_a(1-X)$	$\frac{X}{V_a(1-X)}$

UCN-1081
113 8-67)