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DAVIS ET AL

HYDROGEOCHEMICAL FEASIBILITY STUDIES RELATED TO  
SUBSURFACE FLOW ON YUCCA MOUNTAIN, NEVADA TEST SITE

(USGS CONTRACT NO. 14-08-0001-10190)

FINAL REPORT

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by

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## INTRODUCTION

The thick sequence of altered volcanic tuffs at the Nevada Test Site (NTS) has been identified as a candidate location for the proposed disposal of nuclear wastes in geologic repositories. The U.S. Geological Survey (USGS), in cooperation with the Nevada Nuclear Waste Storage Investigations (NNWSI) and the University of Colorado at Boulder, is conducting hydrologic, geologic, geochemical, and geophysical studies at Yucca Mountain and the surrounding region in order to assess the suitability of the area for a nuclear repository.

The studies conducted by graduate students (Greg Davis and Josh Marvil) at University of Colorado have focussed on the following: (1) the extraction of interstitial fluids from the tuffaceous rocks using centrifugation, and (2) the hydrology of the alluvium which overlies the tuffaceous rocks at NTS.

## EXTRACTION OF INTERSTITIAL FLUIDS

In an effort to better understand the movement and chemistry of water in the unsaturated zone at NTS, Greg Davis is evaluating the possibility of extracting interstitial fluids by means of centrifugation of sections of drillcore. Although centrifugation has been used for removal of fluids from various geologic materials for several decades, the emphasis of such work has generally been on the measurement of the physical properties of rocks rather than on the chemistry of the fluids. The present

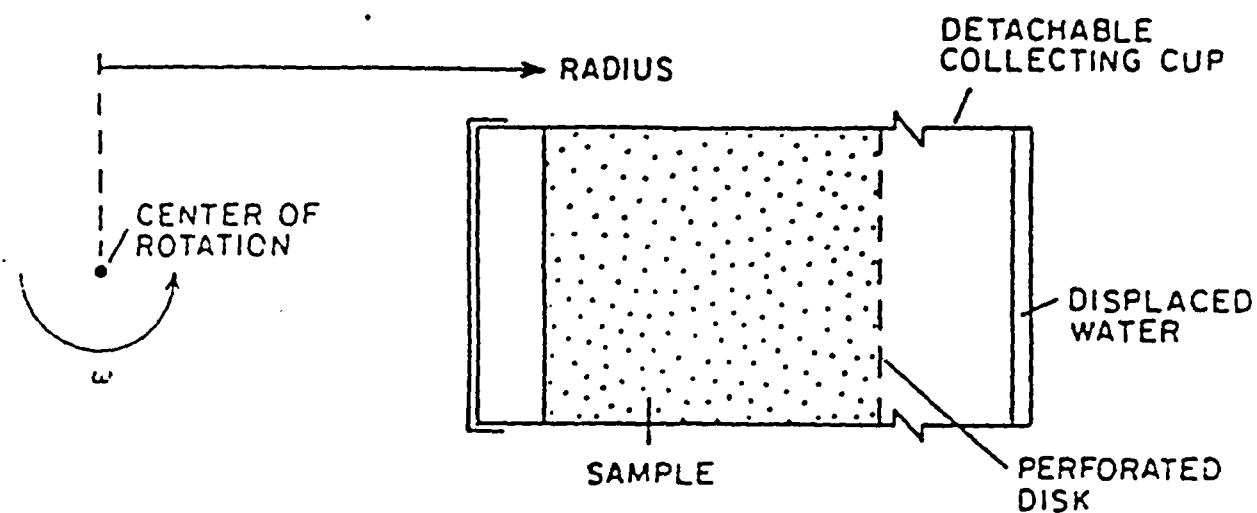
study is designed specifically to compare chemical and physical results from two different methods of centrifugal extraction of interstitial fluids.

A large body of literature exists on the subject of centrifugation of rock cores to determine the relationship of fluid saturation to pore water pressures, especially with regard to rocks that serve as reservoirs for hydrocarbons and for ground water. Recent applications include attempts to recover the interstitial fluids for chemical analysis (Edmunds and Bath, 1976; Kinniburgh and Miles, 1983).

A centrifuge may be used for extracting interstitial fluids in two ways, as shown in Figure 1. In the first technique, the interstitial water is forced through a supporting porous plate and is collected in a cup at the bottom of the centrifuge tube. In the second method, a dense, immiscible fluid is forced through the rock and the water floats to the surface. Both methods utilize crushed samples of the rock core.

Although the precise distribution of forces during the extraction is difficult to define, the general physics of the removal of fluids from porous earth materials by centrifugation is well understood. Water is considered to be displaced only from those pores in which the driving pressure of the centrifugal force is greater than the capillary pressure tending to retain the water in the pores. In theory, the volume of fluid extracted will be a function of the weight of the sample, the distribution of sizes of pores, the degree of initial saturation, the dimensions and

### DRAINAGE METHOD



### IMMISCIBLE DISPLACEMENT

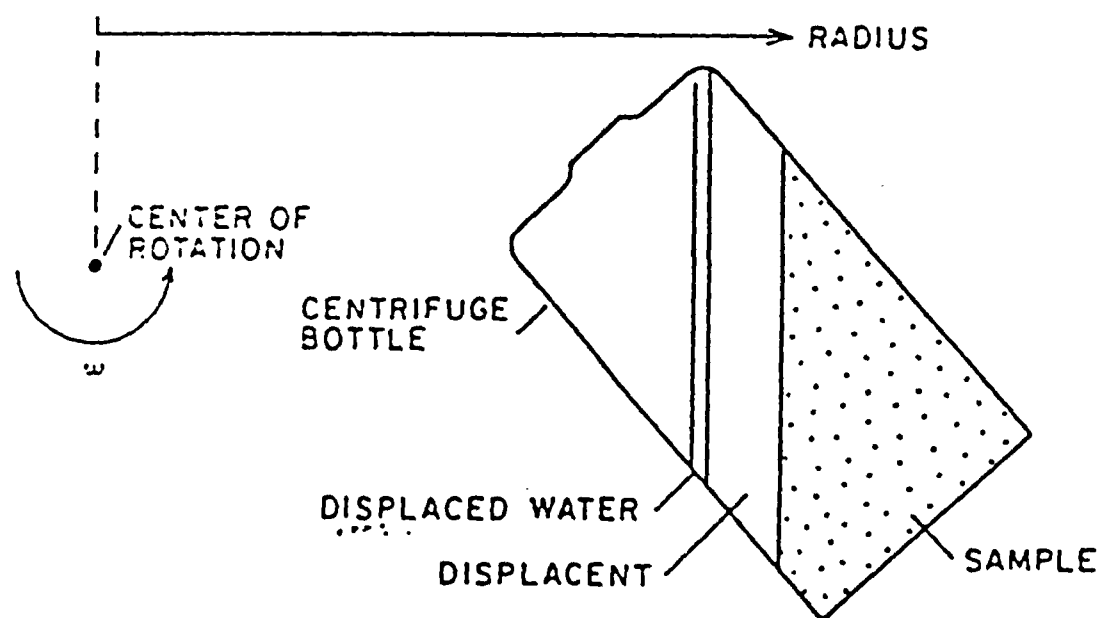


Fig.1. Methods of Centrifugation.

rotational velocity of the centrifuge, and the differences in density between the interstitial fluid and the displacing fluid. Evaporative losses will, of course, reduce the yield.

### Core Samples

Core samples for this investigation came from Wells U24 and U25 adjacent to Yucca Mountain at the NTS. Both wells penetrated approximately 360 feet of unsaturated silicic volcanic tuffs of Miocene age. Four tuff units were identified: Tiva Canyon, Yucca Mountain, Pah Canyon, and Topopah Springs. Layers of bedded and reworked tuff separates each of these four units; for purposes of this report these layers are labeled BR-1, BR-2, and BR-3 (see Table 1).

The air-rotary drillcore has a diameter of 6 cm. Samples were wrapped in aluminum foil or placed in PVC tubing, taped, and sealed with beeswax.

### Equipment and Procedures

Extractions have been carried out using a Sorvall RC-5B high-speed, thermostatically-cooled centrifuge. A variety of rotors are available for this instrument to accomodate various sample sizes and to provide different extraction pressures. Listed below are the specifications for the rotors used in this study:

<u>rotor</u>	<u>max. rpm</u>	<u>max. weight (cup + sample)</u>	<u>radius to cup center</u>
GS-3	8000	780 grams	12.80 cm
SS-34	18000	115	8.26

TABLE 1

ROCK UNIT	IMMISCIBLE DISPLACEMENT						DRAINAGE					
	CRUSHED ROCK 18000 RPM			INTACT 8000 RPM			CRUSHED ROCK 18000 RPM			INTACT 8000 RPM		
	No. OF SAMPLES TESTED	PERCENT MOISTURE CONTENT	VOLUME IN mL EXTRACTED	No. OF SAMPLES TESTED	PERCENT MOISTURE CONTENT	VOLUME IN mL EXTRACTED	No. OF SAMPLES TESTED	PERCENT MOISTURE CONTENT	VOLUME IN mL EXTRACTED	No. OF SAMPLES TESTED	PERCENT MOISTURE CONTENT	VOLUME IN mL EXTRACTED
TIVA CANYON		1					1	28.1	33.8	IN PROGRESS 1		
BEDDED REWORKED # 1	1	12.9	1.4							IN PROGRESS 2		
YUCCA MOUNTAIN	2	8.3 - 10.6	0-2.5							IN PROGRESS 1		
BEDDED REWORKED # 2												
PAH CANYON	3	7.0 - 8.4	0									
BEDDED REWORKED # 3	6	18.6 - 35.7	6.0 - 44.3				2	10-24.7	0-40.7			
TOPOPAH SPRINGS	1	15.3	9				1	7.9	0			

As shown in Figure 2, special centrifuge cups were designed to hold geologic materials in the two rotors described above.

The fluid chosen for immiscible displacement was the halogenated hydrocarbon 1,1,2-trichloro-1,2,2-trifluoroethane, as suggested by Kinniburgh and Miles (1983). This displacement fulfills the desired properties of high density ( $1.57 \text{ gm cm}^{-3}$ ), low solubility in water (90 mg/L), low volatility (B.P. =  $47^{\circ}\text{C}$ ), low toxicity, high chemical inertness, low price (\$75 for 4 liters), and compatibility with polypropylene centrifuge cups.

The exact procedure adopted for work on rock samples will vary according to the type of sample and the exact purpose of the investigation. An overview of the procedures for this study is given here, and a detailed outline of procedural steps is being prepared for a USGS-NHP Quality Assurance Document.

Core samples are unpacked in a nitrogen-purged glove box, weighed, and placed in a plastic bag. The samples are then crushed with a hammer. The sand-size to pea-size fragments are transferred to the centrifuge cups. Immiscible-displacement fluid can be added at this step. The cups are then counterbalanced against each other and placed in the rotor. The rotor is then installed in the centrifuge and the chamber is flooded with nitrogen. After setting the control dials for angular velocity and spin time, the run is begun.

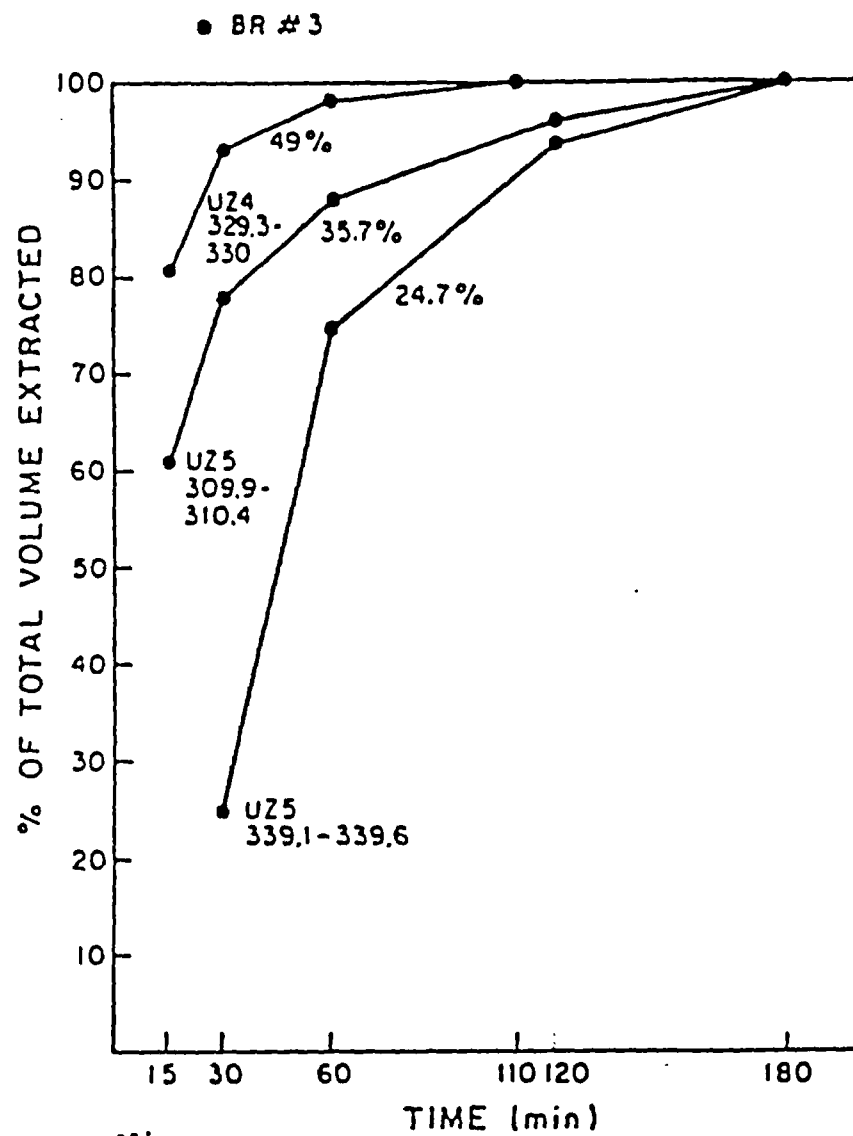


Fig. 2 Percent of Total Pore Water Extracted as a Function of Centrifugation Time.



A second method for preparing the core is now being tested. Intact cores are simply cut to 50 cm length and placed in the large centrifuge cups. Both the drainage and the displacement methods are being tested with the whole cores.

After centrifugation the displaced water is filtered (0.45 um) into an appropriate vial and sent to the analytical laboratory for chemical analysis. Excess immiscible displacing-fluid, if present, is decanted from the centrifuge cups. The remaining solid sample is oven-dried at 105°C for 18 hours. The dry weight is used to determine the initial moisture content.

### Results

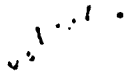
A total of 17 extractions of water have been completed on core samples taken from Wells U2-4 and U2-5. Table 1 summarizes the physical data from these runs. Two units in particular, Tiva Canyon and BR#3, contain sufficient water for multiple chemical analyses. No water can be extracted from the Pah Canyon unit by the centrifugal methods. The remaining rock units yield small amounts of water, sufficient for analysis for cations only.

Past studies have suggested that 30 to 120 minutes of centrifugation ensures maximum recovery of interstitial fluids at a given RPM (Edmunds and Bath, 1976; Kinniburgh and Miles, 1983; Gillman, 1976). Results of centrifugation on NTS tuffs, as illustrated in Figure 2, agree with these findings. A spin-time of 120 minutes was chosen as the standard for the project.

Figures 3 and 4 show plots of percent moisture content versus fluid volumes extracted from crushed rock cores. Rocks containing less than 11% moisture do not yield water by either of the two centrifugation techniques. Greater volumetric yields appear to be obtained by the drainage method.

As with other methods of extraction of interstitial water, centrifugation yields somewhat less than the total amount of pore fluid, as illustrated in Figure 5. It is important to determine if the portion of the fluid that is extracted has the same chemical composition as the remaining interstitial fluid. The variation in chemical composition as a function of yield should indicate whether or not systematic differences exist in the composition of the fluid. The University of Colorado has proposed a one-year extension of the study to further investigate this question.

NONE SPUN



✓✓✓✓✓

TIVA CANYON	*
BEDDED/REWORKED #1	NONE SPUN
YUCCA MOUNTAIN	NONE SPUN
BEDDED/REWORKED #2	NONE SPUN
PAH CANYON	NONE SPUN
BEDDED REWORKED #3	●
TOPOPAH SPRINGS	+

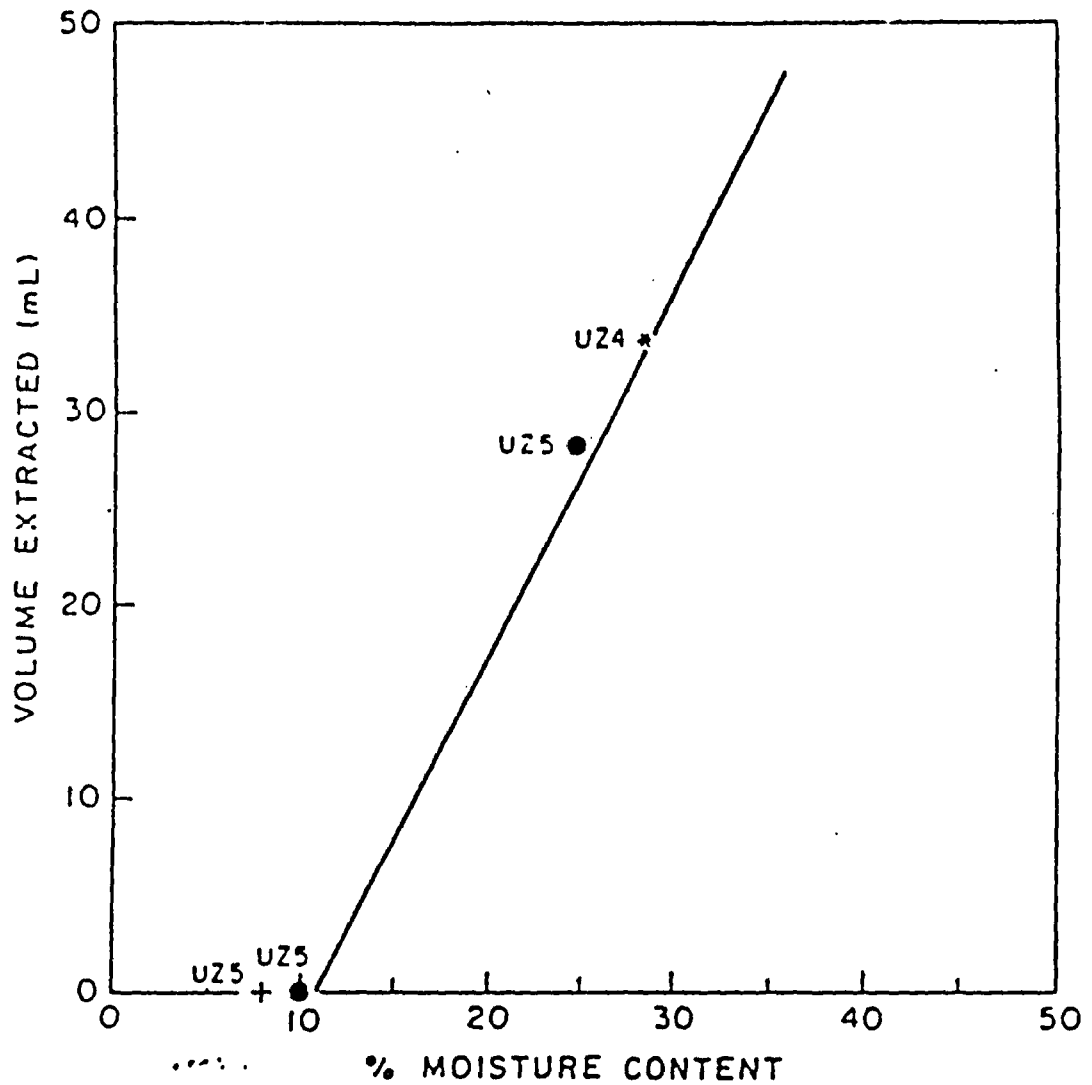


Fig. 4. Extracted Water Volumes from Crushed Rock by Drainage Centrifugation. 4"-HQ Core from Wells UZ4 and UZ5. Centrifuge Speed 1800ORPM Spin-Time 120min..

- DRILLCORE FROM WELLS UZ4 AND UZ5
- ⊙ DRILLCORE FROM WELL UZ5 ARTIFICIALLY RESATURATED TO 50% MOISTURE CONTENT

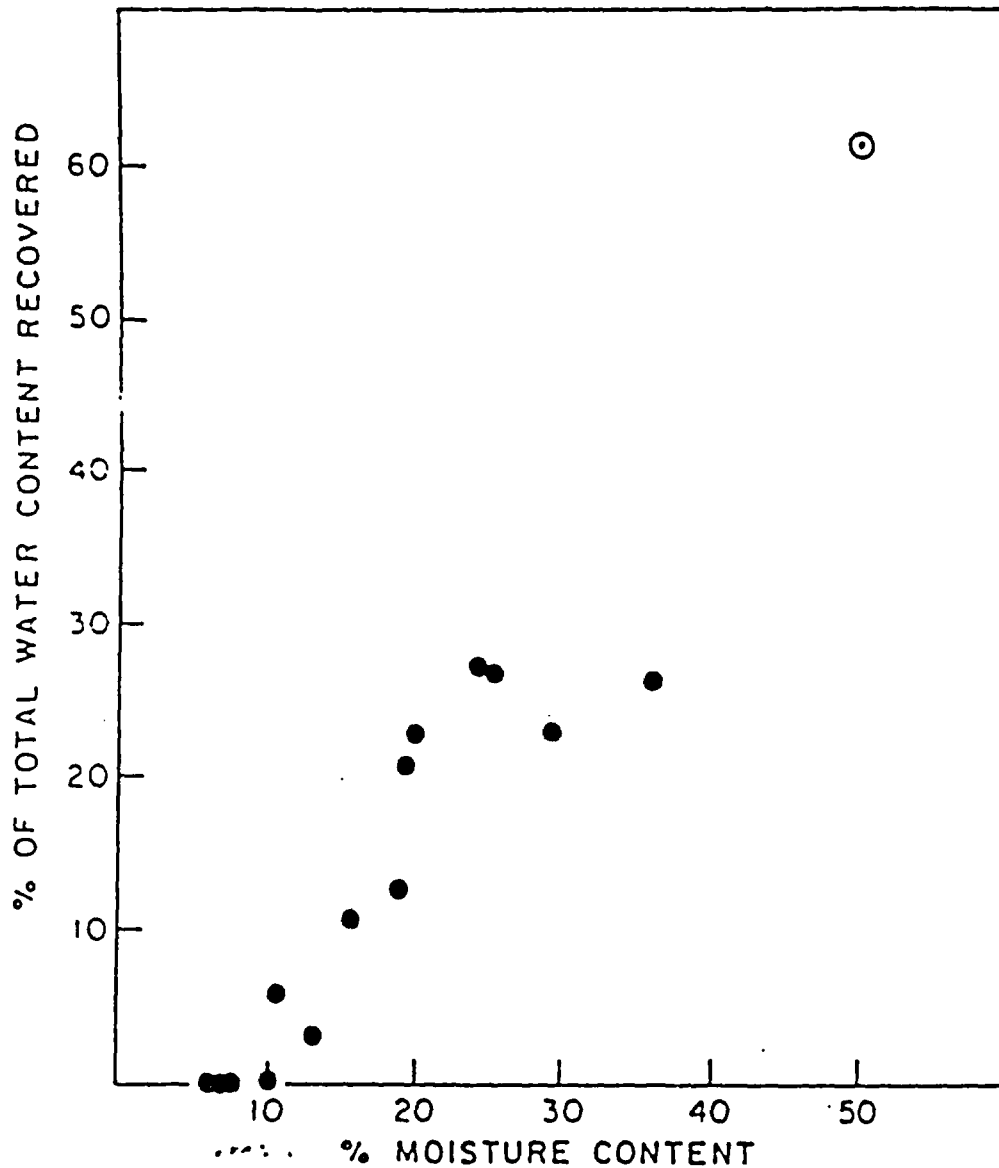


Fig. 5. Percent of Total Water Content Recovered vs. Percent Moisture Content. Centrifuge Speed: 18000 RPM. Including Drainage and Immissible Displacement Techniques.

## HYDROLOGY OF THE ALLUVIUM

The unsaturated zone beneath Yucca Mountain ranges in thickness from 500 to 750 meters (Robinson, 1984). A number of exploratory test holes are currently being drilled to examine the geochemical and hydrologic properties of the main tuffaceous units in the unsaturated zone. However, little quantitative data has been collected to date concerning the alluvium which overlies the tuffaceous rocks. The present study (by Jos. Marvil) focusses on the geochemical and hydrologic properties of the alluvium.

The ultimate objective of the study is to understand the effects of present and past climatic conditions on the geochemistry and hydrology of the alluvial zone. The immediate goal is to gather sufficient field data to obtain a preliminary understanding of the recharge, flow, and transport of water within the alluvium. A longer-term goal is to utilize a predictive computer model (SEGOL) to quantify our understanding of the movement and geochemistry of water within the alluvium.

### Computer Modelling

Much of the first and second quarters of the past year were spent in the modification, debugging, and testing of the computer code SEGOL (Segol, 1976). This code is a Galerkin finite-element model for contaminant transport in variably-saturated porous media. It was our task to make SEGOL compatible with the NHP Prime 9950 operating system, to increase the capability and versatility of the model, and to verify SEGOL by comparison to

other working models. Our efforts met with only limited success. It appears that our initial hope for SEGOL may have been overly optimistic. Although the model is designed for three-dimensional applications, the only verification has been a one-dimensional field experiment (Warrick and others, 1971). As our efforts have focussed more strongly on the field program other USGS researchers have assumed the responsibility of working with SEGOL.

#### Small-plot Rainfall Simulation Studies

It is necessary to increase the data base for the processes of infiltration, percolation, and recharge on Yucca Mountain to permit the modeling of the effects of climatic change. In order to do this, we have been designing and instrumenting experiments for the small-plot simulation of rainfall. Proposals for large-plot rainfall simulation experiments are also being reviewed.

For our small-plot experiments, we chose a rainfall simulator that was designed by the U.S. Bureau of Land Management. It uses small quantities of water and is easily portable. The simulator consists of a 3 by 3 foot precipitation chamber with 23-gauge (0.034 cm ID) hypodermic tubing spaced on a one-inch grid. During rainfall simulation the chamber is rotated in a small circular pattern to prevent drop impact in the same locations. A wind-screen, consisting of a nylon-reinforced plastic tarp, was placed over and around the simulator to minimize the evapotranspiration effects of the arid environment. A water truck

provided sufficient water for the duration of the experiment. Water from Well J-13 was used for the preliminary experiment, but deionized water or actual rainwater could be used in the future. The flow entering the precipitation chamber was regulated with a pressure-reducing valve in line with a flow meter to measure the actual amount of water entering the chamber.

A hole was drilled to a depth of seven feet for instrumentation, using an Odex-115 system (Hammermeister and others, 1985). The monitoring instruments, already attached to an eight-foot length of aluminum tubing, were placed in the hole and the hole was back-filled with screened fines. A bentonite plug was placed around the aluminum tubing at the surface to prevent piping and water flow down the annulus.

The downhole instruments consisted of a series of tensiometers and thermocouple psychrometers to measure water potential and temperature. A neutron moisture-probe was used in the aluminum tubing to measure the content of soil moisture.

Data were gathered for several days prior to infiltration, followed by four days of infiltration. During the infiltration experiment saturation reached a depth of about five feet. On the fifth day the rainfall simulator was blown over in a windstorm.

#### Monitoring Equipment

The instruments used to measure water potential, moisture content, and temperature for the preliminary rainfall simulation infiltration experiment were tensiometers, thermocouple psychro-



meters, and a neutron moisture probe. A data acquisition system was designed to monitor the instruments. Testing was conducted in the laboratory prior to the field experiments.

### Thermocouple Psychrometers

Thermocouple psychrometers were used to measure water potential (matric and osmotic) and temperature during infiltration. The instruments were manufactured by Wescor, Inc. and J.R.D. Merrill Speciality Equipment Company. Thermocouple psychrometers are suitable for measuring water potential values in the range of -3.0 to -70 bar. The theory of the method is described in detail by Brown and Van Havern (1972).

The bulk of our work with psychrometers involved designing a semi-automated system to be used for the dozens of psychrometers purchased for use on this project and on the study involving the drillholes (UZ4, UZ5, UZ6, UZ7, and UZ6S). The calibration system works efficiently and accurately. It uses a Campbell Scientific, Inc. 21X Micrologger, a circuit board for uniform excitation, and a Neslab refrigerated circulating bath for accurate temperature control. The circuit board was constructed for efficiency and accuracy during calibration and field measurements. The board consists of Viking quick-disconnect plugs for easy hookup with the psychrometer leads. A series of switching diodes, resistors, and potentiometers have also been included so that the excitation current passing through the psychrometer tips can be carefully regulated. The magnitude and delay time of the excitation current are important factors in

calibration. The actual calibration procedure is standard and is discussed by Brown and Bartos (1982). Briefly, Peltier psychrometers are calibrated by determining the microvolt output while they are suspended over a salt solution of known water potential and temperature (Brown and Van Haveren, 1972; Brown and Bartos, 1982). Calibration curves are generated for individual psychrometers in the format of bars (or mbars) versus microvolts output for a range of salt solutions and different temperatures.

We have developed a series of interactive computer codes for use on the Prime 9950 system to evaluate and reduce the psychrometer data more efficiently. The data from the 21X can be dumped directly to the computer; subsequent temperature and potential curves are easily generated.

### Tensiometers

Because psychrometers are unable to measure water potential values in the range of 0 to -1.0 bar, tensiometer systems for the measurement of soil matric potential were used downhole during the infiltration experiment. The tensiometers were constructed with 1/2-bar, high-flow, porous ceramic tips (Soil Moisture Equipment Inc.) and 1/8 inch Nylaflow (type H) tubing.

The tubing was cut to the desired lengths and glued into the porous ceramic tips with epoxy cement. Great care was taken to avoid damaging the tips and to avoid having epoxy cement run into the cups, as this would affect the hydraulic connection

between the tensiometer water and the interstitial waters. In addition, Nupro shut-off valves (with 1/8 inch Swagelock fittings) were connected to the loose ends of the "supply" tubes to facilitate flushing of the tensiometry systems.

Similar to the psychrometry data-acquisition system, we utilized a Campbell Scientific 21X Micrologger to collect tensiometer data. We purchased ten MicroSwitch differential pressure transducers which are compatible with the 21X Micrologger. These are small, lightweight, and inexpensive. The "read" tube of each tensiometer was attached to the active port of the pressure transducer and the transducer was attached differentially to the Model 21X Micrologger. The passive port of each transducer remained open to the atmosphere and a gage transducer was attached to the 21X Micrologger to measure relative atmospheric pressure fluctuations. The transducers were calibrated individually with the use of an accurate pressure gauge in the laboratory. Known pressures were applied to the passive port and corresponding millivolt outputs were recorded. The transducers showed good linearity over the calibration range (0-700 mbar) and negligible hysteresis.

#### Neutron Moisture Probe

A Model 503DR neutron moisture probe from Campbell Pacific Nuclear was used to measure soil moisture content downhole during the experiments. The theory of operation is simple - the probe contains a source of high-energy neutrons and a slow

(thermal) neutron detector. The probe is lowered into the two-inch aluminum tubing in the center of the instrument hole. Hydrogen, present in the interstitial water, slows the high-energy neutrons for detection. The moisture data are displayed directly on the screen of the assembly.

The neutron moisture probe data, recorded as counts per unit time versus depth, can be run through a series of computer programs to compare the observed data to calibration curves that are specific for the soils and neutron moisture meter of interest. The calibration curves account for the properties of the soils of interest, thus allowing the neutron counts to be converted to moisture content.

### Summary

In the past year we have made progress toward understanding the processes of percolation and infiltration under different climatic conditions. We have spent much of the last six months designing equipment and instruments and setting up small-plot rainfall-simulation and infiltration experiments.

From the tensiometers and psychrometers we have obtained data on the water potential, and from the neutron probes we have gathered data on the content and flux of moisture in the test plots. We also have analyses of soils, temperatures at the surface and downhole, and rates of sprinkling and infiltration.

We continue to work with new and existing computer programs to increase the efficiency and the reliability of interpretation of the data.

In theory, by use of simple flow equations, we should be able to calculate the hydraulic conductivity at varying degrees of saturation from the water potentials and the fluxes of water into the soil over a given area. The data that we collect will be useful for comparing infiltration rates as a function of different chemical compositions of the water and for comparing field and laboratory methods of determining hydraulic conductivity. If time permits, we will also investigate the effects of soil-type, flora, porosity, and other parameters on the infiltration and recharge through the alluvium. As the data base is expanded, it will be useful for the verification of existing computer models for unsaturated flow and, ultimately, prediction of different hydrologic processes under varying climatic conditions.

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UNIVERSITY OF COLORADO, BOULDER

Department of Geological Sciences



July 30, 1985

Re: Contract No. 14-08-0001-A190

Dr. Warren Hofstra  
U.S. Geological Survey  
Box 25046, M.S. 416  
Denver Federal Center  
Denver, CO 80225

Dear Dr. Hofstra:

Enclosed please find our Final Report for the Fiscal Year 1985.

If you have any questions or comments, please do not hesitate to call or write.

Yours truly,

A handwritten signature in dark ink, appearing to read "D. D. Runnells", written over a horizontal line.

Donald D. Runnells  
Professor

enclosure

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RESULTS OF RADIOISOTOPE MEASUREMENTS AT THE NSF-UNIVERSITY OF ARIZONA  
TANDEM ACCELERATOR MASS SPECTROMETER FACILITY

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In this paper we will describe the operation of the University of Arizona tandem accelerator mass spectrometer (TAMS) facility, present results of some measurements performed to demonstrate the reliability of its performance, and describe several experiments which have been completed on samples of archaeological and geophysical interest.

## 1. Instrument performance

## 1.1. Targets and performance

Most of the work described here has been done with accelerator targets made of a mixture of iron and carbon. After pretreatment, samples to be studied are combusted to  $\text{CO}_2$ , which is reduced to carbon by hot magnesium. The carbon is mixed with iron powder in mass ratio of about  $M(\text{iron})/M(\text{carbon}) \approx 15/1$ , and heated in a vycor tube until the iron melts. For a mixture of 1 mg of carbon and 15 mg of iron, and Fe-C bead with a diameter of about 1.5 mm is formed. This bead is mounted in a holder designed to allow a 1 mm diameter section of the bead to be exposed to the cesium beam in the ion source. Six such target holders are mounted on a wheel which can be rotated to expose, successively, each of the targets to the cesium beam.

In a typical set of experiments, one standard, one blank and four unknown samples are inserted into the ion source. Ions of  $^{14}\text{C}$  and  $^{13}\text{C}$  from a target are counted alternately for a period of fifteen minutes, and the wheel is then rotated to the next target. For a complete set of measurements the wheel is rotated four times, resulting in one hour of exposure for each of the six targets. On the average, the Fe-C beads produce 1.5  $\mu\text{A}$  of  $^{13}\text{C}$ , about 20% of that obtained from graphite targets of similar geometry. For modern carbon, this results in about 2 counts/s of  $^{14}\text{C}$ , so that in 50 min a total of 6000  $^{14}\text{C}$  counts are recorded. Combined with an equal number from a standard target, the ratio of unknown to standard is determined with a statistical precision of about 2%.

## 1.2. Tests of reliability

Fig. 1 illustrates results from a series of measurements made with a set of 24 targets made from AD

1890 wood. The ratio  $^{14}\text{C}/^{13}\text{C}$  for each of the targets was measured for a total time of about one hour, in the manner described above. Plotted in the figure are the ratios

$$R_i = \frac{(^{14}\text{C}/^{13}\text{C})_{2i}}{(^{14}\text{C}/^{13}\text{C})_{2i-1}}$$

for 12 independent ratios which can be deduced from

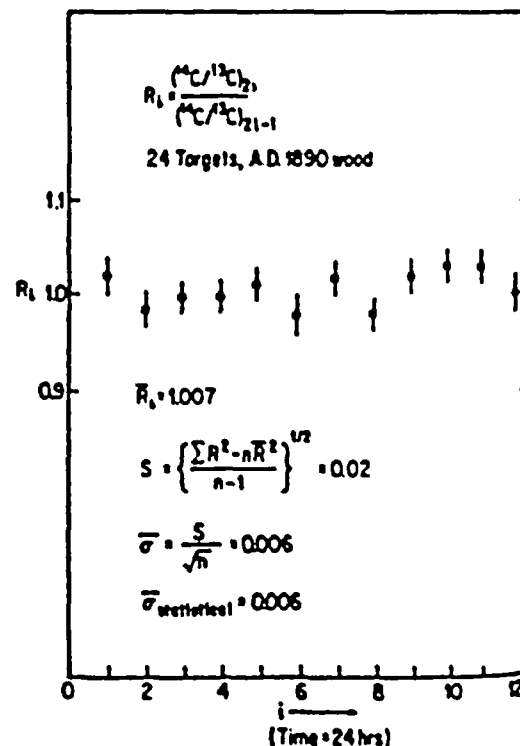


Fig. 1. Twelve values of the ratio  $R$  obtained from  $^{14}\text{C}/^{13}\text{C}$  measurements on 24 targets made of AD 1890 wood



spectrometer (TAMS) facility and describe several experiments

$^{13}\text{C}$  for each of the targets of about one hour, in the plotted in the figure are the

which can be deduced from

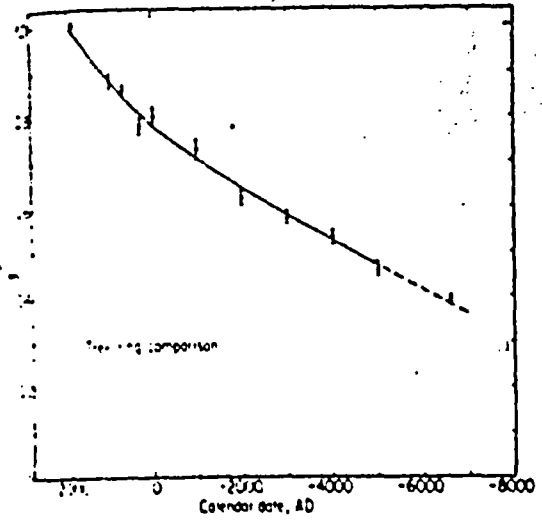
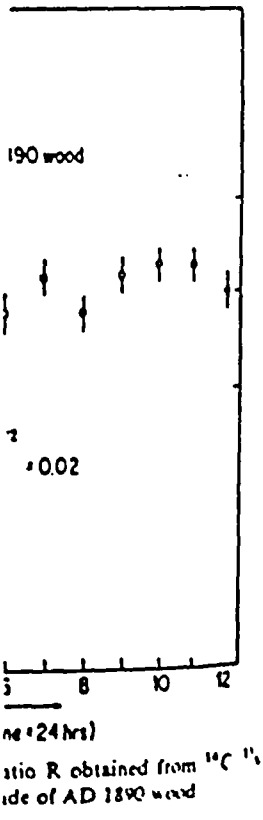


Fig. 2. Accelerator measurements of the ratio  $^{14}\text{C}/^{12}\text{C}_{1000}$  in tree rings plotted vs the calendar date of the tree rings. The curve is a smoothed version of a fit to proportional-counter determinations of the same ratio.

measurements on the 24 targets. As can be seen from the figure, the average value of  $R$  and its standard deviation are  $\bar{R} = 1.007 \pm 0.006$ . The standard deviation of a single measurement of  $R$  from the average is  $\pm 0.002$ . Both the standard deviation of the average and the value of  $S$  are equal to statistical uncertainties. From this we can conclude that, for this series of measurements, to a level of 0.6%, no contributions of instrument fluctuations to random errors are observed. Finally, the fact that the average value of  $\bar{R}$  is within the standard deviation of its expected value of 1.000 indicates that systematic errors are less than 0.7%.

In another series of tests, we have measured the ratio  $^{14}\text{C}/^{13}\text{C}$  in a series of tree rings of known age. Results are presented in fig. 2. The experimental points are plotted as a ratio of  $^{14}\text{C}(\text{tree ring})/^{14}\text{C}(\text{modern})$ . The solid curve is a smoothed version of a fit to proportional-counter measurements on tree rings [1]. The counter data have only been analyzed to 5000 BC, and the smooth curve was extrapolated to include our data at 6600 BC. The agreement between the accelerator data and the smooth curve is consistent with the standard deviations (2-3%) associated with the data.

Table 1  
Summary of measurements

Sample	$^{14}\text{C}/^{12}\text{C}_{1000}$	Equiv. age (a)
Fe-C blanks	$0.015 \pm 0.003$	34000
Catalytic graphite	0.002	50000
Natural graphite	0.0008	57000

### 1.3. Background

Extensive measurements of background associated with  $^{14}\text{C}$  determinations are summarized in table 1. The background for Fe-C blanks is the average of measurements on many blanks. It results from  $^{14}\text{C}$  introduced during chemical preparation of the Fe-C beads. The uncertainty listed in the table is the standard deviation of a single measurement from the average of many measurements.

The results labeled "catalytic graphite" were obtained with targets fabricated by a new method we have been developing in conjunction with scientists in New Zealand [2]. Instead of mixing carbon with iron to produce Fe-C pellets, carbon is combined with a small amount of chromium powder (30% by weight). The mixture is placed in a tantalum tube and heated in a vacuum graphite furnace to a temperature of about  $1900^\circ\text{C}$ . The resultant powder often exhibits an X-ray diffraction pattern of graphite and, when packed into a holder of appropriate geometry in the ion source, yields  $^{12}\text{C}^-$  currents comparable to those from graphite.

Finally, the background from natural graphite targets, which have no chemistry involved in their fabrication, and which produce  $^{12}\text{C}^-$  beams about four times greater than the Fe-C targets, is perhaps the background inherent in the instrument.

### 1.4. Other isotopes

#### 1.4.1. $^{10}\text{Be}$

To detect  $^{10}\text{Be}$  we accelerate molecules from  $\text{BeO}$  targets, disintegrate them in the stripper in the terminal operating at 2 mV, and select ions of  $\text{Be}^{3+}$ . All  $^{10}\text{Be}$  ions are stopped by a gas absorber in front of the detector. The details of this experiment are described in another paper [3]. The results can be summarized with the figures:

- a)  $(^{10}\text{Be}/^9\text{Be})$  background  $= 5 \times 10^{-13}$ .
- b) For  $^{10}\text{Be}/^9\text{Be} = 5 \times 10^{-13}$ ,  
 $^{10}\text{Be}$  counts  $\mu\text{C}$  of  $\text{BeO}^-$  from target  $= 0.1$ .

#### 1.4.2. Trace-element detection

We have done a series of experiments to detect trace elements in semiconductor materials. The accelerator system was calibrated using samples of known composition provided by Dr. M. Anthony of Texas Instruments Corporation. Fig. 3 shows a curve for  $^{11}\text{B}$  in silicon. It indicates that  $^{11}\text{B}$  can be detected in silicon to less than one part per billion.

### 2. Applications

During the nearly two years of operation of the University of Arizona TAMS, most efforts have been

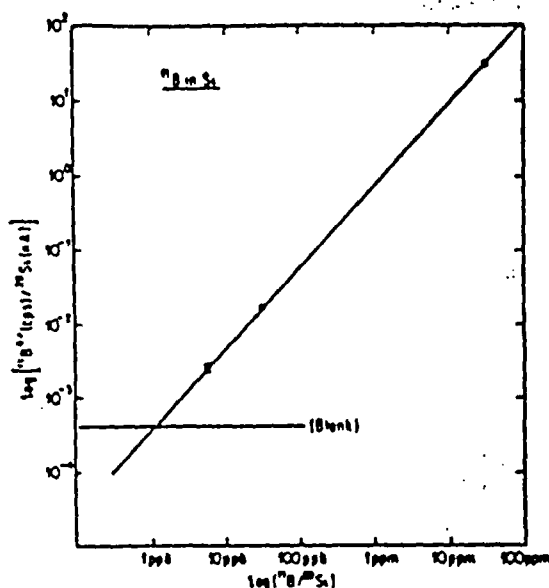


Fig. 3 A plot of known vs measured values of the concentration of  $^{11}\text{B}$  in silicon. The known values on the abscissa were determined at Texas Instruments Corp.

Table 2  
Examples of  $^{14}\text{C}$  studies with Arizona AMS

Agricultural products
Egyptian wheat seeds
North American corn and squash
Alaskan Crustacea
Antarctic Lichen
Atmospheric samples
Bones
Domebo mammoth
Human skeletons
Sunnyvale
Yuha
Anzick
Clovis-site charcoal
Deep-sea cores
Foraminifera
Shells
Coral
Desert Varnish
Earthquake samples
"Historical" artifacts
Hydrological samples
Meteorites
Pack-rat middens; paleobotany
Quaternary extinctions
Textiles
British museum
Coptic
Tree rings

directed toward  $^{14}\text{C}$  measurements. Since January 1991 using targets made of Fe-C beads, approximately 600 real samples have been dated. Table 2 illustrates the variety of measurements which have been made. Details of experiments with atmospheric samples and Coptic textiles are given in other contributions to these proceedings. Several specific measurements are described in more detail below. All errors quoted in the examples below are standard deviations.

### 2.1. Old bones

This work has been done in collaboration with many people, primarily with T.H. Stafford, Jr., C.V. Haynes, Jr., K. Brendel, Austin Long, and P.E. Damon of the University of Arizona, and R.E. Taylor of the University of California at Riverside.

#### 2.1.1. Domebo mammoth

The radiocarbon age of this mammoth, excavated from a site at Domebo, Oklahoma [4], has been determined by conventional counting of associated wood to be about 11000 years old. We have performed a series of experiments [5] to investigate the dependence of the radiocarbon age obtained from bone samples on the particular chemical fraction of the bone used in the measurement.

Some results of these measurements are presented in table 3.

An inspection of the table indicates that results from the first five chemical fractions are in agreement with the results from associated wood, and are reasonably consistent with one another. The remaining chemical fractions yield radiocarbon ages which are too young by 1000 years or more. A more detailed description of the work is being prepared for publication.

Table 3  
Dependence of radiocarbon age on chemical fraction of bone used

Description of sample	Radiocarbon age (years BP)
Wood associated with burial	11450 ± 320
Alpha-hydroxyacids	11350 ± 340
XAD-purified hydrosylate	11450 ± 350
Raw bone after acetic acid treatment	10950 ± 450
XAD-purified gelatin	10850 ± 400
0.6N HCl-insoluble organics	10800 ± 300
Imino acids	10500 ± 350
Gelatin	10450 ± 400
0.6N HCl-soluble organics	9500 ± 400
Inorganic $\text{CO}_2$ from acetic acid leaching	9350 ± 320
$\text{CO}_2$ from combustion of raw bone	8000 ± 450
Bone carbonate	7250 ± 320
Fulvic acids	5100 ± 200

nts. Since January 1981, approximately 60 Table 2 illustrates the have been made. Detrital samples and Coprolites to these measurements are described and quoted in the example

collaboration with marafford, Jr., C.V. Hayne and P.E. Damon of the E. Taylor of the Unive

is mammoth, excavated in Oklahoma [4], has been dating of associated with We have performed a investigation the dependence of the bone samples or of the bone used in the

measurements are presented in

indicates that results from are in agreement with wood, and are reasonably The remaining chemical which are too young to be described in the publication.

chemical fraction of bone

	Radiocarbon age (years BP)
	11450 ± 320
	11350 ± 340
	11450 ± 350
	10950 ± 450
	10850 ± 400
	10800 ± 300
	10500 ± 350
	10450 ± 400
	9500 ± 400
ing	9350 ± 320
	8000 ± 450
	7250 ± 320
	5100 ± 200

### 2.2 Sunnyside and Yuha skeletons

Results have been published elsewhere of measurements made on various chemical fractions derived from the Sunnyside [6] and Yuha [7] skeletons. These skeletons found in the locations indicated in California, were reputed to have ages of from 20000 to 70000 years. The  $^{14}\text{C}$  content of the samples measured in our laboratory indicate that the radiocarbon age of each of the skeletons is less than 5000 years BP.

### 2.3 Agricultural products

#### 2.3.1 Egyptian wheat seeds

In collaboration with Prof. F. Wendorf of Southern Methodist University and his colleagues, measurements have been made of the  $^{14}\text{C}$  content of several barley and wheat seeds discovered in a late Paleolithic site at Wadi Kubbaniya, in Egypt. Charcoal from the same site has previously been determined by conventional  $^{14}\text{C}$  measurements to have a radiocarbon age of about 18000 years. Results of our measurements on several seeds and on two samples of charcoal from the site are shown in table 4.

Our measurements of the age of charcoal (7 and 8 in table 4) are consistent with previous conventional measurements. The fact that two of the seeds (3 and 5) had  $^{14}\text{C}$  contents greater than that of modern material led us to discover that the laboratory in which seeds nos. 3, 4 and 5 were gold-coated and subjected to SEM measurements had previously been used for  $^{14}\text{C}$  tracer experiments. Therefore, results for these three seeds were considered invalid. There is no reason to expect that the remainder of the seeds (nos. 1, 2, and 6) were contaminated. The  $^{14}\text{C}$  contents of all of these seeds yield radiocarbon ages of less than 5000 years BP and indicate that the seeds were intrusions on the 18000 year old site. The results discussed here have been submitted for publication in another journal.

#### 2.3.2 Early corn in the Southwestern USA

In collaboration with A. Long of the University of

Table 4  
Measurement results from the Wadi Kubbaniya site

Sample	$\frac{(^{14}\text{C}/^{13}\text{C})_{\text{sample}}}{(^{14}\text{C}/^{13}\text{C})_{\text{std}}}$	Radiocarbon age (years BP)
1) Barley seed, brown, site E-78-3	0.90 ± 0.06	820 ± 500
2) Barley seed, black, site E-78-3	0.87 ± 0.06	1100 ± 500
3) Barley seed, Au-coated, site E-78-4	2.39 ± 0.05	modern
4) Barley seed, Au-coated, site E-78-4	0.72 ± 0.02	2670 ± 250
5) Barley seed, Au-coated, site E-78-4	1.33 ± 0.05	modern
6) Barley seed, site E-78-4	0.55 ± 0.01	4850 ± 150
7) Charcoal, site E-78-3	0.114 ± 0.014	17500 ± 1000
8) Charcoal, site E-78-4	0.107 ± 0.007	18000 ± 525

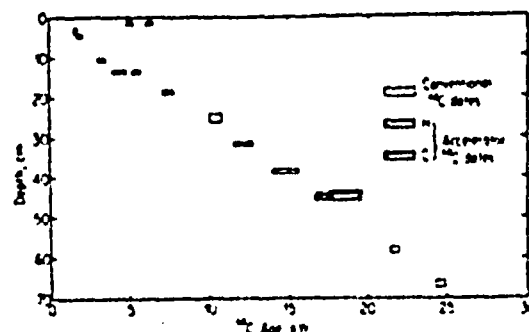


Fig. 4. Radiocarbon ages of samples from a deep-sea core vs the depth at which the samples were taken. The accelerator radiocarbon dates were obtained from foraminifera which were either combusted (C) or hydrolyzed (H) to produce  $\text{CO}_2$ .

Arizona, 12 corn samples have been collected from various sites in the western United States and radiocarbon-dated in the accelerator. Contrary to expectations, no corn has been found with a radiocarbon age of greater than about 2500 years BP.

### 2.3. Deep-sea cores

Experiments directed toward measurements of foraminifera, shells, and coral in deep-sea cores have begun in collaboration with scientists at Scripps Institute and at Wood's Hole. Preliminary results of some of these measurements are shown in fig. 4, where accelerator measurements on specific components of a deep-sea core are compared with conventional measurements. The two types of measurements agree well, except at depths of less than about 15 cm, where the accelerator measurements indicate a degree of mixing not seen by the conventional measurements.

### 3. Summary

We have presented results which indicate that for measurements in the Arizona tandem accelerator mass

spectrometer, to a level of 0.6%, the standard deviation of the ratio  $R = (^{14}\text{C}/^{13}\text{C})_{\text{sample}} / (^{14}\text{C}/^{13}\text{C})_{\text{std}}$  is determined by statistical uncertainties only. Measurements of the  $^{14}\text{C}/^{13}\text{C}$  ratio in about 600 samples have been made in the past 15 months, and a selection of results from these measurements is described. The precision of these measurements has been limited by statistical uncertainties which are determined by the output of the Fe-C heads used for targets. For targets made of modern carbon, the standard deviation of a measurement is about 2%. A new method of target fabrication is being developed which uses catalytically produced graphite. Such targets produce  $^{12}\text{C}^-$  beams about a factor of four greater than the beams from Fe-C targets and shall extend the age limit as well as improve precision of TAMS determinations.

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USGS TECHNICAL PROCEDURE HP-160. R0

Methods for Collection and Analysis of Samples for  
Gas Composition by Gas Chromatography

1.0 PURPOSE.

1.1 To assure the accuracy, validity, and applicability of the methods used to collect and analyze gas samples for composition by chromatography from unsaturated-zone test holes, this procedure provides a guide for USGS personnel and contractors to perform the described activity. From this procedure, the Department of Energy (DOE) and the Nuclear Regulatory Commission (NRC) can evaluate these activities for meeting requirements of the NNWSI Project, and competent, trained personnel can reproduce the work.

1.2 This procedure describes the components of the work, the principles of the methods used, and their limits. It also describes the detailed methods to be used for calibration, operation and performance verification of any equipment. In addition, it defines the requirements for data acceptance, documentation, and control; and it provides a means of data traceability.

2.0 SCOPE OF COMPLIANCE.

2.1 This procedure applies to all USGS personnel and their contractors who may perform work referred to in Para. 1.1, or use data obtained from this procedure if it is deemed to potentially affect public health and safety as related to a nuclear waste repository.

2.2 All data derived from this procedure that are presented to support licensing of the NNWSI Project repository, and any equipment calibrations or recalibrations that may be required shall be in accordance with this technical procedure. Variations are allowed only if and when this procedure is formally revised, or otherwise modified, as described in Section 8.

3.0 PERSONNEL RESPONSIBILITIES. The Principal Investigator (PI) is responsible for assuring full compliance with this procedure. Per QMP-2.02 and QMP-2.03, the PI shall require that all personnel assigned to work under this procedure shall have the necessary technical training, experience, and personal skills, to adequately perform this procedure; and they shall have a working knowledge of the USGS QA Manual. Responsibilities of others - including the reviewer(s), contributing investigators, Branch/NHP Chief, QA Office and the Chief, Branch of NNWSI are as described in Para. 4.3, QMP-5.01.

4.0 DETAILED PROCEDURE. Unsaturated zone gas composition, including carbon dioxide, methane, hydrogen, sulfur hexafluoride, freon 11 and 12, ethylene, ethane, and various other gas concentrations may be determined by gas chromatography. Gas composition information can be used to infer the gaseous-

diffusion properties of the unsaturated porous media to trace-gas diffusion. Such information is needed to assess the dispersion of radioactive nuclides due to the burial of high-level radioactive wastes.

4.1 Objective: To provide instructions for collecting and analyzing gas samples for composition by gas chromatography.

4.2 Methods Used: Glass syringes equipped with two-way stopcocks are used to collect gases from tubing leading to various unsaturated zone horizons. The gases may either be pumped from the tubing into the syringe by peristaltic pump or drawn from the tubing into the syringe by the syringe plunger. The gases collected in the syringe are then injected into a high performance laboratory gas chromatograph and analyzed.

#### 4.2.1 Collection of Gas Composition Syringe Samples

4.2.1.1 Connect the tubing from downhole to the two-way stopcock on the syringe. If tube is being pumped, allow gas to flow into the syringe by opening the syringe stopcock. If tubing is not being pumped, pull back on the syringe plunger to draw gas into the syringe.

4.2.1.2 Eject gas from the syringe by opening the syringe stopcock to the atmosphere and pushing the plunger in.

4.2.1.3 Repeat steps 4.2.1.1 and 4.2.1.2 three times to thoroughly flush the syringe.

4.2.1.4 Allow gas to flow into syringe according to step 4.2.1.1 and close the syringe stopcock to hold gas in syringe.

4.2.1.5 Collect duplicate or triplicate samples at each time and location by the above methods.

4.2.1.6 Label syringes with: borehole #, probe #, date, time, and location of sample collection, i.e., before molecular sieve (BMS), after molecular sieve (AMS), etc.

4.2.1.7 Transport syringe samples to the field laboratory and analyze for gas composition concentrations.

#### 4.2.2 Analysis of Gas Composition Samples

4.2.2.1 Packard 437A Gas Chromatograph: Facing the instrument, the FID exit is on top of the GC, left side, front tube; the ECD exit is about two inches to the rear. Figure 1 shows a diagram of a front view of the GC.

##### 4.2.2.1.1 Definitions for Packard 437A:

Gas Chromatograph (GC) - A gas chromatograph is a high performance laboratory instrument capable of separating a sample into its component parts for analysis. Analyses

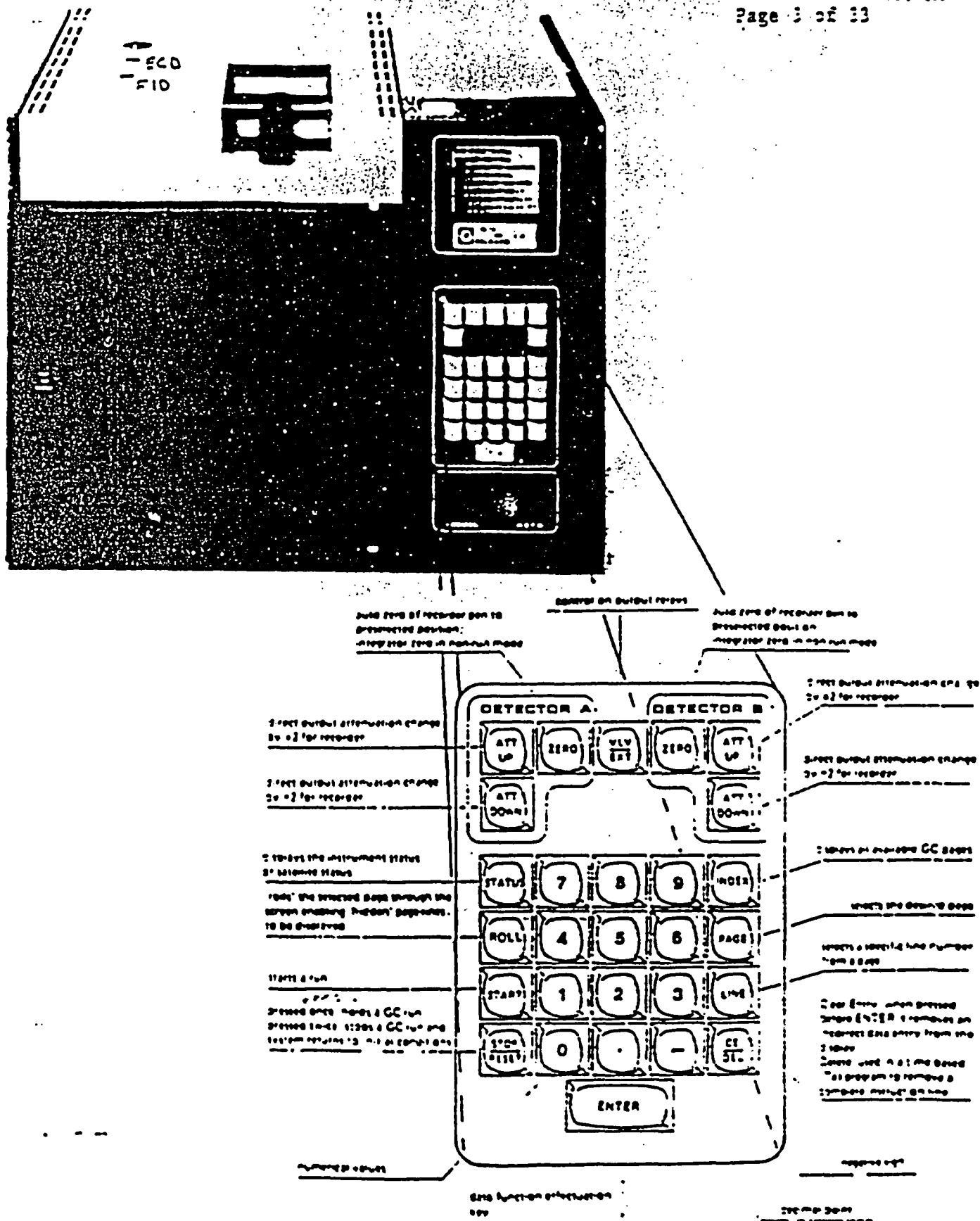


Figure 1. - Packard 437A Gas Chromatograph and Keyboard.

performed by a GC depend upon the type of column, detector, and carrier gas chosen.

**Gas sampling valves** - The sample is introduced through an external inlet port, through an eight-way valve that is solenoid operated, through a 1 Ml sample loop, and excess sample is expelled through an external outlet port. The solenoid valve switches the sample in the sample loop onto the column.

**Detectors** - Small concentrations of gaseous compounds exit the column and enter the detector. The detector responds to these gases and emits an electrical signal proportional to these concentrations. The Packard 437A GC is equipped with two complete detectors and associated analytical systems. A flame ionization detector (FID) is coupled with a methanizer and with a Porapak N column and is used to analyze for halogenated compounds, particularly freons and selected tracers, such as SF<sub>6</sub> and BCF.

**Columns** - The columns are located within a temperature controlled oven. Sample components are retained by column packing material so that their movement through the column is at different rates, thus achieving separation of the various components of the sample. The two columns used are (1) a Porapak N, 80/100 mesh, 2 meter by 1/8 inch stainless steel; and (2) a Carboxpack B, 60/80 mesh, 2 meter by 1/8 inch stainless steel.

**Carrier Gas** - The sample components are transported through the columns by an inert gas, in this case, at least 99.995% pure nitrogen.

**Integrator** - An instrument which receives the detector's signal and mechanically calculates definite integrals. The integrator used with the Packard 437A GC is the Spectra Physics 4290 computing integrator. A front view of this integrator is shown in Figure 2.

**4.2.2.1.2 Apparatus Assembly** - The gas chromatograph requires a draft free, relatively constant temperature laboratory environment. It must be placed on a vibration free bench with sufficient area around it to hold auxiliary equipment such as an integrator, syringes, standards, etc. An outlet to provide 115 volt A.C. service is required.

**External Gas Requirements** - Nitrogen (at least 99.995% purity) is the recommended carrier gas. The FID (a combustion detector) and methanizer require hydrogen gas (99.995% pure) and highest quality compressed air. The ECD requires only the nitrogen carrier gas. In both cases compressed air is necessary to operate the solenoids. These gases should be supplied at a working pressure of 600 kPa (about 85 psi).



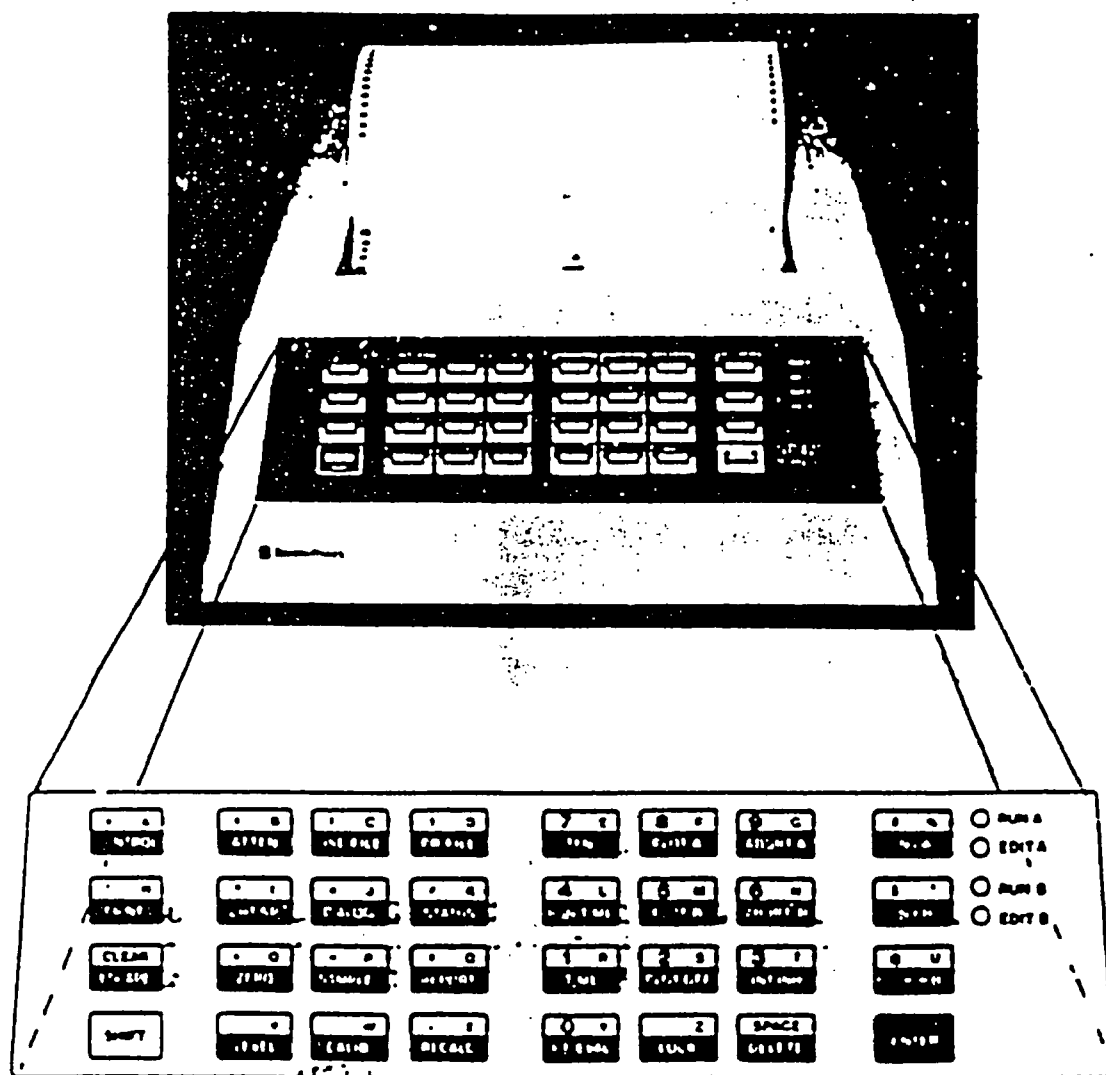


Figure 2. - The SP4290 Computing Integrator and SP4290 Keypad

Various traps should be installed in the gas flow line to eliminate contamination, and possible column and/or detector damage. Oxygen traps should be installed in line in the carrier gas to remove oxygen and trace amounts of sulfur and chlorine compounds. The ECD will be damaged by oxygen, so an indicating oxygen gas trap is used downstream of the oxygen gas trap. A molecular sieve/drierite trap should be used to remove moisture and dust from all gases.

4.2.2.1.3 Instrument start up - Upon receipt of the GC or a prolonged period of non-use (about one year) a verification of good operation might be necessary. In general, every time you are in doubt about the correct functioning of the instrument, a "Performance Evaluation Test" must be performed. See section 3.4 of the Packard manual for this procedure.

4.2.2.1.4 Initial Start Up after unit off for several days to several months.

A) Using both FID and ECD detectors.

- 1) Turn carrier gas (nitrogen) on at the main tank, and set at 600 kPa or about 85 psi. The "CG" regulator on the GC should be set at 300. The GC "air" regulator and "H2" regulator should be closed.
- 2) On the lower front of the gas chromatograph, turn power on and oven on.
  - a) Using a gas flow meter or a soap film flow meter, the carrier gas exiting the FID should be 15 cc/min. with the instrument cool. If it is not, adjust with GC needle valve #1. (See Figure 3.)
  - b) Gas exiting the ECD should be 60 cc/min. if the ECD is to be used. If the FID is to be used and not the ECD, carrier gas flow can be 30 cc/min. in the ECD. NOTE: When the detector temperature is set to 200° C, both detectors are heated to 200° C. If the ECD does not have a good flow of carrier gas or if it should have air introduced while hot, it will be destroyed. If gas exiting the ECD is not 30 (or 60) cc/min., close GC needle valve #3; adjust GC needle valve #2 to 15 or 30 cc/min.; then open GC needle valve #3 for a total reading of 30 or 60 cc/min.
- 3) Turn compressed air on at main tank, and set at 600 kPa or about 85 psi.
- 4) Set the GC hydrogen gas regulator at 200 kPa, and measure the outflow from the FID. It should be 15

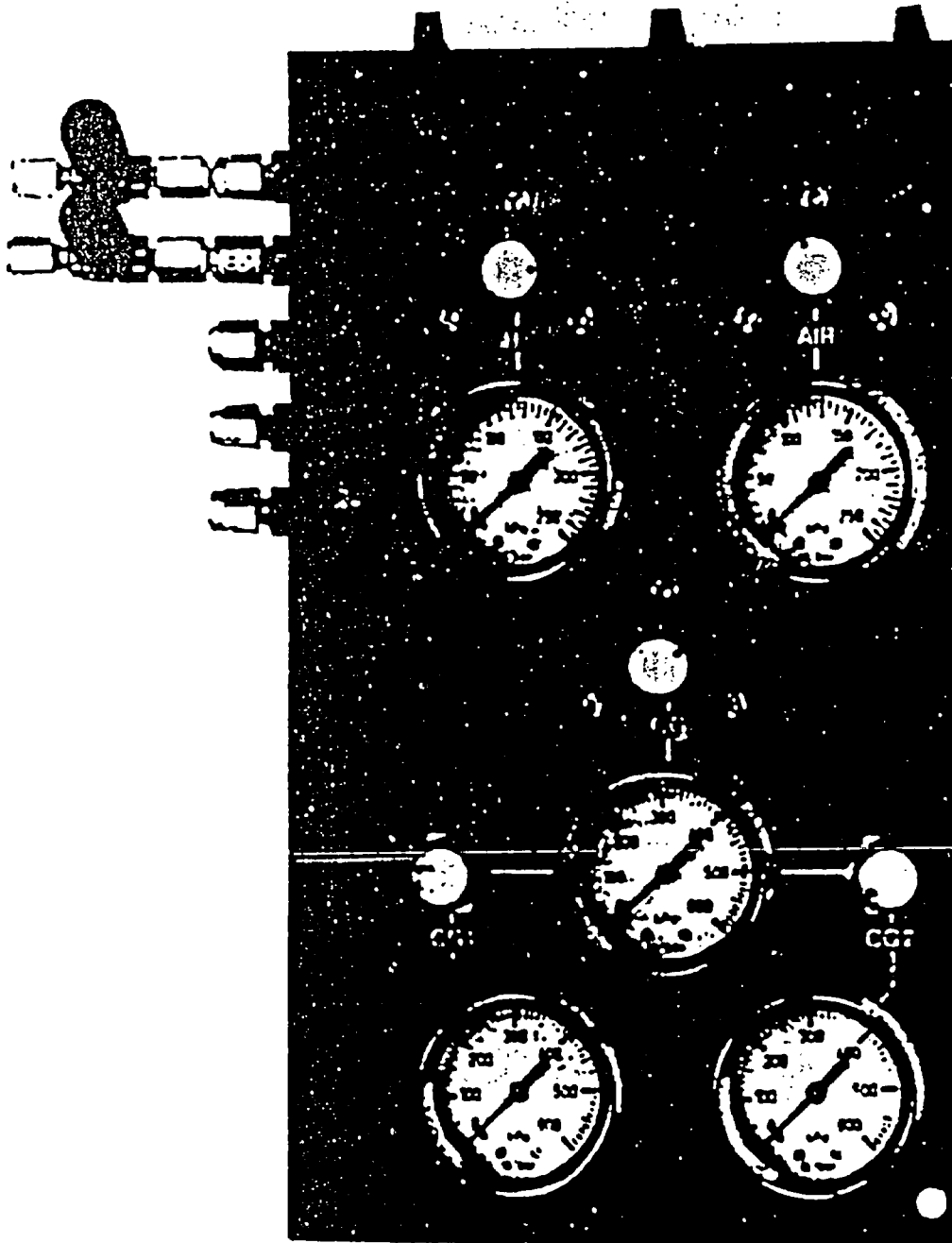


Figure 3. - Gas flow adjustment valves.

c min. hydrogen for a total of 40 cc/min. If it is not, close the hydrogen needle valves #1 (under the hydrogen gas GC regulator) and #2 (far right). Open needle valve #2 to allow 15 cc/min. of hydrogen to go through the mechanizer; then open needle valve #1 to allow 10 cc/min. of hydrogen to go through the FID for a total of 25 cc/min., above the 15 cc/min. nitrogen. Last, turn the GC air regulator to 70 kPa. The outflow from the FID should now be 15 cc/min. nitrogen, plus 25 cc/min. hydrogen, plus 250 cc/min. air, for a total of 280 cc/min. If it is not, adjust the air needle valve #1. The ECD does not receive air or hydrogen. Once the flow of gases through the GC has been adjusted, it tends to be quite stable and rarely needs readjusting. Flows should be checked, however, and readjusted when necessary.

- a) Make a note of the readings on each dial after the GC is at operating temperatures and check each day of use to be sure there is no substantial change in these readings. There could be a change if a compressed gas tank is replaced or becomes too low in pressure or if a leak developed in the system. Rarely, there will be a change with time or by accidentally altering a valve. Changes of a few kPa, assuming the system continues to operate normally, is not cause for concern. More substantial changes would indicate a need for recalibration.

- b) Compressed gas tanks should be replaced when the pressure reaches 400 psi at the gas tank gauge. If the carrier gas tank must be replaced, the detectors should be cooled. Loss of carrier gas while the detectors are hot can result in damage.

- 5) Programming the GC - The LCD display and keyboard on the right front of the instrument (see Figure 1) are used to program temperatures, ranges, and valve operations. This information is currently stored as "Methods" and, barring malfunction or accident, are retained even when the instrument has been shut down.

- a) When the instrument is turned on, the LCD shows "Page Index." Four of the pages are applicable. Pages 1 through 3 contain all of the information necessary to analyze the samples. Page 1 is primarily temperatures; page 2 is primarily ranges for the detector; page 3 is timing for sample injection onto the column. Information contained in these pages is stored on methods

contained on page 5. Method 1 is for analysis with either ECD or FID; Method 2 is overnight standby.

- b) To enter a method, press "Page" "5" "Enter", and the methods page will be displayed. Then press "Line" "2" "Enter", which asks which method is to be loaded. Press "1" "Enter". Method 1 is now loaded.
- o If methods are lost or if minor changes, such as oven temperature or detector range, are required, the following outlines the organization, information, and keystrokes to effect these changes.
  - o To display page 1, for example, press "Page" "1" "Enter". The display shows only part of the total lines making up the page. To display hidden lines press "Roll". When a page is first called up, line number 1 will be blinking. If line number 1 requires an entry (150 for example), press "1" "5" "0" "Enter" and 150 is now entered at line 1 and line 2 will start blinking. If no entry is to be made at line 2 press "Enter" and line 2 will remain unchanged and line 3 will begin blinking. The display will automatically roll to the hidden lines using this method.
  - o Page 1 controls the temperatures at which the GC is operated and turns on the TX mode for controlling the solenoid valves.

Page 1 entries for the FID are as follows:

Line 1.	Column limit	190
2.	Det. Temp.	200
3.	Inj. Temp.	150
4.	Aux. Temp.	350
5.	Oven Init.	50
6.	Oven Fin.	50
7.	Oven Rise	0
8.	Time Init.	4
9.	Time Final	0
10.	Stability	1
11.	Cycles	1
12.	TX Mode	1
13.	Sampler	0

Page 1 for the ECD is the same with the exception of:

Line 4. Aux. Temp. 25 auxiliary  
temperature is used to heat the  
methanizer, which is not used with  
the ECD)  
5. Oven Init. 70  
6. Oven Fin. 70

Page 2 entries for channel A (FID) and chan-  
nel D (ECD) follow:

Line 1. Independ. 12.0  
Channel A.  
5. Range A 2.0 (Range 1 is  
most sensitive and range 3 is least  
sensitive for FID)  
6. 7. and 8. (see note)  
Channel B.  
9. Range B 4.0 (Range 4 is  
most sensitive and range 1 is least  
sensitive for ECD; outside air would  
be done on range 4; a contaminated  
sample might use range 1 or 2)  
10, 11, and 12. (see note)

NOTE: These lines apply to strip-chart recorders.  
There is no recorder used with this GC so  
entries in these lines have no effect.

- o Page 3 is used to operate the solenoid valves  
that switch the gas in the sample loop onto  
the column and then switch back, so a new  
sample can be introduced into the sample  
loop. The TX program, page 3 is as follows:

Line 1. TX time 0.17  
valve/ext. 1 (This switches  
the sample loaded into the loop onto  
the column 0.17 sec. after the start  
of the run; valve 1 is part of the  
FID system)  
2. TX time 4.0  
valve/ext. -1 (four minutes  
after the start of the run the  
solenoid switches the sample loop  
off the column and back into posi-  
tion to receive a new sample injec-  
tion)  
3. TX time 0.17  
valve/ext. 2 (same thing  
but for valve 2, part of the ECD  
system)  
4. TX time 4.0  
valve/ext. -2

As entries are made, the TX program will arrange them in chronological order. To change numbers if desired or reload the program if lost:

- Page 1, line 12 must be "1" to activate the TX program.
- "Page" "3" "Enter" to call up the TX page.
- "Line" "1" "Enter" will ask for a TX time; press "0.17"; the screen will ask for the TX code. Press "VLV/EXT" "1" "Enter".
- Line 1 is complete; now press "Line" "2" "Enter" and continue.

If it is desired to store pages 1, 2, and 3 as a method, go to page 1, line 1: Enter the method number where the program is to be stored, and press "Enter" two times. With the second "Enter", the method is stored.

- o Once the information on pages 1, 2 and 3 are entered, the results can be seen on the status pages. There are 4 pages: one shows the actual and set temperatures for the oven, detector, injector, and auxiliary heating block; one shows the signal and range for the ECD; and another shows the same information on the FID. Lastly, a page that shows the time elapsed since the start of an analysis and the condition of the solenoid valves (if no valve number shows, the valves are set for the injection of a sample into the GC; if valve 1 and 2 are shown, then the valves are on the column, and any sample injected into the GC will be lost). The status pages can be seen by pressing "status" and then "roll" to view the 4 pages.

- 6) Analysis of carbon dioxide, methane, ethane, and ethylene using the FID, methanizer, valve 1, and channel A cord to integrator. Press "Status" and "Roll" buttons on the front of the unit, in that order, to observe the actual and set temperatures.
- 7) When the actual temperatures equal set temperatures ignite the hydrogen gas. This is done by holding the switch on the top of the unit forward, to FID 1 position, for three to five seconds.
- 8) Press "Status" and "Roll" buttons to determine whether hydrogen ignited or not. On \*\*Status\*\* page, detector signal A should be some number other than 0.0. Normally the detector signal on range 2

is 0.6 to 2.5. If detector signal A is approximately 0.03 the hydrogen did not ignite.

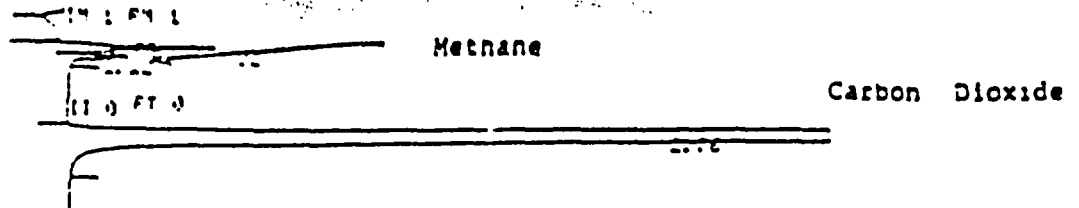
- 9) Try to ignite Hydrogen again using switch on top. If again this doesn't work, open the hood on top of the machine and turn the hydrogen gas pressure level to about 150 to 200. Try to ignite again. If detector signal A is something other than 0.0 ignition was successful and the hydrogen pressure level on top of the machine should be tuned back down to the original setting (the detector signal will decrease when this is done).
- 10) The Spectra-Physics Sp4290 integrator utilizes a three function keyboard (the edit lights - located on the right hand side of the keypad - indicate which key section is currently being assessed for which channel). The blue lower section of each key initiates a system function (edit light does not blink), while the upper portion represents numeric/punctuation characters (upper left) (steady blink) and alpha characters (upper right) (irregular blink). The "shift" key is used to shift the keypad from one key section to the other.
  - a) Turn the integrator on (rear of machine). Connect channel A cable (banana plugs).
  - b) Integrator will ask for date. Input date in the following format: MO/DAY/YR "enter" and time HR:MIN:SEC: "enter".
  - c) For analyses of carbon dioxide, ethane, and ethylene, the only programming required on the integrator is to turn on the peak markers, tic marks which show the beginning and end of the peak, so the analyst can judge if the integration is a proper one (see Figure 4 for good and poor integrations of carbon dioxide).
  - d) If methane analyses are desired, further integrator programming is necessary because the methane peak is on the trailing edge of an injection peak, which in turn follows a negative segment of the injection peak. To get a good, reproducible integration for the methane peak, two steps are necessary: (1) integration must be inhibited during the negative segment of the injection peak; and (2) the positive portion of the injection peak must be forced to tangent skim the trailing downslope so the methane peak will be calculated from the point it takes off from the downslope to the point it rejoins the downslope (see Figure 4).



1141FT EVAL:  
97% 12

CHANNEL 4 INJECT 12-02-87 09:14:15

lab-air  
Good Integration



GASES 12/03/87 09:14:15 CH= "A" PS= 1.

FILE 1. METHOD 2. RUN 1 INDEX 1

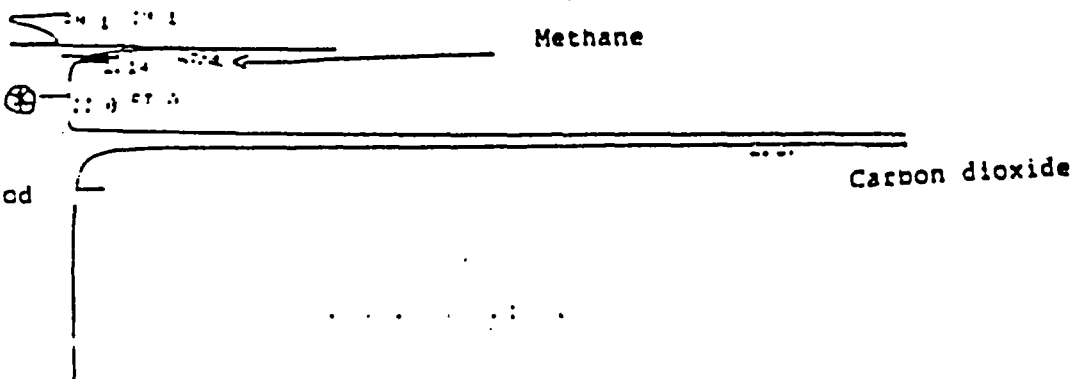
PEAKS	AREA	RT	AREA EC
1	0.474	0.75	0.005 02
2	0.455	0.92	0.007 03
3	0.23	1.12	0.003 04
4	0.001	2.75	0.000 01
TOTAL	100.		10212.00

Methane "05" code indicates a properly  
tangent skimmed peak

Carbon dioxide - tic marks show good  
beginning and ending  
of carbon dioxide peak integration.

CHANNEL 4 INJECT 05-28-87 12:23:20

Methane good,  
Carbon dioxide not good



GASES 05-28-87 12:23:20 CH= "A" PS= 1.

FILE 1. METHOD 2. RUN 1 INDEX 1

PEAKS	AREA	RT	AREA EC
1	0.124	0.77	0.005 02
2	0.040	0.92	0.001 03
3	0.154	1.14	0.003 04
4	0.001	2.75	0.000 01
TOTAL	100.		10030.00

methane - good peak and integration

carbon dioxide - poor integration  
(early tic mark ⊕ )

Figure 4. - Methane and Carbon Dioxide Integrations

- e) To program peak markers and methane analysis, press "Dialog" on the integrator. The integrator will ask for the name of the program: a name can be keyed in or this can be skipped by pressing "Enter". Now the integrator will print "TT-", which is asking for the time of the function. For peak markers, press ".1" "Enter". The integrator will then print "TF-", which asks for the function. Press "P" "M" (code for peak markers) "Enter". Lastly, the integrator will print "TV-" (time function value). In this case, this is an on/off command, so press "1" "Enter". ("1" is on; "0" is off). After the third entry on a line is finished, the integrator automatically goes to the next line and starts again with "TT-".

These timed events for peak markers and for methane analyses are:

TT- .1 TF- PM TV- 1 (peak markers on at .1 sec)  
TT- .15 TF- IM TV- 1 (inhibit integration on at .92 sec.)  
TT- .92 TF- FT TV- 1 (force tangent skim on first peak after .92 sec.)  
TT- 1.5 TF- IM TV- 0 (inhibit integration off at 1.5 min.)

- f) After the final line is entered, keep pressing "Enter" until an "End of Dialog" message is printed. To print out the timed event program just entered, press "PR File" "Enter".
- g) The peak width used is 6, which is the default value for the integrator and so is automatically set. Attenuation is set at 8 ("Atten" "8" "Enter"). Neither attenuation or chart speed affect the integration; they only affect the integrator display.
- 11) After a minimum of 1 hour of warm-up time, press detector A "Zero" "Enter" on the GC keyboard and press "Level" on the integrator keyboard. A number will be printed by the integrator, and it should be somewhere around 1000. Next press "PT Eval", which monitors baseline noise and is an essential step in obtaining good integrations because it effects the beginning and end of the integration of the peaks (indicated by the peak markers). In 50 seconds, the Pt. Eval. is printed out. It is usually around 12, but can be as high as 30. Redo the Pt. Eval. 3 or 4 times to be sure of a stable reading. The GC and integrator are now ready to receive a sample.

- 12) Prior to running unsaturated zone gas samples, collect a couple of samples of atmospheric air and analyze them to see if the baseline, programming, etc. is correct.

Inject a sample of laboratory air to see if the peak markers and programming seem to be operating properly (see Figure 4). If the instrument has been unused, you will probably find extra peaks and noise, particularly around the methane peak. If this happens, raise the oven temperature to 110° C for a minimum of an hour, preferably overnight. Return the oven temperature to 50° C, and the analyses should be clean.

- 13) A minimum of three carbon dioxide standards are with the GC: A 0.50% (v) carbon dioxide standard is the primary standard; a 0.051% (v) carbon dioxide and a 1.0% (v) carbon dioxide standard are the working standards. All of these standards have been verified against a 0.51% (v) carbon dioxide standard located in the U.S. Geological Survey laboratory in Reston, VA. Everyday the 0.051 standard should be verified against the 0.50 standard. If samples are encountered in the 0.5 to 1.0% carbon dioxide range, then the 1% standard should also be verified against the 0.50 standard. The response of the GC has been linear in this range, so the 0.051 standard may be used as the working standard to be used throughout the day.

The 0.051 carbon dioxide standard also contains 3.0 ppm (v) methane and serves as the primary and working methane standard. There is a 2.34 ppm (v) and a 9.123 ppm (v) methane standard for ethylene (2.0 ppm (v)) and ethane (2.1 ppm (v)) is also with the GC.

- 14) Injection of samples into this system is open ended; which means that analyses are done at ambient barometric pressure. As the barometer changes, the analytics change. For this reason, a standard must be analyzed every 6 analyses. If the standard changes over the course of 6 analyses the change should be verified by reanalyzing the standard in duplicate or triplicate. Each 6 samples are calculated based on the initial and final standards bracketing them.

B) ECD operation - To use the ECD for tracer or Freon analyses requires only a few changes from those outlined for the ECD and FID.

- 1) The ECD requires only nitrogen as the carrier gas. No hydrogen is used, and air is used only to operate

the solenoids. The adjustment of carrier gas to 30 cc/min. + 30 cc/min. is described in Para. 4.2.2.1.4 A 2 b).

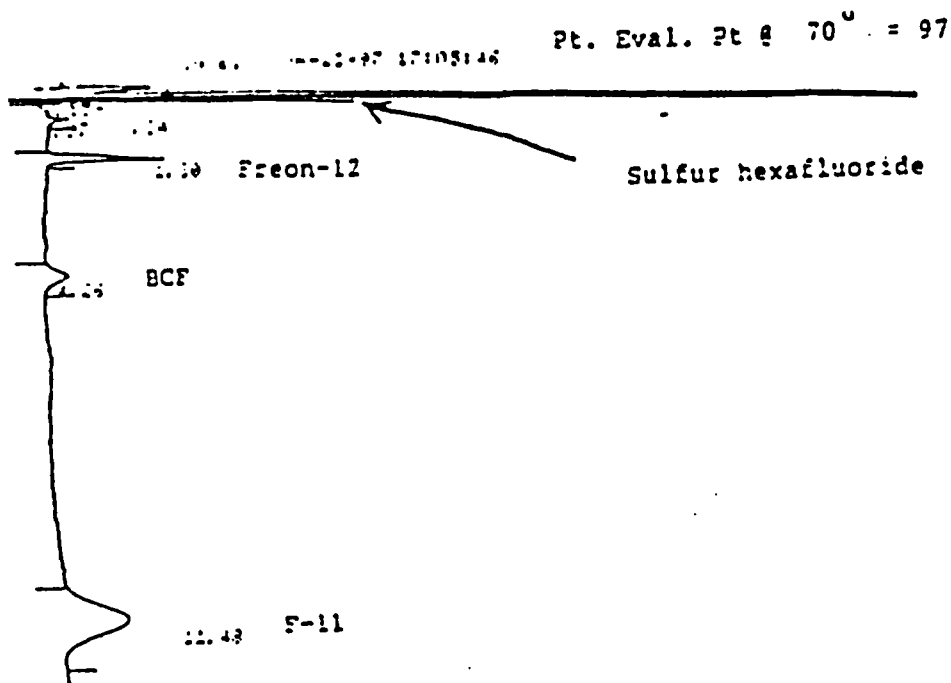
- 2) Temperature settings for the injector (150° C) and detector (200° C) are the same as for the FID. The oven is set at 70° C for analysis and 110° C for overnight standby. The auxiliary can be set to room temperature because it is used only to heat the methanizer, used only with the FID.
- 3) Samples are now injected into the sample inlet marked ECD. The zeroing of the baseline is now done with Detector B "Zero". The GC status page for Channel B shows the ECD signal. The GC range adjustments are now on Page 2. Channel 3. Low level. near atmospheric samples should be analyzed on range 4, the most sensitive ECD range. The integrator must have the Channel B cord (banana plugs) plugged in, and it need be programmed only for peak markers. The Pt. Eval. ms be near 100. Depending on range setting, the integrator attenuation may be put at 8, 32, or even 64.

Figure 5 shows an analysis for SF6, F-12, and F-11. A 1 ppm (v) standard for each of these is with the GC.

- 4) If the GC is being used daily, it is best to leave it up and running. Overnight the column temperature (oven temperature) should be raised to 110° C. If, to conserve compressed air and hydrogen it is desired to put the GC on overnight standby, use the GC keyboard to set the detector to 25° C, injector to 25° C, auxiliary to 25° C, and oven to 110° C (this may be stored as a method - see Paras. 4.2.2.1.4 A 5 a) and b) above) turn hydrogen and compressed air off at the tank. Leave carrier gas flowing.

#### 4.2.2.1.5 Start up for carbon dioxide analyzer after Gas Chromatograph has been on overnight standby.

- A) Turn compressed air tank on at tank.
- B) Turn hydrogen gas on at tank.
- C) Use the keyboard on the front of the unit to enter the working method (Method 1) Press the buttons in the following order: "Page", "5", "Enter"; "Line", "2", "Enter"; "1", Enter.
- D) Press "Status" and "Roll" buttons on the front of the unit, in that order, to observe the result. Tempera



04-22-87 17:05:46 CH= "A" FS= 1.

FILE 1.	METHOD 0.	SUM 2	INDEX 3
PEAK	AREA	ST	AREA BC
1	0.14	0.12	12155 02
2	29.875	0.42	3562741 02
3	0.115	0.35	11122 01
4	0.023	0.34	1023 02
5	0.029	0.27	2458 01
6	0.182	1.3	12157 01
7	0.075	4.25	7249 01
8	0.522	12.43	45055 01
TOTAL	100.		1622082

— SF6

— F-12

— BCF

— F-11

Figure 3. - Satisfactory integration of freons and tracers.

tures that the unit is set for the oven, detector, injector and auxiliary will be visible.

- E) Wait for the actual temperatures to equal the set temperatures.
- F) When the actual temperatures equal set temperatures ignite the hydrogen gas. This is done by holding the switch on the top of the unit forward, to FID 1 position, for three to five seconds.
- G) Press "Status" and "Roll" buttons to determine whether hydrogen ignited or not. On \*\*Status\*\* page, detector signal A should be some number other than about 0.03. If detector signal A is near 0.03 the hydrogen did not ignite.
- H) Try to ignite hydrogen again using switch on top. If again this doesn't work, open the hood on top of the machine and turn the hydrogen gas pressure level to about 150 to 200. Try to ignite again. If detector signal A is something other than about 0.03 ignition was successful and the hydrogen pressure level on top of the machine should be turned back down to the marked level.
- I) On the front of the gas chromatograph check to see if the signal detector A has stabilized (Paras. 4.2.2.1.4 A 10 a) and b) above). If the signal has stabilized, on front of GC, press detector A "Zero" to zero the baseline.
- J) On the integrator press "Level". A number will be printed by the integrator. If this number is close to 1000 then the integrator and GC are ready to run samples. Press "PT EVAL", in about 50 second a number near 12 or possibly as high as 30 will be printed out. Redo the "PT EVAL" several times to be sure of a stable reading.
- K) Prior to running unsaturated zone gas samples, collect a couple of samples of atmospheric air and analyze them to see if the baseline, programming, etc. is correct.

#### 4.2.2.1.6 Running Samples

- A) Connect syringe to "sample in" injection port on the back of the gas chromatograph.
- B) Gently inject the sample.
- C) Push "Start/Reset" button on the top of the gas chromatograph (the light in the button will be off - not blinking - prior to pressing it). Upon pressing the button the integrator will begin operation.

- D) Wait, without disturbing the syringe, until the solenoid clicks. The click occurs when the sample is injected into the GC column. The syringe can be removed from the injection port after the solenoid clicks.
- E) When the solenoid clicks again (4 minutes), and if all of the constituent values desired have come off on the integrator printout and have been terminated by a tick mark, push "INJ A" on the integrator and analytical results will be printed out. The GC will automatically reset itself for the next sample.
- F) Write the sample identification on the integrator printout.
- G) Write the sample ID, Date, Time, and desired constituent areas in GC log book (Attachment 1). Fill out a Sample Inventory Form (SIF) (Attachment 2).

#### 4.2.2.1.7 Setting the Gas Chromatograph on overnight standby.

- A) Turn off hydrogen gas at tank.
- B) Turn off compressed air at tank.
- C) Use the keyboard on the front of the unit to enter overnight standby (Method 2). Press the buttons in the following order: "Page", "5", "Enter"; "Line", "2", "Enter"; "2", "Enter".

#### 4.2.2.1.8 GC shutdown procedures.

- A) Turn hydrogen off at the main regulator.
- B) Turn compressed air off at the main regulator.
- C) Set oven, injection, detector, and auxiliary temperatures to room temperature.
- D) When detectors have cooled to room temperature, turn the carrier gas off.
- E) Close the GC regulators for compressed air, hydrogen, and the carrier gas.
- F) Turn oven off.
- G) Turn main power off.

#### 4.2.2.1.9 Troubleshooting

- A) The FID will not ignite, even when the hydrogen GC regulator is turned to the maximum setting. This

probably is an indication that the ignitor has shorted or broken a filament. Put hydrogen GC regulator back to its normal setting, and light with a butane lighter (NEVER WITH A MATCH).

- B) Peak markers are indicating that integration of the peaks is starting early or late (Figure 4). This can be caused by changes in baseline noise; redo Pt. Eval. a couple of times, redo standards. If integration is proper, continue analysis. This can also be caused by a contaminated sample. If this does not work, baking the column at 110° C may help. The oven must be returned to 50° C, and standards analyzed before continuing with samples.
- C) Nonlinearity of 0.05% (v) and 1.0% (v) carbon dioxide standards. Go to GC page 2, and change the range to 3 for detector A and redo the standards. If they are now linear, analyze samples in the 1.0% (v) and greater range on 3. Whenever ranges are changed, the detector should be zeroed, the "Level" checked, "Pt. Eval" done, and standards must be reanalyzed.
- D) Methane is not being tangent skimmed or is not being integrated properly. In order for methane to be tangent skimmed, the forced tangent skim must be started just prior to the retention time for the positive injection peak. Sometimes retention times change a little, so the integrator must be reprogrammed for FT (force tangent skim). Put the integrator in "Dialog" mode, hit "Enter" until you come to the FT line; then for "TT-" enter the time now entered as a minus time, enter the remaining two entries exactly as they are. When the integrator starts a new line with "TT-" put in a corrected time for the positive injection peak, enter the remaining two entries exactly as they are. Continue to push "Enter" until you are out of Dialog, and test the new entry with an air sample.
- E) You inject a sample, push Start, and nothing happens. The solenoid valves have accidentally gotten out of phase. Go to "Status" and "Roll" to look at the "Time Elapsed" page. "VLV" gives the position of the valves. If this line shows "VLV 1 (and/or) 2", this means the valves are switched onto the column and you cannot inject a sample. If this line shows "VLV " (no number shown), this means that the valves are ready to accept a sample and start an analysis. If the valve numbers are shown on the page, they can be switched by the following strokes on the GC keyboard: "EXT/VLV" "-." "1" "Enter". Valve 1 will switch to accept a sample injection, and the number will disappear off of the screen.



4.2.2.2 Hydrogen Analyzer - The hydrogen analyzer is a RGD2, reduction gas detector manufactured by Trace Analytical. A front view of the RGD2 is shown in Figure 6.

4.2.2.2.1 Definitions specific to hydrogen analyzer

Sample injection valve - A six-way rotary valve is used for sample injection.

Detectors - Small concentrations of gaseous compounds exit the column and enter the detector. The detector responds to the gases and emits an electrical signal proportional to their concentrations. This detector is a Trace Analytical Reduction Gas Detector (RGD2), sensitive to hydrogen in the low ppb to low percent concentration range.

Columns - The column is plumbed between the sample injection valve and the detector. It is supported by a ring-stand and is in the open. Analyses are done at room temperature. The column is a five foot by 1/8-inch stainless steel 100/120 mesh Carbosieve SII (Supelco).

Integrator - An instrument which receives the detectors signal and mechanically calculates definite integrals. The integrator used for hydrogen analysis is a Hewlett Packard 3390A. A front view of the HP 3390A is shown in Figure 7.

Gas Chromatograph (GC) - A gas chromatograph is a high performance laboratory instrument capable of separating a sample into its component parts for analysis. Analyses performed by a GC depend upon the type of column, detector, and carrier gas chosen.

Carrier Gas - The sample components are transported through the columns by an inert gas, in this case, at least 99.995% pure nitrogen.

4.2.2.2.2 Apparatus Assembly - The gas chromatograph requires a draft free, relatively constant temperature laboratory environment. It must be placed on a vibration free bench with sufficient area around it to hold auxiliary equipment. An outlet to provide 115 volt AC service is required.

External gas requirements - Nitrogen (at least 99.995% purity) is the recommended carrier gas.

A catalytic combustion filter is supplied with the detector. Carrier gas must pass through the catalytic combustion filter, and finally through a water/organic trap before going to the column and detector.

4.2.2.2.3 Instrument start up



Figure 6. - Hydrogen Analyzer.

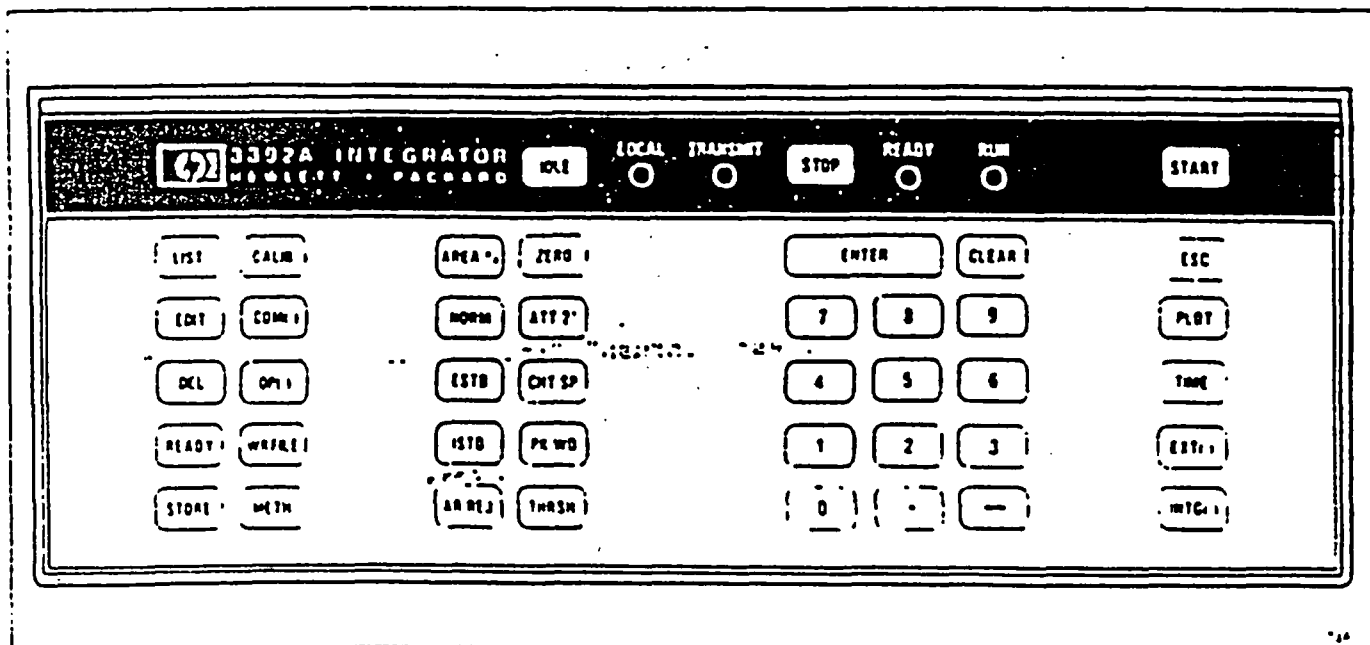
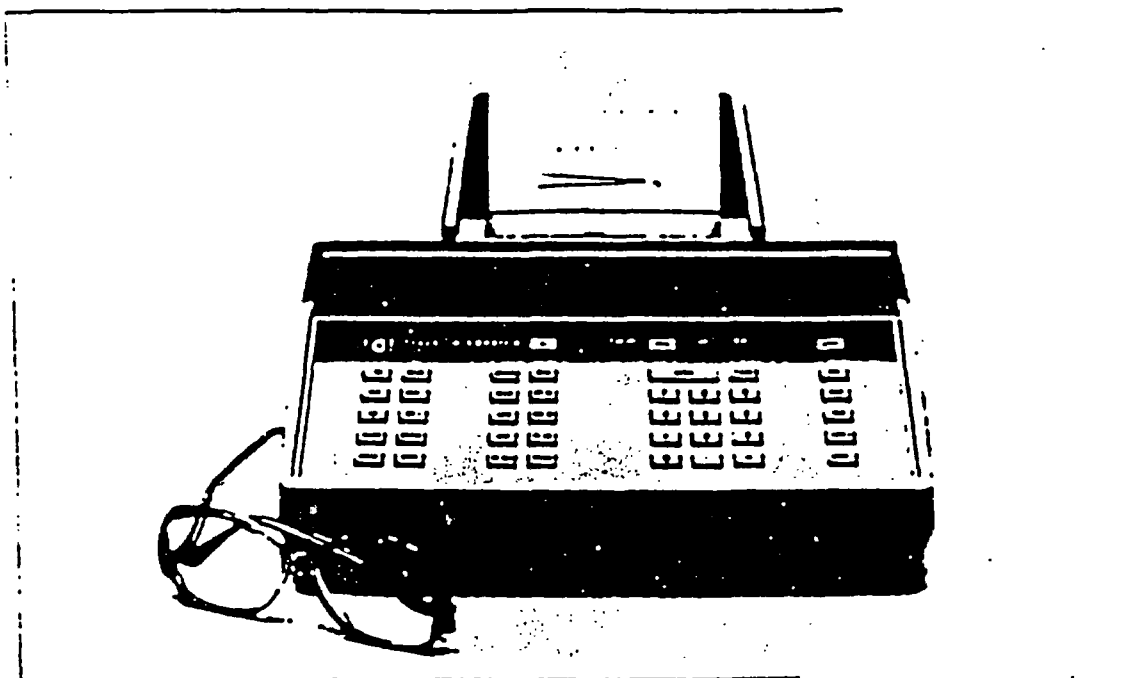


Figure 2-1. HP 3390A Keyboard

Figure 7. - Hewlett Packard 3390A computing integrator.

- A) Turn the carrier gas on at the main tank and set at 30 psi. A plug is on the exit of the detector (back of the detector; end of trap). This should be removed.
- B) Adjust flow using the needle valve between the tank regulator and the catalytic filter.
- C) Turn the catalytic filter on. Attach a Gasmet or other flow meter to the downstream side of the filter on the back of the detector. The flow should be about 20 cc/min. (This is not critical: 18-25 cc/min. will give good results.)
- D) Facing the instrument, turn the "heater" (right front of instrument) on. The "heater" needs to have at least four hours warm-up and overnight warm-up is better. The "heater" should remain on for the duration of use. As long as the "heater" is on, carrier gas must flow through the detector.
- E) After the "heater" has been on for a minimum of four hours, turn the "Photometer" (left front of instrument) on. The "Photometer" needs about an hour of warm-up before starting use. The "Photometer" should be turned off overnight. The "range", front left, should be set at 1.
- F) Turn the integrator on (switch is on the back of the instrument).
- G) After a minimum of one hour warm-up with the "Photometer" on, do the following keystrokes: "Att 2" "4" "Enter" to set integrator attenuation to 4. "CHT SP" "0.5" "Enter" to set chart speed to .5 cc/min. Peak width is set to 0.04 by default. Press "List" "Zero" and a number will be printed. On the detector, turn the "Zero" knob until "List" "Zero" on the integrator prints "0.00". Press "Thrush" "Enter" and in a few seconds a number will be printed. The number will probably be 5 or 6. This is a measurement of baseline noise. Redo the above steps to be sure the "Thrush" number is consistent.
- H) Two entries must be placed in the "Time" table.
  - 1) First, the following keystrokes will make the integrator stop 6 minutes after the analysis began. "Stop" "Time" "6.0".
  - 2) Before the second and final entry, laboratory air samples must be analyzed to obtain the retention time for the hydrogen peak.

- a) Analyze three laboratory air samples, and note the retention time for the hydrogen peak. With greatest weight given to the final lab air analysis, the final step in programming the integrator is to make it consider the hydrogen peak as a solvent peak, and thereby continue integrating its trailing edge until it is back to baseline. The following are the keystrokes: "INTG()" "3" "Time" "(set the time 2 to 3 seconds before the retention time of the hydrogen peak)" "Enter".
  - b) Analyze another laboratory air sample. If the time entered is working properly, the analytical report should show under "Type" (see Figure 8) an "SBB", "SPB" or "SBP". The "S" indicates the hydrogen was treated as a solvent peak. The other letters indicate the peak was integrated from baseline to baseline or from a baseline penetration to baseline.
  - c) If the current report does not indicate "S" for the hydrogen peak, delete the current retention time by typing exactly the same thing, but put a "." in front of the "3" and then retype the entire entry with another retention time and test again.
  - d) Once the hydrogen is indicated as a "S" peak, all of the above can be stored as a method. This is done by the following: "Delete" "Meth" "1" "Enter", then "Store" "Meth" "1" "Enter", then "Meth" "1" "Enter". The method is now stored, and it is loaded and ready for standards and samples. If the power does not fail, the method will remain stored. To print the method (see Figure 8), press "List" "Meth" "1" "Enter".
- I) Each day, the "Thrush" must be done and the retention time of the hydrogen peak must be checked, and if necessary, the method changed accordingly. The three steps above of deleting the method, storing it, and entering it must be done in order to change the method. Always have the method printed out for both verification and for a record to go with the day's analysis.
- J) A 5 ppm (v) standard is with the GC: clean outdoor air (away from building and/or traffic) samples should be analyzed against the 5 ppm (v) standard every morning. Outdoor air should have a hydrogen concentration of 0.45 to 0.55 ppm (v).
- K) Injection of samples into this system is open ended, which means that analyses are done at ambient barometric

Hydrogen standard = 5ppm

Hydrogen - good integration

indicating hydrogen  
peak created as  
a solvent

1012 4442 1325500  
 00 72(1)R 1 40000000

CA

## Hydrogen

26(AM)			
81	DATE	TUES	NR(AM)
" 17	1953	(C) 1	" 128
" 42	1952	"	" 316
" 17	1954	"	" 464

[illegible]

Figure 8. - Integrator printout for hydrogen analyzer.

pressure. As the barometer changes, the analytics change. For this reason, a standard must be analyzed every six analyses. If the standard changes over the course of the six analyses, the change should be verified by reanalyzing the standard in duplicate or triplicate. Each six samples are calculated based on the initial and final standards bracketing them.

#### 4.2.2.2.4 Running samples

- A) The sample injection valve is a 6-way valve. The various positions are numbered on the bottom of the valve and color coded on the tubing extending from the valve. The sample loop is a 1 ml loop and is color coded: red (position #2) and green (#5). Sample injection is color coded: black (#3); when flushing and loading a sample, the pointer on top of the valve must be in the "Load" position (marked on side of valve).
- B) After injecting the sample, wait 5 seconds, supporting the valve in one hand, move the pointer to the "On Col." position and quickly press "Start" on the integrator. The retention time for hydrogen is about .45 to .55 minutes (Figure 8). The valve may be switched back to "Load" position anytime after the hydrogen peak is completed. (Peaks at 2 to 4 minutes are carbon monoxide peaks).

4.2.2.2.5 Overnight Standby - The only necessary step is to turn the photometer off. Carrier gas must continue to flow.

#### 4.2.2.2.6 Hydrogen Analyzer shutdown procedure.

- A) Turn photometer off.
- B) Turn heater off.
- C) Turn integrator off.
- D) When the detector is cool turn the catalytic filter off.
- E) Turn the carrier gas off.
- F) Plug the outflow from the trap on the back of the detector.

#### 4.2.2.2.7 Troubleshooting

- A) The only problem encountered has been in turning the 6-way valve. If the valve does not seat properly, gas flow may be cut off. The baseline will suddenly go off-chart. If the Gasmat flowmeter has been left connected to the outflow at the back of the detector, a glance will indicate what the problem is. This is serious

because the detector can be damaged if it is hot and has no carrier gas flowing through it. Jiggling the valve will seat it and gas flow should immediately be restored. The instrument will require some stabilization time before continuing with the analyses. The "Thrush" should be checked.

- 4.3 Alternative Method(s) Considered: No alternate methods apply. Collecting and analyzing gas samples for gas compositions while in the field can only be done by these methods.

4.4 Materials/Equipment Required:

- o Packard 437A Gas Chromatograph and its associated parts, i.e., electrical connections, gas plumbing connections, columns, detectors, oven, etc.
- o Spectra Physics SP 4290 computing integrator and its associated parts, i.e., electrical connections, printer/plotter paper, etc.
- o (name and #) Hydrogen Analyzer and its associated parts, i.e., electrical connections, gas plumbing connections, columns, detectors, etc.
- o Hewlett Packard 3390A computing integrator and its associated parts, i.e., electrical connections, printer/plotter, paper, etc.
- o External gases, i.e., Nitrogen, Hydrogen, Compressed air
- o Gages, reducing valves and pressure regulators associated with external gas use
- o Standard gases, i.e., carbon dioxide (between .05% and .5%), methane (between .01% and .1%), Sulfur Hexafluoride, Freon, Hydrogen and other gases at the required concentrations
- o Gas filters, i.e., molecular sieve filter/dryer, charcoal filters, and oxygen filters.
- o 220V/50Hz or 115V/60Hz power supply and possibly a voltage stabilization unit.
- o Assorted spare fuses, see GC operators manual
- o 10 cc glass syringes with 3-way stopcock
- o Tool kit, includes crescent wrenches, screwdriver, allen wrenches, open end wrenches, socket wrench set.
- o Operators manuals for the gas chromatographs and integrators
- o Gas chromatograph lab book (Attachment 1 shows format)
- o Field Summary data sheet (Attachment 2)
- o HP-160, R0
- o HP-56, R1

4.5 Assumptions Affecting the Procedure:

4.5.1 It is assumed that the gas analyzed is collected in such a manner so as to be representative of uncontaminated formation gas.

4.5.2 It is assumed that the external gases and the standard gases are of the necessary quality and that the stated standard concentrations are indicative of the actual concentrations.

- 4.6 Data Information: Data type and form are as described in Attachments 1, 2 and 3.



4.6.1 Quantitative/Qualitative Criteria

4.6.1.1 Gas filters will show if there is contamination of the external gases.

4.6.1.2 Knowing the approximate concentration of atmospheric carbon dioxide and hydrogen the correct relative range for integrator curve areas of other standards and samples can be determined.

4.6.1.3 Integrator level values allow determination of proper start up conditions.

4.6.1.4 Detector signal values allow determination of proper start up conditions.

4.7 Limitations:

4.7.1 The accuracy of the determined gas compositions are within the limits of the gas chromatograph's accuracy.

4.7.2 Possible contamination of formation gases by borehole construction and stemming materials.

4.8 Other: This procedure interfaces with technical procedure NWM-USGS-HP-56, R1.

5.0 CALIBRATION REQUIREMENTS. Calibration is required as a part of this technical procedure. When calibrations are required, all instruments and methods when applicable, will be calibrated in compliance with the Instrument Calibration Procedure (NNWSI-USGS-QMP-12.01) prior to obtaining data that will be cited to support licensing the NNWSI Project.

5.1 Calibration Responsibility: The PI is responsible for calibrations required by this procedure. Calibration will be in accordance with procedures described or referenced in Para. 5.2. Maintenance of all calibration records described in Para. 5.3 may be done by a contributing investigator under the direct supervision of the PI.

5.2 Calibration Procedure: The equipment which must be calibrated for this hydrologic procedure are the flow meter, and the gas chromatographs.

5.2.1 Calibration of the flow meter is performed before and after each sampling trip. A displacement curve is drawn for each calibration, and is used to determine the flows for specific meter readings. Details of this calibration procedure can be found in HP-56, R1.

5.2.2 Calibration of the Gas Chromatographs

5.2.2.1 Column conditioning - to condition new columns follow the instructions on p. 26 of the Packard operator's manual, section 2.13.

5.2.2.2 Flow measurement - The flow of the carrier gas, hydrogen, and compressed air must be accurately measured. The flow meter can be directly attached to the detector exit.

5.2.2.3 Leak testing - After the installation of the columns check the column connections for leaks. All other gas line connections should also be checked. It is also important to check the main pressure regulators at the gas cylinders to ensure that all gas connections to the gas chromatograph are absolutely leak tight.

5.2.2.4 Gas settings - The gas settings for the flame ionization detector (FID) are fairly critical. The nitrogen carrier gas should be set at an optimum rate of 15 ml/min. A hydrogen flow rate of about 250 ml/min. is required for correct flame burning. A flow of 25 ml/min. is the required minimum for compressed air.

5.2.2.5 Performance evaluation test - After a prolonged period of non-use this test may be necessary. This test is performed under standard conditions, with a standard sample and will lead, under normal conditions, to a chromatogram equivalent to the example in the operator's manual.

5.2.2.6 Zeroing the integrator output - Each time when a new input range is selected, an integrator output zero is performed. Zero A and Zero B keys are used to zero the integrator. These keys are active in the non-run mode only.

5.2.2.7 Standard gases - Standard gases and an atmospheric sample should be run prior to running unknown samples. Standard gases should be run after every three or four samples until the standard sample concentration has stabilized. Once the standard has stabilized the standard gases need be run only every six to eight unknowns. The formula for determining unknown sample concentrations using standard gases is: unknown sample area times known standard concentration in percent divided by the mean of the standard gas area of the standard run prior to and after the unknown.

5.3 Calibration Records: Calibration data will be entered in a notebook or other organized documentation. A field notebook will be used if the test equipment is used in the field. These notebooks or other documents shall be maintained as described in the Document Control Procedure (NNWSI-USGS-QMP-6.01) and stored in accordance with the QA Records Management Procedure (NNWSI-USGS-QMP-17.01). Minimum data will include instrument type, its identification and location, calibration procedure used, its date, the standard used, its range and accuracy, recalibration due date, responsible division subunit, any pertinent observations and the name of the person calibrating the instrument. Calibration entries shall be signed and dated by the person performing the calibration and filed with the QA Office.

5.4 Labeling of Equipment Calibration Status: In compliance with NNWSI-USGS-QMP-12.01, a sticker will be affixed to each piece of equipment

used in this procedure denoting the calibration status according to one of the following three categories:

- a) Equipment identification, date calibrated, date recalibration is due, procedure number and calibrator;
- b) Equipment identification, "OPERATOR TO CALIBRATE", and the procedure number; or
- c) Equipment identification and "NO CALIBRATION REQUIRED".

6.0 IDENTIFICATION AND CONTROL OF SAMPLES. Samples will be collected as part of this procedure.

6.1 Sample Identification. As part of the data records and documentation, and in compliance with QMP-8.01, all samples will be identified as follows: borehole number, probe number, replicate number, collection date, collection time, and collection location.

6.2 Control and Storage: In compliance with QMP-8.01, the collected and identified samples shall reside in the custody of the sample collector until analysis. The gas syringe samples are analyzed immediately after collection and are destroyed as a part of the gas composition analysis and thus control and storage procedures will not be necessary.

6.3 Special Treatment: Gas composition samples collected in glass syringes should be analyzed as soon as possible after collection.

7.0 QUALITY ASSURANCE RECORDS. All information collected and recorded under this procedure that is to be used in support of the NNWSI Project licensing process is required to be a part of the official USGS record. Input needed to process the information as a record includes: title or description, subject, originator, date of the document, and whether it is an original, a revision or an addendum.

Specific items from this procedure that will constitute a record are:

- o Field log book
- o GC lab book (Attachment 1)
- o Gas chromatograph log book
- o Flow meter calibration log book
- o Copy of HP-56, R1
- o Field Data Summary Sheet (Attachment 2)

7.1 Notebooks or other organized documentation will be prepared as appropriate by the PI or a contributing investigator to record data from this procedure and shall include any information considered by the originator to be pertinent. When data are kept in loose-leaf form, each page will be numbered consecutively and chronologically. All documents will be signed or initialed and dated by the investigator on a daily basis when entries are made. Any revisions will be lined out, initialed, and dated.

- 2.2 All data collected and the applicability of methods used in this procedure will be reviewed and cosigned by a peer or supervisor of the investigator knowledgeable with the objectives of this procedure in accordance with MM-USGS-OMP-6.01, Para. 4.2.2; and as such are acknowledged by both the investigator and the reviewer to be acceptable and meaningful data that meet appropriate quantitative and qualitative acceptance criteria. Unacceptable data shall be identified appropriate to the form of the data.
- 3.0 MODIFICATIONS. When field modifications become necessary, per Para. 4.8, OMP-6.01, the PI shall fully document the changes, submit the documentation for the same review signature and distribution process as for the original procedure, and indicate whether the change should result in a subsequent revision to the technical procedure. The documentation will be reviewed within 30 days.
- 9.0 REFERENCES CITED.
- Spectra-Physics. 1985. SP 4290 Computing Integrator operators manual. San Jose, California. p. 160.
- Packard Instruments. 1983. Operation manual for Packard Gas Chromatograph 437A. The Netherlands. p. 144.
- Trace Analytical. RGD2- Reduction Gas Detector - Operators Manual. Menlo Park, California. p. 29.
- Hewlett-Packard Co.. 1983. HP-3392A Integrator Operators Manual. Avondale, Pennsylvania. p. 134.
- 10.0 ATTACHMENTS. The following attachments are included with this technical procedure for the purpose of examples as described:
- Attachment No. 1 - GC Lab Book Data Analysis Format  
Attachment No. 2 - Field Data Summary Sheet

- 11.0 APPROVAL. This technical procedure shall become effective upon its approval as noted by completion of all the following signatures and dates.

Charles A. Peters  
Prepared by: C. A. Peters

6-9-88  
Date

Jean Woodward  
Technical Reviewer: J. Woodward

June 10 1988  
Date

K.W. Causseaux  
NHP QA Coordinator: K. W. Causseaux

6-16-88  
Date

Daniel C. Gillies  
Acting NHP Chief: D. C. Gillies

6-16-88  
Date

L. R. Hayes  
Chief, Branch of NNWSI: L. R. Hayes

6/16/88  
Date

J. R. Willmon  
Quality Assurance: J. R. Willmon

6/10/88  
Date

# Attachment 1 -- Gas Chromatograph Lab Book Data Analysis Format

Date: MM/DD/YY  
Integrator Level: \*\*\*\*

Lab Air Area: \*\*\*\*  
Carbon Dioxide .05% Standard Area: \*\*\*\*  
Carbon Dioxide .5% Standard Area: \*\*\*\*  
Methane .234% Standard Area: \*\*\*\*  
Other Standards Area: \*\*\*\*

Borehole Number: \*\*\* Date: MM/DD

Probe Number: aa	Tube Number: a	Sampling Location: aaa	Collection Time: tmm	Gas Area: ****	Gas Concentration: aa
Probe Number: aa	Tube Number: a	Sampling Location: aaa	Collection Time: tmm	Gas Area: ****	Gas Concentration: aa
Probe Number: aa	Tube Number: a	Sampling Location: aaa	Collection Time: tmm	Gas Area: ****	Gas Concentration: aa
Probe Number: aa	Tube Number: a	Sampling Location: aaa	Collection Time: tmm	Gas Area: ****	Gas Concentration: aa
Probe Number: aa	Tube Number: a	Sampling Location: aaa	Collection Time: tmm	Gas Area: ****	Gas Concentration: aa
Probe Number: aa	Tube Number: a	Sampling Location: aaa	Collection Time: tmm	Gas Area: ****	Gas Concentration: aa

Carbon Dioxide Standard Area: \*\*\*\*  
Methane Standard Area: \*\*\*\*  
Other Gases Standard Area: \*\*\*\*

An Example of This format:

3/31/87  
1036

Lab air - 351323  
CO2 .05% - 505116  
CO2 .5% - 4673333  
CH4 .234% - 2082

U21	3/31	CH4	CO2	CH4	CO2
B - C - BMS - 1015	392	1135770	.042	.112	
B - C - BMS - 1016	383	1152302	.041	.114	
B - A - BMS - 1017	426	1138313	.044	.112	
B - A - BMS - 1018	392	1133821	.042	.112	
B - A - BSG - 1019	408	1137681	.043	.112	
B - A - BSG - 1020	400	1140000	.043	.112	

CO2 .5% - 504856  
CH4 .234% - 2154

Attachment 3. - Field Summary Data sheet.

GENERAL INFORMATION

CARBON DIOXIDE

OTHER GASES

BONE HOLE	PHONE #	DEPTH FI	TUBE #	COLLECT POINT	DATE	TIME	GAS PUMPED	CO2 CONC.	VOL. CO2 CALCULATED	VOL. CO2 DEGASSED	AVG. CO2 CONC.	CH4 CONC	H2 CONC	SF6 CONC	F11 CONC	F12 CONC
U21	1	42														
U21	1	42														
U21	1	42														
U21	2	62														
U21	2	62														
U21	2	62														
U21	3	93														
U21	3	93														
U21	3	93														
U21	4	131														
U21	4	131														
U21	4	131														
U21	4	131														
U21	4	131														
U21	4	131														
U21	4	131														
U21	5	201														
U21	5	201														
U21	5	201														
U21	5	201														
U21	5	201														
U21	5	201														
U21	5	201														
U21	6	266														
U21	6	266														
U21	6	266														
U21	6	266														
U21	6	266														
U21	7	348														
U21	7	348														
U21	7	348														
U21	8	421														
U21	8	421														
U21	8	421														
U21	9	501														
U21	9	501														
U21	9	501														
U21	10	621														
U21	10	621														
U21	10	621														



Environment  
Canada

Environnement  
Canada

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## Some Characteristics of Ion-Selective Electrodes

Ivan Sekerka and Josef F. Lechner

GB

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**TECHNICAL BULLETIN NO. 72**  
(Résumé en français)

INLAND WATERS DIRECTORATE,  
CANADA CENTRE FOR INLAND WATERS,  
BURLINGTON, ONTARIO, 1973.



# Some Characteristics of Ion-Selective Electrodes

Ivan Šekerka and Josef F. Lechner

## INTRODUCTION

The most common application of ion-selective electrodes is in direct potentiometric measurement, where the measured cell potential is directly related to the activity of the ion in the solution (Durst, 1969). Ion-selective electrodes are used to measure the concentration of an ion of particular interest by making use of such methods as single known addition (Orion Research, 1969) or double known addition (Orion Research, 1970a), subtraction (Orion Research, 1970b), anionate addition and subtraction (Orion Research, 1970c). The application of these electrodes is of specific interest in water quality and pollution measurements, since they offer a fast and simple method of determining some of the common ions. These devices are relatively inexpensive, and when used with proper understanding of their characteristics, the results are as accurate as those obtained by the conventional analytical techniques (Riseman, 1969; Andelman, 1968).

Although the theory, operation, application, and the analytical usefulness of these electrodes has already been presented for a number of systems, many problems in their application for routine analytical purposes remain unresolved (Frant *et al.*, 1968; Smrcek *et al.*, 1958; Eisenman, 1969; Ross, 1969; Pungor, 1967, and Light, 1969). The following data, for example, are not satisfactorily covered in the literature:

- i) time of response
- ii) precision
- iii) stability of the potential over a long time period
- iv) effect of the temperature
- v) effect of the room temperature and light intensity.

The present paper discusses these characteristics for different types of ion-selective electrodes.

## EXPERIMENTAL

### Reagents

All chemicals were of reagent grade. Double-distilled water was used for all solutions.

### Apparatus

The ion-selective electrodes listed in Table 1 were used in this study and were prepared according to the manufacturer's directions. All data herein reported were obtained with the Orion 801 digital pH/mV meter, the Orion 855 six-channel automatic switch, the Orion 851 digital printer system and the Hewlett-Packard 7004A recorder. The constant signal source was a Keithley 260 nanovolt secondary standard. The solution temperature

TABLE 1. Types of ion-selective electrodes

	Orion	Beckman	Coming
Chloride	94-17	39604	
Bromide	94-35	39602	
Iodide	94-53	39606	
Sulphide	94-16	39610	476129
Cyanide	94-06		
Cupric	94-29		476133
Lead	94-82		
Cadmium	94-48		
Fluoride	94-09	39600	476042
Sodium	94-11		476210
Calcium	92-20		476041
Divalent cation	92-32		476235
Potassium	92-19		476132
Fluoroborate	92-05		
Nitrate	92-07		476134
Chloride	92-17		476131
Perchlorate	92-81		

was maintained with a Haake K42 circulating thermostated water bath, and the air temperature with a Lab-line Imperial II incubator. Single-junction Orion 90-01 or double-junction Orion 90-02 electrodes were used as reference electrodes immersed directly into the solution or with an intermediate electrolytic bridge. The apparatus and its component parts are shown schematically in Figure 1. The stirring was identical and constant for all measurements. The estimation of the influence of light intensity on the ion-selective electrode potential was accomplished with the help of a microscopic illuminator using a variable voltage source to achieve the changes of light intensity. The light was focused directly onto the surface of the ion-selective electrode crystal. A more accurate measurement of this phenomenon would be beyond the range of this study.

The measurements were conducted in pure standard solutions as well as in the presence of total ionic strength adjustors and in the concentration ranges of  $1 \times 10^{-2}$  M to the lower detection limit of the electrode. For an electrode responding to univalent ion, an overall error of 1 mV corresponds to a 3.9% relative error in activity and for an electrode sensing divalent ion, the relative error is 7.8% per 1 mV.

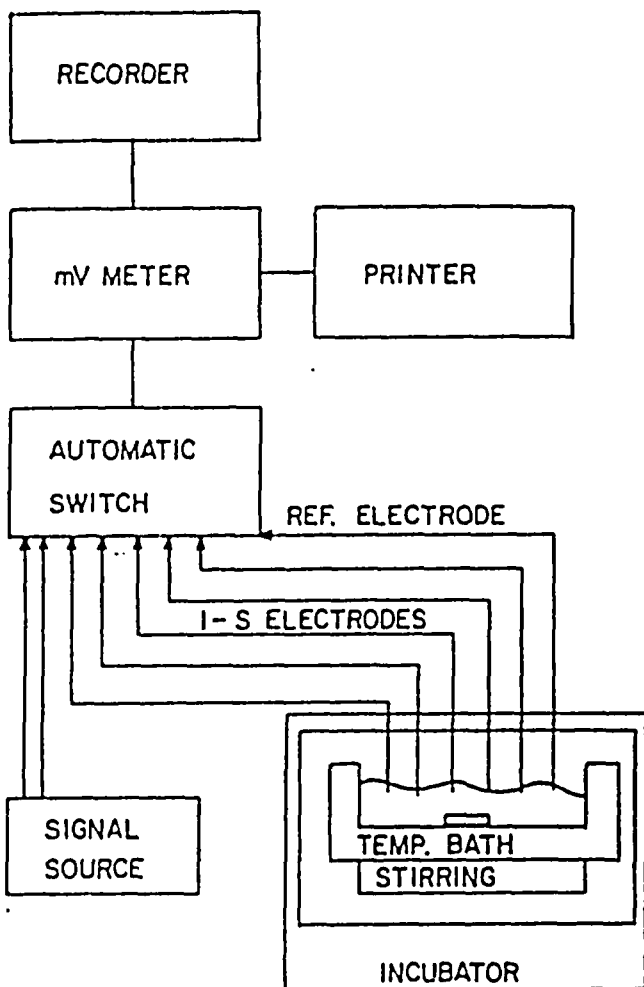


Figure 1. Apparatus for measuring characteristics of ion-selective electrodes.

## RESULTS

### Time Response

The time period was measured during which the initial electrode potential was unstable and changed to a relatively constant value. The point dividing the area of the instability and the relatively stable potential, was derived from the recorded potential-time curve as an empirical point from which the electrode potential varied due to the drift of the potential and the noise of the instruments. A typical example of this curve is shown in

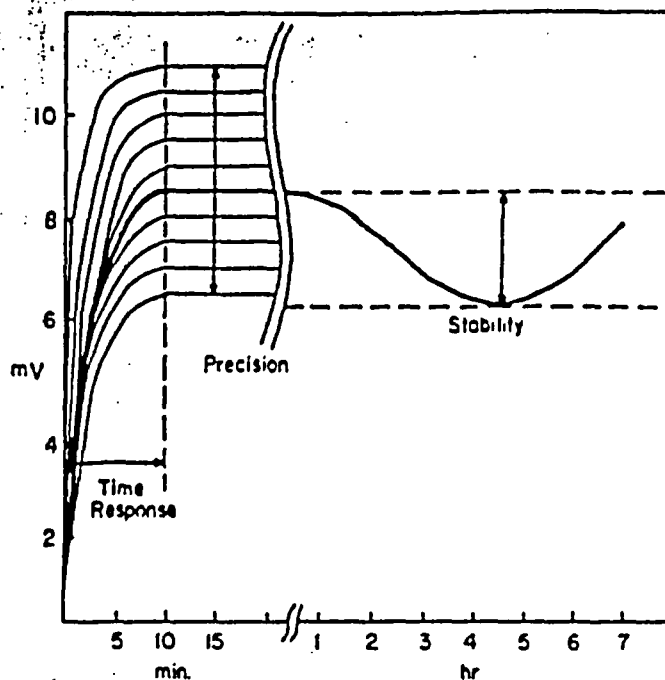


Figure 2. Potential-time curve of an ion-selective electrode.

Figure 2. The speed of response depended very much on the "state of readiness" of the device. Optimum readiness occurred after soaking the electrodes in a nearly similar concentration of the prime ion, resulting in short-time response. Unprepared electrodes taken out of dry storage or electrodes used previously under different conditions have a much slower speed of response. The observed differences in the time responses were probably due to the formation or rebuilding of the active surface layer of the sensing element. It is, therefore, necessary to allow enough time for stabilization of the potential and this time period has to be determined individually for each electrode and its application. In our experiments the electrodes were presoaked in the double-distilled water and the measurements were accomplished with increasing levels of the ion of interest. The results are summarized in Table 2. The time response was reasonably short for the high concentration range and lengthened with the decreasing concentration of the ion of interest. This time period increased very rapidly as the detection limit was approached and measurement became difficult. The electrodes in pure standard solutions and in solutions with constant ionic strength behaved in a similar manner. Practically no difference was found between the electrodes of different manufacturers.

### Precision

An important factor in using the ion-selective electrode for direct potentiometric measurements is the precision which can be related to the reproducibility of the measurements. The precision as the concordance of a series of measurements of the same quantity was deter-

TABLE 2. Time response in minutes

Electrode	Manufacturer	Concentration (m)					
		$1 \times 10^{-2}$	$1 \times 10^{-4}$	$1 \times 10^{-5}$	$1 \times 10^{-6}$	$1 \times 10^{-7}$	$1 \times 10^{-8}$
Sulphide	Orion	3	4	5	5	10	15
	Beckman	3	3	5	5	10	15
	Corning	2	4	5	5	10	15
Silver	Orion	2	4	5	5	10	
	Beckman	2	3	5	5	10	
Chloride	Orion	2	5	15			
	Beckman	3	5	20			
Iodide	Orion	6	5	10	10	15	
	Beckman	3	4	5	10	15	
Mercury	Orion	2	2	3	5	10	15
Bromide	Orion	4	5	10	10	20	
	Beckman	3	5	10	10	20	
Cyanide	Orion	5	5	10	15	30	
Fluoride	Orion	1	1	2	3		
	Beckman	1	1	2	3		
	Corning	1	1	2	3		
Cupric	Orion	1	1	1	2	3	5
	Corning	1	1	1	2	5	10
Lead	Orion	2	2	4	10		
Cadmium	Orion	1	1	1	3	5	
Sodium	Orion	2	2	5	10		
	Corning	3	3	5			
Calcium	Orion	2	2	5			
	Corning	2	2	5			
Divalent Cation	Orion	2	2	5			
	Corning	2	2	5			
Potassium	Orion	2	2	2	5		
	Corning	2	2	5	5		
Fluoroborate	Orion	2	2	20			
Perchlorate	Orion	2	2	4			
Nitrate	Orion	3	4	20			
	Corning	3	4	20			
Chloride (liquid exchanger)	Orion	2	2	5			
	Corning	2	2	5			

mined by recording the electrode potential after 10 times repeated immersion (15 min) and withdrawal (15 min) of the electrode. The electrode was blotted dry after each withdrawal. A 15-minute period was used to allow the electrode enough time to reach the relatively stable potential. The results of these measurements are given in Table 3 and indicate a decrease of precision with the decreasing concentration of the ion of interest. Serious limitations of the electrodes' performance were observed close to the detection limits. The precision of the measurements was slightly better in a solution with a constant ionic strength than in a pure standardizing solution. The electrodes of different manufacturers behaved in similar manner.

#### Stability of the Potential

The stability of the electrode potential over a long time period is the important characteristic of the ion-selective electrode. (This is particularly important for the incorporation into the continuous monitoring system.)

This characteristic — the drift of the mean potential after passing the point limiting the area of the time response — was measured during a six-hour period. The values of the stability expressed in mV are presented in Table 4. The instability of the potential rose markedly in concentrations close to the detection limit, where the drift of the electrode potential limited the use of the electrode. The drift was somewhat smaller in solutions with constant ionic strength than in pure standard solutions. No significant difference was observed between the electrodes of different manufacturers.

#### Temperature Coefficient

The temperature coefficient, as measured, was the overall effect of changing the temperature of the solution while holding the reference electrode (intermediate electrolytic bridge) at room temperature. This experimental coefficient consisted of the standard temperature coefficient of the solution and the coefficient of the liquid junction potential. A summary of the results is presented

TABLE 3. Precision in  $\pm$  mV

Electrode	Manufacturer	Concentration (m)					
		$1 \times 10^{-3}$	$1 \times 10^{-4}$	$1 \times 10^{-5}$	$1 \times 10^{-6}$	$1 \times 10^{-7}$	$1 \times 10^{-8}$
Sulphide	Orion	3	3	2	3	6	10
	Beckman	2	2	2	3	5	10
	Corning	3	3	2	5	5	12
Silver	Orion	3	3	3	4	5	
	Beckman	2	3	3	3	4	
Chloride	Orion	2	3	5	9		
	Beckman	3	3	4	9		
Iodide	Orion	2	3	4	3	5	6
	Beckman	2	2	3	4	4	8
Mercury	Orion	2	2	2	4	5	8
Bromide	Orion	2	2	4	5		
	Beckman	2	3	4	5		
Cyanide	Orion	3	4	6	10		
Fluoride	Orion	1	1	1	2		
	Beckman	1	1	1	2		
	Corning	1	1	1	2		
Cupric	Orion	0.5	0.5	0.5	1	1	1.5
	Corning	0.5	0.5	0.5	1	1.5	1.5
Lead	Orion	0.5	1	1.3	1.5		
Cadmium	Orion	0.5	1	1	1.5	2.5	
Sodium	Orion	2	2	4			
	Corning	2	2	5			
Calcium	Orion	2	3	5			
	Corning	2	2	5			
Divalent cation	Orion	2	3	5			
	Corning	2	2	5			
Potassium	Orion	2	2	3	10		
	Corning	2	2	2	8		
Fluoroborate	Orion	1	1	3			
Perchlorate	Orion	2	3	5			
Nitrate	Orion	2	2	4			
	Corning	2	2	4			
Chloride (liquid exchanger)	Orion	3	3	5			
	Corning	3	4	5			

in Table 5. The temperature coefficient of all ion-selective electrodes in the temperature range of 5–40°C remained practically constant (1.2–1.3 mV/°C). Only in concentration representing the lower detection limit, did the coefficient rise to a value of 1.7 mV/°C. It is important to mention that the dependence of the electrode potential on the temperature was not exactly linear. The potential versus temperature curves possessed a drift, probably due to individual electrode characteristics (long-term change in mean potential) and to the many variable contributions of the potential mentioned above.

#### Room Temperature and Light Intensity

It was observed that the potential of some ion-selective electrodes was very sensitive to varying room temperature, even though the solution temperature remained constant. For the purpose of illustration, variations in room temperature of  $\pm 2^\circ\text{C}$ , which are customary in air-conditioned laboratories, may result in a relative error of  $\pm 15\%$  in concentrations. The  $\text{Ag}_2\text{S}/\text{AgX}$  elec-

trodes (sulphide, silver, chloride, iodide, mercury, bromide and cyanide) were the most sensitive to varying room temperature, having a coefficient  $\pm 2\text{mV}/^\circ\text{C}$ . The values of the external temperature coefficients of  $\text{Ag}_2\text{S}/\text{AgMe}$  electrodes (cupric, lead and cadmium) were in the range of 0.1–0.5 mV/°C. All remaining electrodes were not sensitive to changes in room temperature.

The potentials of  $\text{Ag}_2\text{S}/\text{AgX}$  electrodes were sensitive to changes in light intensity. The change of the electrode potential in our experiments reached values of up to 50 mV. The changes of the potentials of  $\text{Ag}_2\text{S}/\text{AgMe}$  electrodes due to varying light intensity were found to be negligible. The other types of ion-selective electrodes were not sensitive to changes in light intensity.

To obtain reproducible results by using  $\text{Ag}_2\text{S}/\text{AgX}$  and  $\text{Ag}_2\text{S}/\text{AgMe}$  electrodes it is essential that temperature and light intensity in the laboratory be kept at constant levels during calibration and measurement. If constant conditions are not guaranteed, it is necessary to determine and use correction factors.

TABLE 4. Stability of the potential in mV

Electrode	Manufacturer	Concentration (m)					
		$1 \times 10^{-2}$	$1 \times 10^{-4}$	$1 \times 10^{-5}$	$1 \times 10^{-6}$	$1 \times 10^{-7}$	$1 \times 10^{-8}$
Sulphide	Orion	3	2	3	2	5	5
	Beckman	2	2	2	3	4	7
	Corning	2	2	3	3	3	6
Silver	Orion	1	4	4	4	10	
	Beckman	2	3	5	5	10	
Chloride	Orion	1	4	10	17		
	Beckman	1	5	10	18		
Iodide	Orion	2	2	3	3	5	10
	Beckman	2	3	3	5	2	10
Mercury	Orion	2	2	2	3	5	5
Bromide	Orion	2	3	3	7	10	
	Beckman	1	2	3	5	10	
Cyanide	Orion	2	2	2	5		
Fluoride	Orion	1	1	1	1		
	Beckman	1	1	1	1		
	Corning	1	1	1	1		
Cupric	Orion	0.2	0.5	0.5	0.5	2	4
	Corning	0.4	0.5	0.5	1	2	4
Lead	Orion	1	1	1.5	2		
Cadmium	Orion	1	1	1	1.5	2	
Sodium	Orion	2	2	5			
	Corning	2	2	5			
Calcium	Orion	1	1	3			
	Corning	1	2	3			
Divalent cation	Orion	1	1	3			
	Corning	1	2	3			
Potassium	Orion	5	5	10	20		
	Corning	3	4	8	15		
Fluoroborate	Orion	1	1	2			
Perchlorate	Orion	2	2	5			
Nitrate	Orion	1	2	3			
	Corning	1	3	5			
	Orion	2	3	5			
Chloride (liquid exchanger)	Corning	1	3	5			

## CONCLUSIONS

From the characteristics measured in the experiments it can be concluded that the fluoride, cupric, cadmium, and calcium electrodes will be superior in application to the other electrodes. It is also obvious that when measurements involving ion-selective electrodes are made, conditions of measurements must be maintained constant if meaningful results are to be obtained.

Although the application of ion-selective electrodes for certain problems is dependent on many factors such as selectivity, sensitivity, detection limit, mode of use, required accuracy etc., the characteristics estimated and presented in this study are of fundamental importance and must be taken into account in any studies involving the use of ion-selective electrodes.

## ACKNOWLEDGMENTS

The authors would like to thank Mr. J. P. Lively and Dr. P. D. Goulden for encouragement and Mr. F. R. MacDonald and Mr. K. Conn for helpful suggestions.

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- Frant, M.S. and Ross, J.W. Jr. 1968. The application of specific-ion electrodes to water pollution monitoring. Paper presented at the 155th National Meeting of the American Chemical Society, San Francisco, Cal., April 4.
- Light, T.S. 1969. Industrial analysis and control with ion-selective electrodes. In: *Ion-Selective Electrodes*. (Ed. R.A. Durst).

TABLE 5. Temperature coefficients in mV/°C

Electrode	Manufacturer	Concentration (m)					
		$1 \times 10^{-2}$	$1 \times 10^{-4}$	$1 \times 10^{-5}$	$1 \times 10^{-6}$	$1 \times 10^{-7}$	$1 \times 10^{-8}$
Sulphide	Orion	1.1	1.3	1.2	1.2	1.5	1.6
	Beckman	1.2	1.3	1.3	1.3	1.4	1.6
	Corning	1.2	1.2	1.3	1.3	1.6	1.6
Silver	Orion	1.2	1.2	1.3	1.4	1.5	
	Beckman	1.2	1.3	1.3	1.5	1.6	
Chloride	Orion	1.1	1.3	1.3	1.6		
	Beckman	1.2	1.2	1.3	1.6		
Iodide	Orion	1.2	1.2	1.2	1.3	1.4	1.7
	Beckman	1.2	1.4	1.3	1.3	1.5	1.7
Mercury	Orion	1.2	1.3	1.3	1.3	1.4	1.6
	Beckman	1.2	1.3	1.5	1.8	1.8	
Bromide	Orion	1.2	1.3	1.5	1.8	1.8	
	Beckman	1.3	1.4	1.4	1.7	1.8	
Cyanide	Orion	1.2	1.2	1.4	1.5		
	Beckman	0.2	0.2	0.3	0.5		
Fluoride	Orion	0.2	0.2	0.2	0.5		
	Beckman	0.2	0.2	0.2	0.5		
Cupric	Corning	0.2	0.2	0.3	0.4		
	Orion	0.8	0.8	0.9	1.0	1.5	1.7
Lead	Corning	0.9	0.9	1.0	1.0	1.4	1.6
	Orion	0.5	0.6	0.7	1.2		
Cadmium	Orion	0.5	0.5	0.5	0.6	1.3	
	Orion	0.4	0.8	1.0			
Sodium	Corning	0.5	0.8	1.1			
	Orion	0.2	0.2	0.4			
Calcium	Corning	0.3	0.3	0.4			
	Orion	0.2	0.2	0.4			
Divalent Cations	Orion	0.2	0.2	0.4			
	Corning	0.3	0.3	0.4			
Potassium	Orion	0.2	0.2	0.5	0.6		
	Corning	0.3	0.2	0.6	0.6		
Fluoroborate	Orion	0.4	0.5	0.7			
	Orion	0.2	0.2	0.4			
Perchlorate	Orion	0.2	0.2	0.4			
	Orion	0.2	0.3	0.6			
Nitrate	Corning	0.3	0.3	0.6			
	Orion	0.2	0.2	0.4			
Chloride (liquid exchanger)	Orion	0.2	0.2	0.4			
	Corning	0.3	0.3	0.5			

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