UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THE USE OF VACUTAINER TUBES FOR COLLECTION OF SOIL SAMPLES FOR HELIUM ANALYSIS

by

M. E. Hinkle and J. E. Kilburn

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Abstract

Measurements of the helium concentration of soil samples collected and stored in Vacutainer-brand evacuated glass tubes show that Vacutainers are reliable containers for soil collection. Within the limits of reproducibility, helium content of soils appears to be independent of variations in soil temperature, barometric pressure, and quantity of soil moisture present in the sample.

Introduction

Evacuated glass tubes are widely used in the medical profession for the collection and analysis of blood samples. These evacuated tubes are sealed by airtight rubber stoppers that reclose after being pierced by a hypodermic needle. We have found that Vacutainer[1/] brand evacuated tubes are also useful for collecting and storing soils for analysis of helium.

Sample Treatment

Collection

At each sample site, the top 4-8 cm of soil is scraped away with a trowel, and the soil below that is placed in a 20-ml-size Vacutainer tube, to within 2-3 cm of the top. Care is taken that small stones and organic debris are not collected. If the soil contains gravel, sieving to less than 600 μm (-30 mesh) may provide more homogeneous samples. Dirt is brushed away from the inside neck of the Vacutainer tube, and the tube is resealed with its airtight rubber stopper.

Preparation and Analysis

The samples in Vacutainer tubes are placed in an ultrasonic cleaning bath for one hour to disaggregate clumps of clayey soil. The tubes are left standing in the laboratory for three days to allow the helium from the disaggregated soil to equilibrate with the helium in the dead-air space in the tube.

[1/] Use of brand names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

At the time of analysis, a side-hole needle is inserted through the rubber stopper and 5 cm^3 of ambient air is injected into the tube from a hypodermic syringe attached to the needle. To mix the added air with air in equilibrium with soil in the tube, the sample in the tube is stirred vigorously for 30 seconds by pressing the tube against a vortex stirrer.

After stirring, a side-hole needle with empty syringe attached is inserted through the rubber stopper to receive the air that is expelled from the tube. The expelled air is immediately analyzed for helium by means of a modified DuPont leak detector (Friedman and Denton, 1975). This detector has been further modified by the use of polyphenyl ether in place of oil in the diffusion pump, and by the use of a liquid-nitrogen-cooled charcoal trap on the inlet to adsorb gases such as hydrocarbons, which might cause interferences with the helium measurement (Reimer and Denton, 1978).

The detector is calibrated three to four times a day against a standard air mixture containing a known quantity of helium. Ambient laboratory air samples are run between each soil-gas sample. Precision of the helium measurement is $\pm$ 15 ppb. Helium measurments are obtained as parts per billion helium in excess of helium in laboratory air (5,240 ppb).

To calculate the quantity of helium released from the soil sample in the Vacutainer, the dead-space volume of the Vacutainer and the weight of the soil must be considered. The dead-space volume of the Vacutainer tube

is determined by inserting a needle that is attached to a hose connected to a vacuum pump through the stopper and evacuating the tube for 30 seconds. Then another needle attached to a syringe containing 20 cm^3 of air is inserted through the stopper. The amount of air drawn into the evacuated tube is recorded as the dead-space volume, that is, the volume occupied by 5,240 ppb He in atmospheric air sealed in the Vacutainer tube with the soil sample plus the helium derived from the sample itself. The tube is then opened and the soil is weighed.

Calculations

The concentration of helium in the sample may be expressed in different ways, depending on which portion of the sample is assumed to contain all of the excess helium. The concentration may be calculated as volume of helium per gram of undried soil sample, per gram of dried soil sample, in the pore-space volume of the dried soil sample, or in the volume or weight of soil moisture in the sample. Helium derived from the sample is calculated from the total helium measured by the leak detector.

$$He_{measured} = He_{added\ air} + He_{in\ tube\ originally} + He_{excess,\ from\ sample}$$

$$He_{sample} = He_{measured} - (He_{added\ air} + He_{in\ tube\ originally})$$

In the following equations, the excess helium measured is expressed as $10^{-9} cm^3$ per unit weight or volume of a sample portion.

If helium is assumed to be derived from the total undried sample:

$$\frac{He \times 10^{-9} cm^3}{\text{gram undried sample}} = \frac{\text{excess He measured} \times 10^{-9} \times (5 cm^3 + \text{dead-space})}{\text{weight of undried soil}}$$

If helium is assumed to be derived from the dried sample only, the concentration of helium in soil moisture must be subtracted from the helium measured. Because this quantity cannot be measured separately, the theoretical concentration of helium in water equilibrated with atmospheric air in the laboratory is used; in Denver this concentration is approximately $37 \times 10^{-9} cm^3$ He per cm^3 or gram of H_2O.

$$\frac{He \times 10^{-9} cm^3}{\text{gram dry sample}} =$$

$$\left[\frac{\text{excess He} - 37 \times 10^{-9} cm^3 He \times \text{weight } H_2O \text{ in sample}}{\text{weight of dry soil}}\right] \times (5\ cm^3 + \text{dead volume})$$

If helium is assumed to be derived from the soil moisture alone:

$$\frac{He \times 10^{-9} cm^3}{cm^3 \text{ of soil moisture}} = \frac{\text{excess He} \times (5 cm^3 + \text{dead volume})}{\text{volume of soil moisture}}$$

If helium is derived solely from the pore spaces of dry soil, the volume of the pore space is calculated by difference from the following measurements:

22 cm^3 (actual measured volume of nominal 20-ml Vacutainer tube) =

pore-space volume (cm^3)

+ approximate volume of soil $\left[\frac{\text{dry weight of soil}}{2.65 \text{ (average specific gravity of dry soil)}}\right]$

+ volume of soil moisture (difference in weight between undried and dried soil)

+ dead-space volume

The theoretical concentration of helium in soil moisture is subtracted from the helium measured in this calculation, also.

$$\frac{\text{He} \times 10^{-9} cm^3}{cm^3 \text{ of pore space}} =$$

$$\frac{\left[\text{Excess He} - 37 \times 10^{-9} cm^3 \text{ He} \times \text{weight } H_2O \text{ in sample}\right]}{cm^3 \text{ of pore space}} \times (5\ cm^3 + \text{dead-space})$$

Results

Concentrations of helium in distinct portions of the sample may be expressed wherever they appear useful or desired to illustrate a point. All of these calculations yield similar patterns of concentrations. For example, in soil samples collected in a traverse across the Puhimau Thermal Area, at the Hawaii Volcanoes National Park, the quantities of helium expressed as concentrations in different portions of the sample were all lower over the thermal area and higher away for the area (fig. 1). Because concentration of helium in undried soil is the easiest to measure, this quantity is more often used in our studies. When a finite quantity of soil is collected and degassed, the measured helium may be considered to be derived from a combination of the soil moisture, the pore space, and the crystal lattices of the soil minerals; however, the measured helium is not necessarily the total helium, but only that which has achieved equilibrium.

Reproducibility

Replicate soil samples were analyzed to check the reproducibility of the helium measurement. Helium concentration was calculated on the basis of weight of undried soil. Reproducibility was poor for samples containing essentially no helium and was $\pm$ 31-36% for samples containing measurable helium (table 1).

PUHIMAU THERMAL AREA

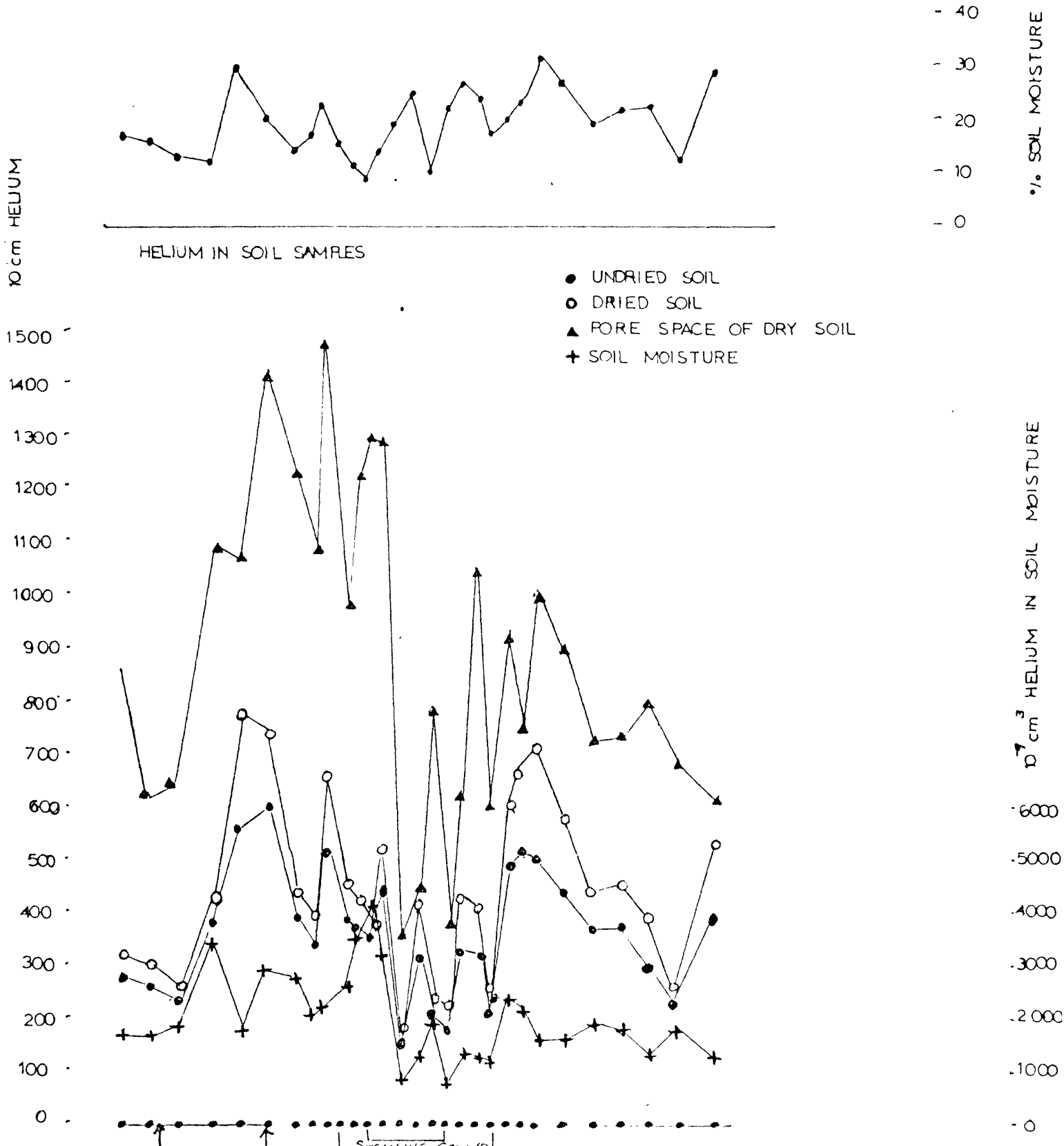


Table 1.--Reproducibility of helium measurement

Sample Location	How Collected	Number of Determinations	Helium Found $\frac{10^{-9} \times cm^3}{g \text{ undried soil}}$			
			Low	High	Mean and Std. dev.	Relative Std. dev.
Golden, Colorado	4 Vacutainers of soil at one place, at same time.	4	0	21	10 ± 12	115.5%
Leyden, Colorado	6 Vacutainers of soil at one place, at same time.	6	40	104	80 ± 25	31.3%
Milford, Utah	8 Vacutainers of soil at one place, on 8 different days	8	22	64	44 ± 16	36.4%

Effect of Temperature and Barometric Pressure

Although temperature and barometric-pressure changes should cause changes in the concentration of helium, large changes in helium content have not been observed in our samples, within the limits of reproducibility. The helium content of the soil samples from Milford, Utah (table 1), did not show any conclusive relationship when compared to soil temperature, barometric pressure, or weight of moisture in the soil sample (fig. 2). However, seasonal variations in helium content of soils may be expected, due to long-term temperature and moisture conditions.

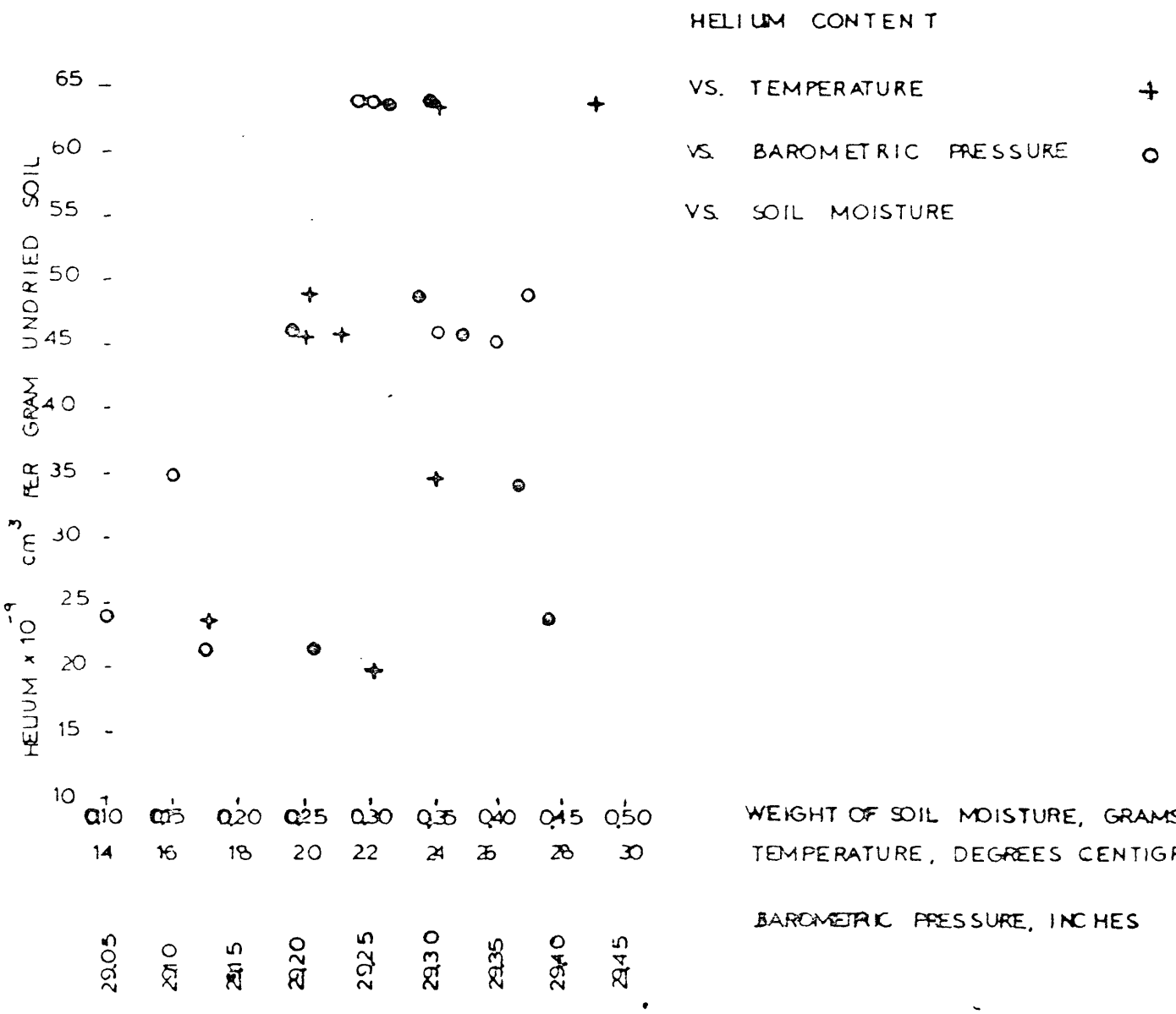
Flushing the Vacutainers

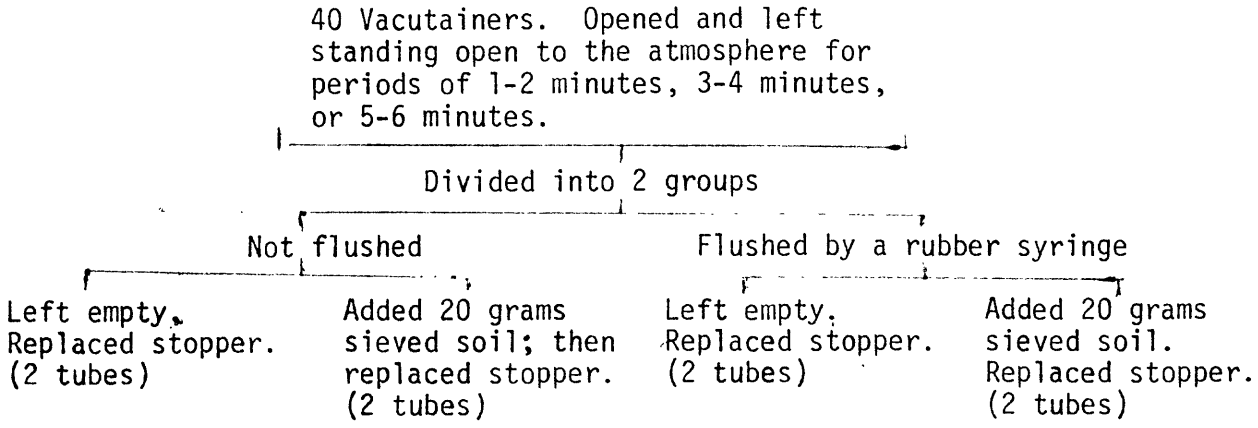
Unopened Vauctainer tubes regularly contain residual helium when received from the manufacturer. The source of this helium may be atmospheric helium that has diffused through the stopper into the partially evacuated tube. E. H. Denton (writtern communication, 1979) calculated that the time required for a 20-ml Vacutainer tube to gain 524 ppb helium (10% of the normal abundance of helium in the atmosphere) is 3.18 months, which is at least as long as the time that elapses between manufacture and use of a Vacutainer.

To determine if residual helium is purged during normal handling of the samples, we took 120 Vacutainer tubes of the same lot number and divided them into three sets according to the times the tubes would be left standing open to the atmosphere. The tubes were treated according to the flow chart below:

FIG. - 2

SOIL SAMPLES COLLECTED ON DIFFERENT DAYS; MILFORD, UTAH





The tubes were allowed to stand for 3, 6, 12, 24, and 48 days before the contents were analyzed for helium. Helium measurements of duplicate samples were within $\pm$ 50 ppb. Only the two unflushed empty tubes that stood open for 1-2 minutes contained appreciable helium. The unflushed tubes that stood open 1-2 minutes and then had soil added contained very little helium; soil pouring into the tube evidently flushed out residual helium (figs. 3, 4, and 5). During the 48-day test, no large leakage of helium occurred either into or out of the Vacutainer tubes.

FIG. - 3

VACUTAINERS LEFT OPEN TO THE ATMOSPHERE FOR 1-2 MINUTES BEFORE FILLING WITH SOIL

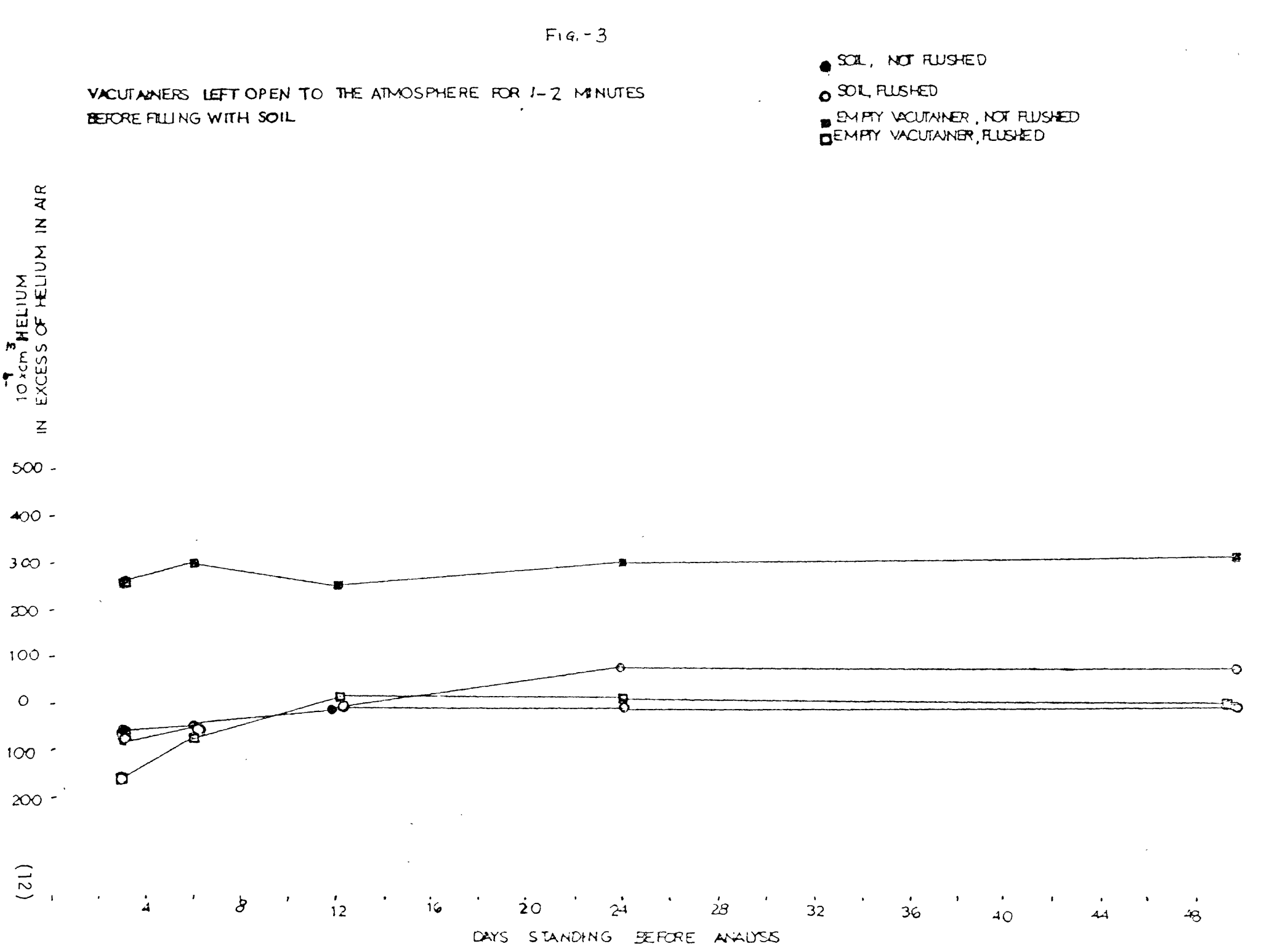


FIG. - 4

VACUTAINERS LEFT OPEN TO THE ATMOSPHERE FOR 3-4 MINUTES BEFORE FILLING WITH SOIL

● SOIL, NOT FLUSHED
○ SOIL, FLUSHED
▪ EMPTY VACUTAINER, NOT FLUSHED
□ EMPTY VACUTAINER, FLUSHED

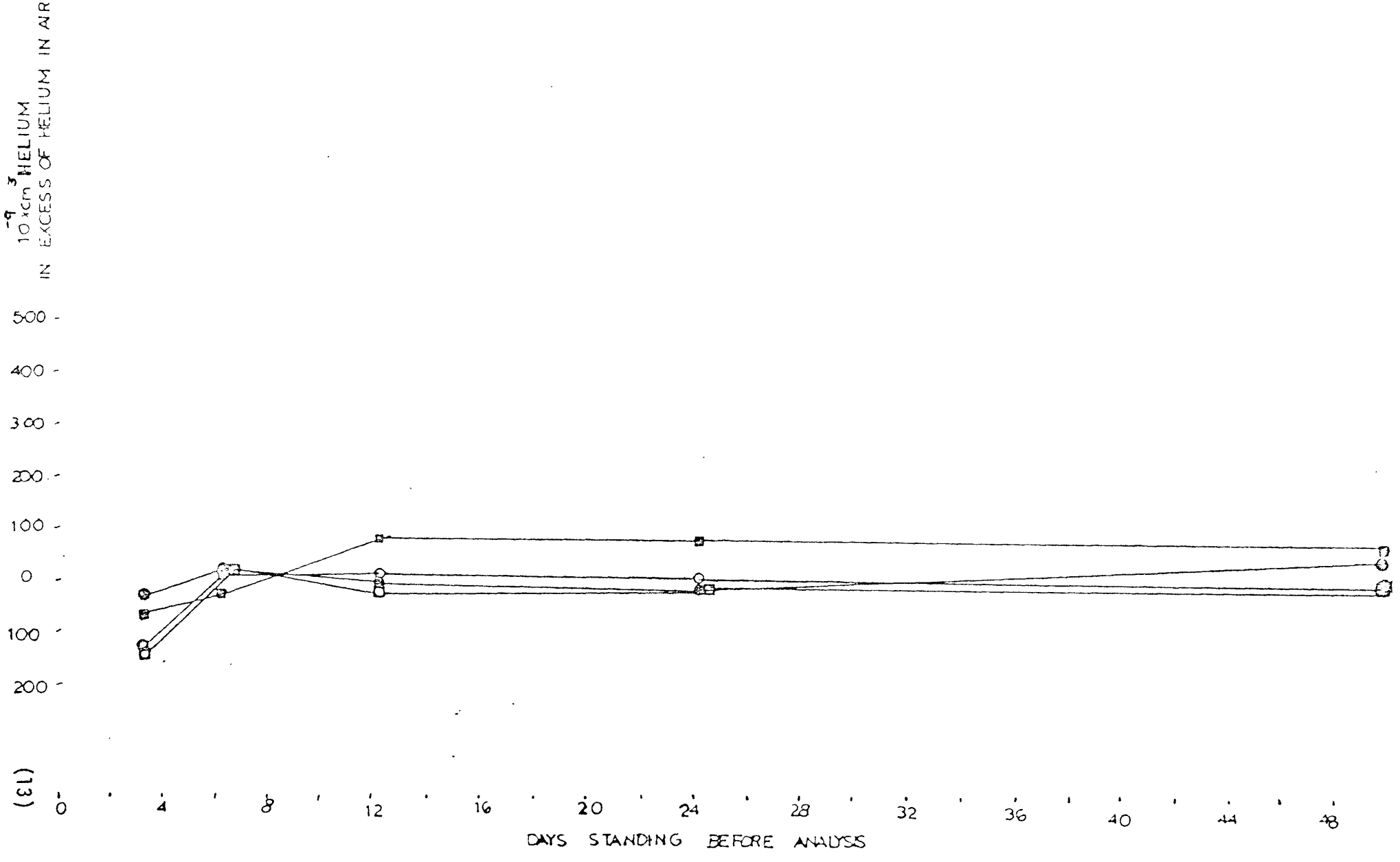
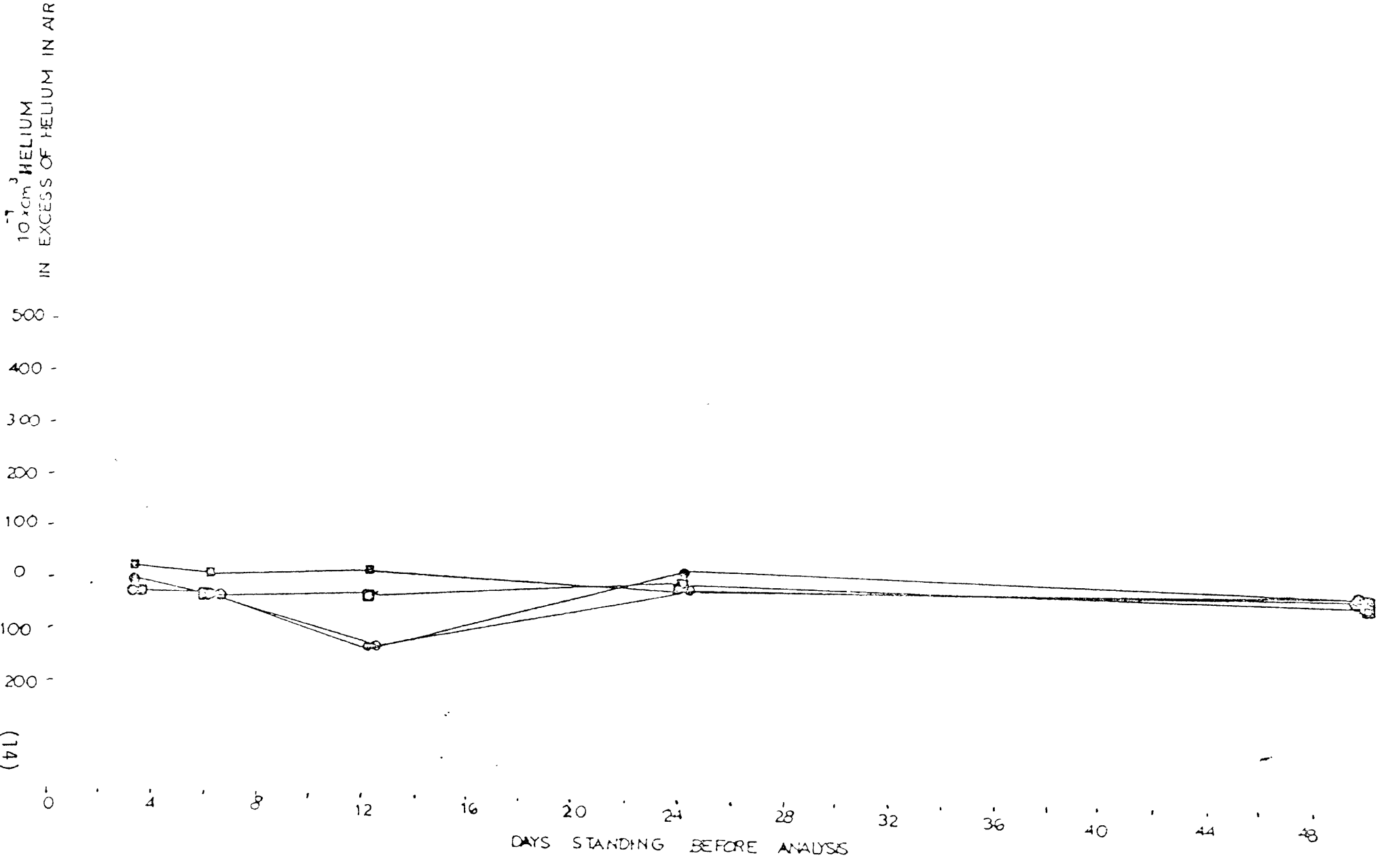


FIG.-5

VACUTAINERS LEFT OPEN TO THE ATMOSPHERE FOR 5-6 MINUTES BEFORE FILLING WITH SOIL

● SOIL, NOT FLUSHED
○ SOIL, FLUSHED
■ EMPTY VACUTAINER, NOT FLUSHED
□ EMPTY VACUTAINER, FLUSHED



Effect of Moisture on Helium Concentration

Water in equilibrium with atmospheric air contains about 30 to 50 x 10^{-9} cm^3 helium per cm^3 of water (Mazor and Fournier, 1973), depending on the temperature and barometric pressure. The amount of helium contributed by the soil moisture should increase with increasing quantities of moisture. Negligible helium will be contributed from the moisture of desert soils, which generally contain less than 1 cm^3 of water in a Vacutainer of soil. Helium dissolved in the moisture of ordinary soils that contain 1-2 cm^3 water per Vacutainer may or may not be a significant part of the total helium.

Helium in soils containing more than 10 percent moisture does not correlate well with soil moisture. Concentrations of helium in soil samples collected in the traverse across the Puhimau Thermal Area were compared to the percent moisture in the soil. Moisture in these soils appeared to either flush helium out of the sample (fig. 6b) or to trap upward-migrating helium beneath wet surficial soil (fig. 7b).

Moisture in surficial soil samples should be in equilibrium with atmospheric air and is not likely to be supersaturated with helium. If the total helium measured in the sample is assumed to be derived from the soil moisture alone, small quantities of moisture can appear highly supersaturated with helium. Therefore, while the concentration of helium may be expressed as volume helium per volume of moisture and the pattern of helium concentrations in moisture is similar to the patterns of helium concentrations expressed in other ways, the concentrations obtained are usually highly supersaturated and are useful for a

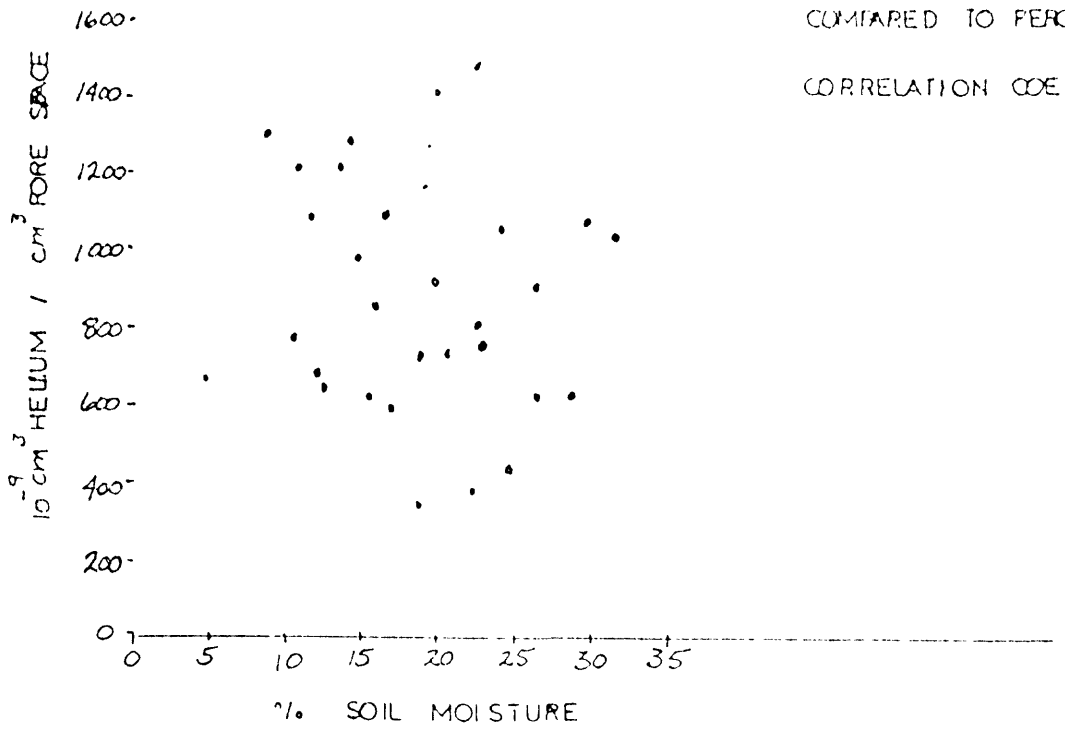
FIG. - 6

PUHIMAU THERMAL AREA

NW - SE TRAVERSE

(a) HELIUM CONCENTRATION IN PORE SPACE OF DRY SOIL COMPARED TO PERCENT SOIL MOISTURE

CORRELATION COEFFICIENT = -0.20



(b) HELIUM CONCENTRATION IN SOIL MOISTURE COMPARED TO PERCENT SOIL MOISTURE

CORRELATION COEFFICIENT = -0.50

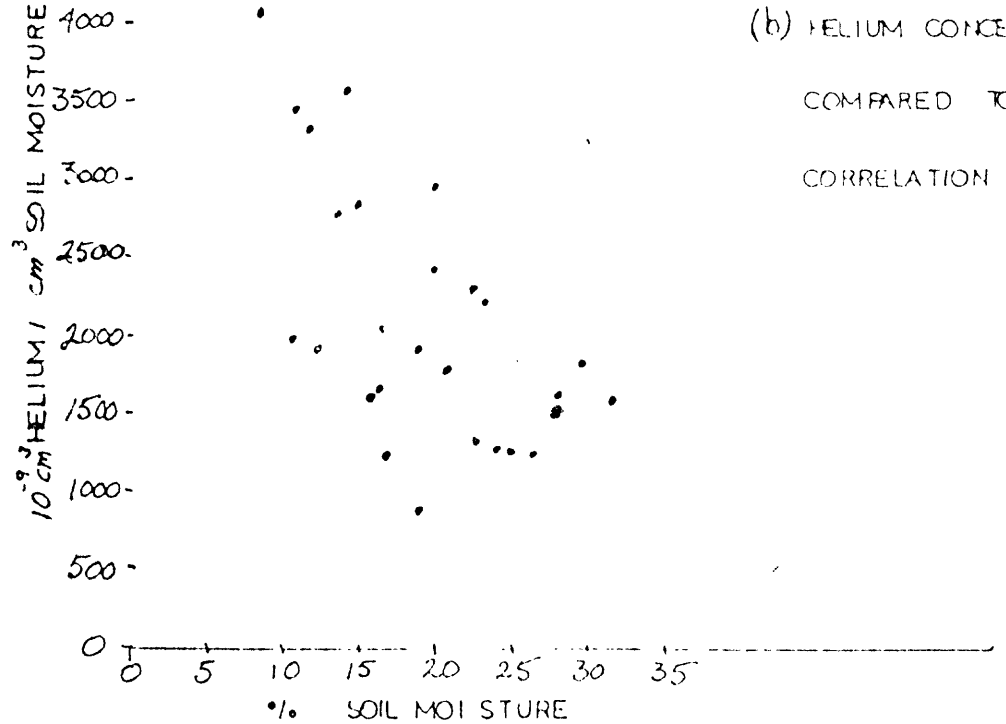
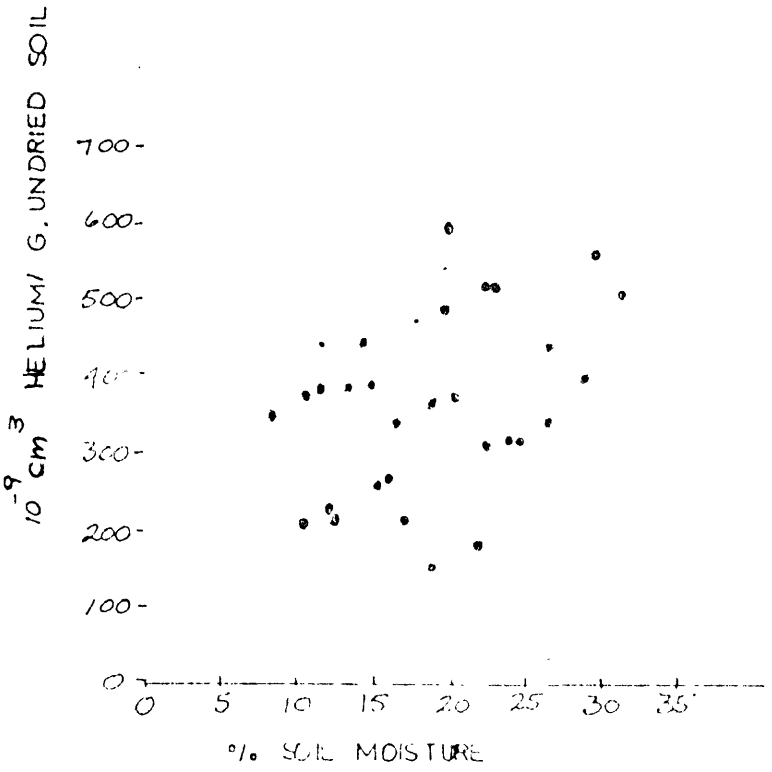


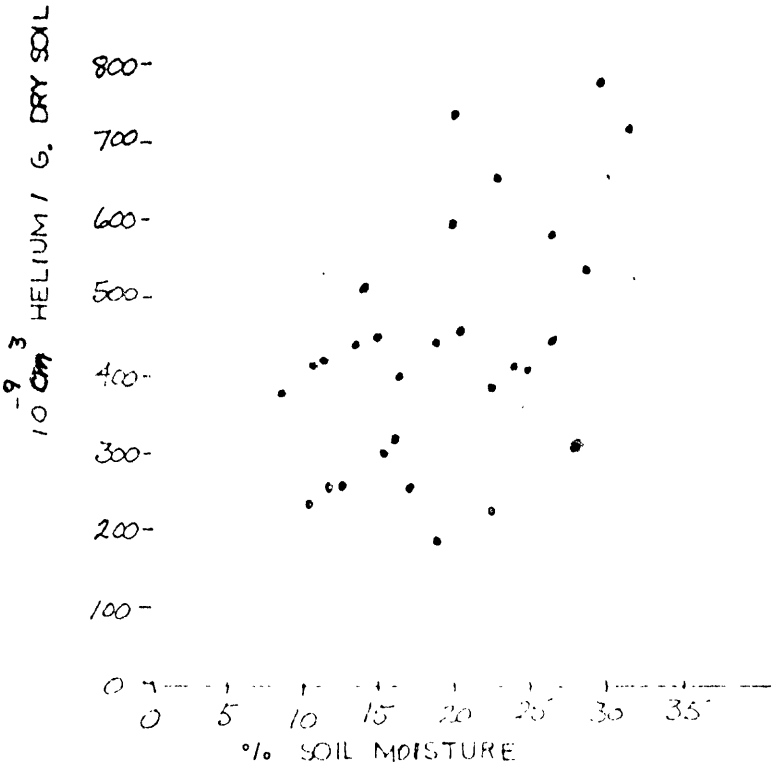
FIG.-7

PUHIMAU THERMAL AREA
NW-SE TRAVERSE

(a) HELIUM CONCENTRATION OF UNDRIED SOILS COMPARED TO PERCENT SOIL MOISTURE
CORRELATION COEFFICIENT = 0.40



(b) HELIUM CONCENTRATION OF DRY SOILS COMPARED TO PERCENT SOIL MOISTURE
CORRELATION COEFFICIENT = 0.57



comparison of relative concentrations, but are not useful as absolute concentrations of helium.

Equilibration Time

Duplicate soil samples were collected every 160 m in three parallel traverses 400 m apart near Casa Grande, Arizona. One sample of each pair was analyzed after 3 days of equilibration. The other sample was run after 26 days. The concentration of helium in the duplicate samples was similar for most sites; however, some of the samples that equilibrated for 26 days contained more helium than the duplicate samples that equilibrated for only 3 days (fig. 8).

To determine the number of days of equilibration needed to maximize the helium produced from a soil sample, two sites near Leyden, Colorado, were sampled. Thirty Vacutainers of soil were collected at each site. The helium content of six samples at each site was measured after 1, 4, 8, 18, and 60 days. The maximum concentration of helium appeared after 18 days. However, distinct differences in concentration were observed after 8 days, and differences could be measured after shorter times by taking an average of replicates. One of the Leyden samples showed a large increase in helium content after a few days, while the other sample did not show an increase in helium (fig. 9).

Average percent moisture contents of the samples collected at each Leyden site were very reproducible (table 2). The samples that showed a large increase in helium content contained roughly twice the moisture of the samples that did not show a large increase in helium. Although higher moisture content appears to be the cause of the large increase in

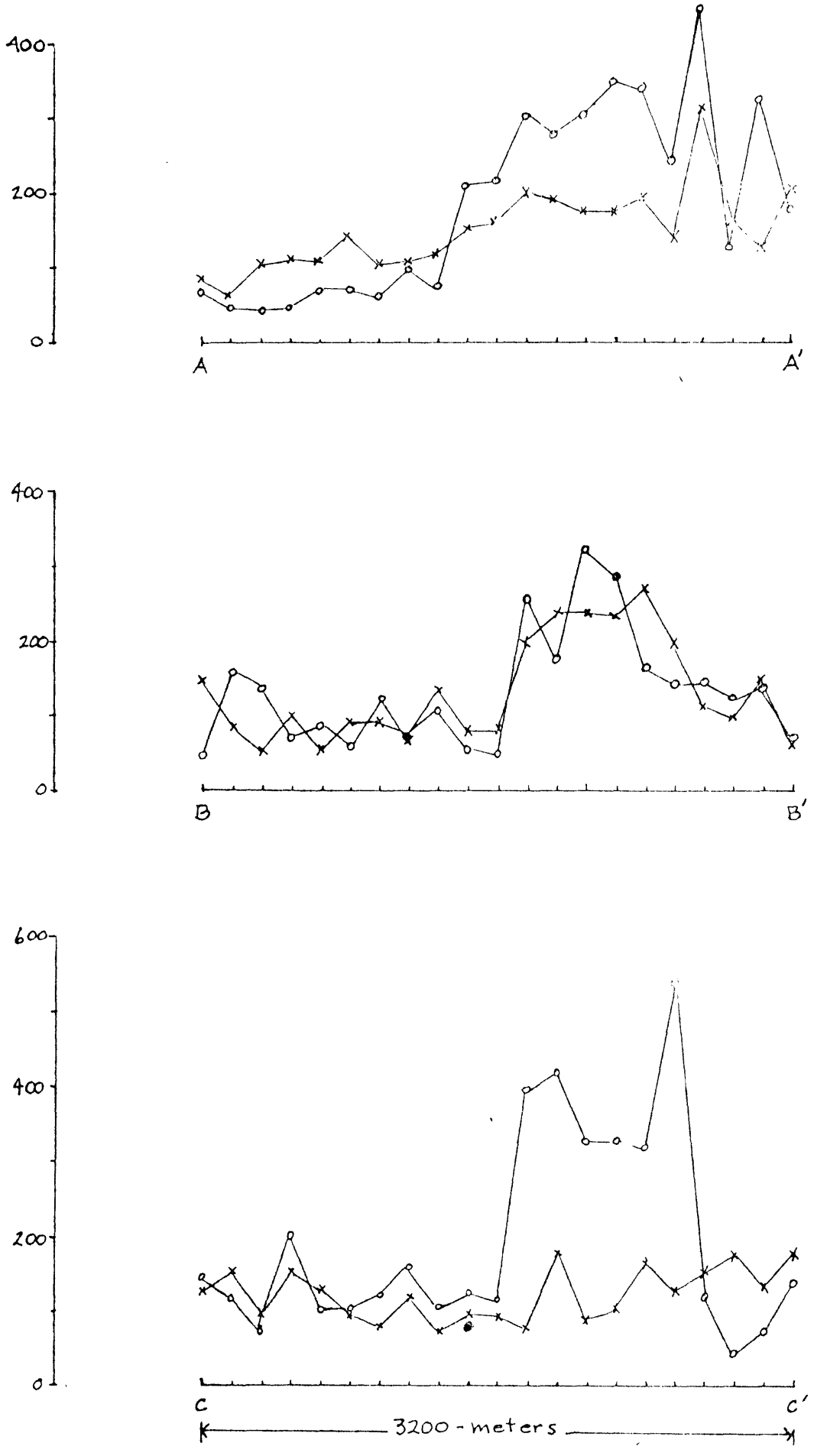


FIG. - 8

COMPARISON OF EQUILIBRIUM TIMES

HELIUM IN SOIL SAMPLES

× 3 - DAYS

o 26 DAYS

FIG.-9

EFFECT OF EQUILIBRATION TIME
ON HELIUM CONTENT OF SOILS

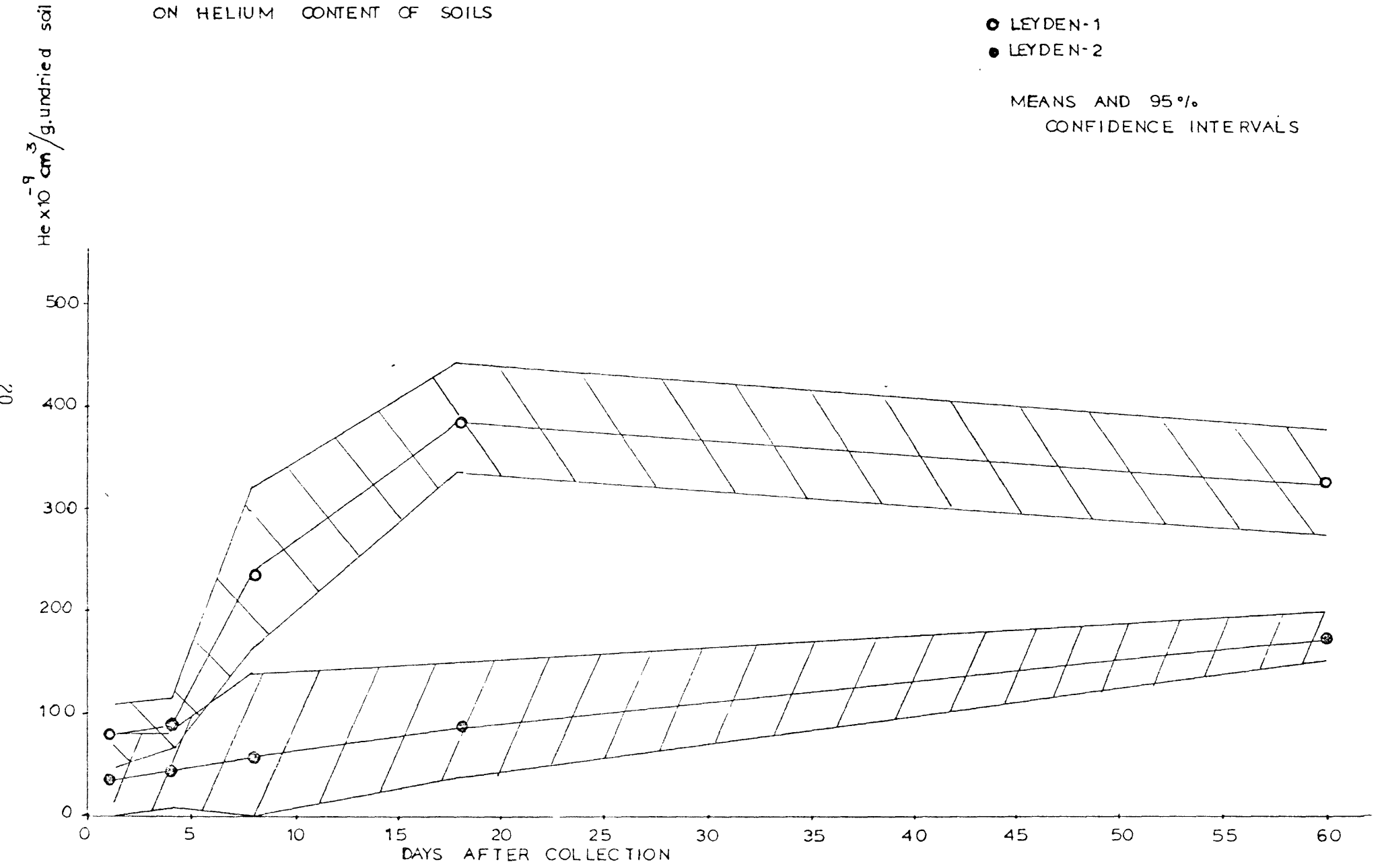


Table 2.--Moisture contents of samples at two sites.

Days after Collection	Number of Samples	Percent Moisture		
		Range	Mean and Std. Dev.	Relative Std. Dev.
		Leyden-1		
1	6	13.8-15.4	14.6 ± 0.6	4.3%
4	6	12.3-14.1	13.4 ± 0.6	4.8%
8	5	11.2-14.1	13.1 ± 1.2	8.9%
18	6	12.4-13.5	13.1 ± 0.4	3.1%
60	6	11.2-14.0	12.7 ± 1.2	9.2%
		Leyden-2		
1	6	5.5- 7.5	6.3 ± 0.7	11.5%
4	6	4.9-10.6	7.1 ± 2.0	28.2%
8	6	4.1- 5.5	4.5 ± 0.5	11.6%
18	6	4.7- 7.1	5.7 ± 1.0	17.0%
60	6	5.5- 6.1	5.7 ± 0.2	4.0%

helium content of samples from the one site at Leyden, moisture may not be the only factor producing the higher helium measurements. The large increase in helium content seen in some of the samples along traverses A-A' and C-C' at Casa Grande (fig. 8) is greater than would be expected for samples of equivalent moisture contents; longer equilibration time appears to be the cause of these differences in helium concentration.

Our data suggest that the concentration of helium in many samples may be compared after less than a week of equilibration, provided that the samples are treated in the same manner and are analyzed after an equal number of days. Because we cannot yet predict which samples will show an increase in helium content after equilibrating for longer perids of time, we recommend that samples be equilibrated for at least two weeks and that samples be analyzed after equal equilibration times.

Conclusions

Vacutainer evacuated glass tubes with airtight stoppers are useful for the collection and storage of soil samples for helium analysis. Helium leaks neither into nor out of the tubes for periods as long as 48 days. Concentrations of helium may be expressed in terms of undried soil weight, dried soil weight, volume of soil moisture, or volume of pore space in the dried soil sample. Reproducibility of the measurement of helium in the undried soil averages $\pm$ 30 to 35%.

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