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A PYROLYSIS TECHNIQUE
FOR DETERMINING MICROAMOUNTS OF HYDROGEN IN LUNAR SOIL
USING THE HELIUM IONIZATION DETECTOR

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ABSTRACT

A method has been developed which will determine hydrogen in sub-milligram samples of lunar soil. It consists of heating the sample in a pyroprobe followed by the gas chromatographic determination of hydrogen using the helium ionization detector. Using a 7 foot, 1/8" OD stainless steel column packed with Carbosieve S, 120/140 mesh, hydrogen was well-separated from the other gases released from lunar soil.

Standards of hydrogen in helium were used for calibration. The limit of detection under the conditions used was about 2 ng. The method was linear from 2 ng to 270 ng.

The method was checked using some actual lunar samples. Results were typical of those obtained for lunar soils using other methods.

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INTRODUCTION

Many times chemical analyses must be run on samples which are limited in amount or which cannot be destroyed. In most instances, a few tenths of a milligram can be spared for analysis. With increasing information about a future lunar base, there is a renewed interest in the soils returned from the moon. Hydrogen is a solar wind species whose concentration in lunar soil is very small. In order to predict the potential usefulness of this lunar hydrogen for propellants and consumables, it is desirable to determine the hydrogen content not only of bulk soil but of various size fractions and of different particle types within a given size fraction. This necessarily limits the amount of sample available for analysis.

A method has been developed which will determine hydrogen in sub-milligram samples. It consists of heating the sample in a pyroprobe followed by the gas chromatographic determination of hydrogen using the helium ionization detector.

EXPERIMENTAL

An Antek 300 gas chromatograph fitted with a helium ionization detector was used in this study. The detector was operated at room temperature and at an applied potential of 150 volts. The column was a 7 foot, 1/8" OD stainless steel tube packed with Carbosieve S, 120/140 mesh. The column was conditioned at 220°C overnight with a helium

flow of 25 ml/min. A schematic diagram of the system is shown in Figure 1. Experimental conditions are given in Figure 2.

A Chemical Data System 122 Micro-extended Pyroprobe was used. The coil was heated to 900°C for 1 minute immediately prior to introducing the weighed sample. The sample was contained in a quartz tube sealed on one end. The tube was placed directly into the pyroprobe coil. The coil served as both the sample holder and the heating element. After reassembling the pyroprobe, the sample was heated to 150°C to eliminate any adsorbed surface moisture. When a steady base-line was obtained, valves were closed, isolating the pyroprobe. The sample was then heated for 1 minute, after which the released gases were introduced onto the column where hydrogen was separated from the other components. Prior to use, the quartz tubes were heated at 900°C for several hours and then stored in a desiccator. A blank was run on each quartz tube prior to sample determination. Blanks typically showed no hydrogen peak or a peak too small to be integrated by the central processor.

The carrier gas was helium which contained 104 ppm nitrogen. Standards of hydrogen in helium were used to calibrate the system. They were injected by means of a Valco gas sampling valve with a 100 µl sampling loop. Chromatographic signals were recorded on an OmniScribe recorder, using 0.001 Volt full scale, and were integrated on a Spectra-Physics 4000 central processor. The smallest peak which could be integrated corresponded to about 1 ppm of hydrogen.

RESULTS AND DISCUSSION

After preliminary evaluations were made of Carbosieve S, Carbosieve B, Molecular Sieve 5A, Molecular Sieve 13X, and Porapak Q; Carbosieve S was chosen for the column packing material because it gave the best separation of hydrogen from the other gases released from lunar soil. Figure 3 shows a chromatogram of a typical pyrolysis of a lunar soil sample. The helium ionization detector gives the best response when ultrapure helium is used as the carrier gas (Andrawes et al., 1981a). However, under these conditions, hydrogen sometimes gives a negative peak and sometimes a W-shaped peak. Andrawes et al. (1981b) discussed the relationship between purity of the carrier gas and peak shape. In order to always obtain hydrogen peaks with the same polarity which could be integrated by the data system, helium containing 104 ppm nitrogen was chosen as the carrier gas. To eliminate the detector instability problems caused primarily by water in the carrier gas line, a liquid nitrogen trap for condensibles was placed in the line.

Preliminary runs showed that hydrogen began to be evolved around 700°C. The amount of evolved hydrogen increased with temperature until around 900°C but showed a marked decrease at 1000°C. Thus, the temperature for pyrolysis was chosen as 900°C.

The valves in the carrier gas line served a two-fold purpose. Closing the by-pass valves made it possible to isolate the pyroprobe during sample change so that a minimum amount of air entered the carrier gas line. This

effected a considerable time savings because the helium ionization detector is very sensitive to air and requires a long time to stabilize after a significant amount of air hits the detector. Isolating the pyroprobe from the rest of the system also made it possible to heat the sample and subsequently to introduce the released volatiles onto the column as a plug when the valves were opened. The pyroprobe controller is a versatile one, allowing heating intervals from 20 milliseconds to 4 hours. A pyrolysis time of 1 minute was found to be optimum for this study because 1) most of the hydrogen was released during the first minute of pyrolysis, and 2) not enough air diffused into the pyroprobe in 1 minute to result in interference. Longer heating times showed this interference. One-minute pyrolyses were continued on the same sample until no more hydrogen was released. This usually required from 2 to 4 pyrolyses.

When standards are introduced onto the column by a gas sampling valve, the retention time for a particular species is different from that obtained by using a pyroprobe to release the species into the carrier gas line. Pyrolysis of an actual sample usually releases many more components than the standards contain; thus, the peak for the species in question may not be obvious. To establish retention times using the pyroprobe system, individual pyrolyses were run using calcium hydride, potassium chlorate, and ammonium dichromate to get retention times of hydrogen, oxygen, and nitrogen, respectively. This method was not used for standardization of the hydrogen because reagent grade calcium hydride was not available for this study.

Standards of hydrogen in helium were used for calibration. The limit of detection under the conditions used was about 2 ng. The method was linear from 2 ng to 270 ng.

The method was checked using some actual lunar samples. Results are shown in Table 1 for 12 bulk lunar soils. Values are typical of those obtained for lunar soils (Chang et al., 1974; DesMarais et al., 1974; Epstein and Taylor, 1970, 1973, 1975; Friedman et al., 1970; and Merlivat et al., 1974). Hydrogen was determined in different particle size fractions for two lunar soils. Figures 4 and 5 show that hydrogen concentration decreases with increasing particle size. This is predictable because more solar wind hydrogen could be implanted in the large surface area provided by small particles. DesMarais et al. (1974) obtained similar trends for other lunar soils.

The pyrolysis technique is simple, fairly rapid, and very sensitive. It can be adapted for the determination of volatiles in a variety of materials.

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SCHEMATIC OF EQUIPMENT

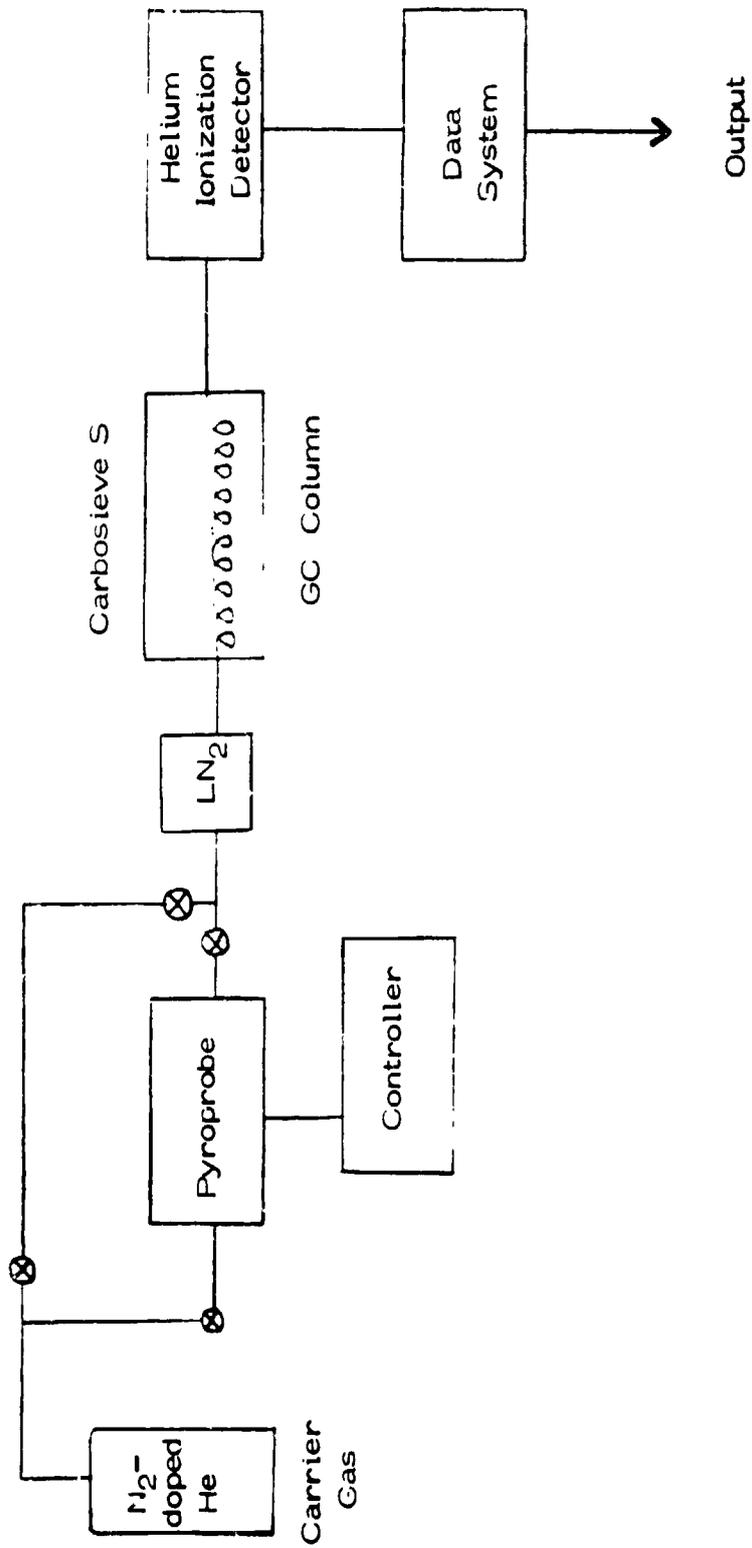


Figure 1

EXPERIMENTAL CONDITIONS

Column 7 ft. Carbosieve S, 120/140 mesh

Column Temperature 60°C

Detector Helium Ionization Detector

Carrier Gas Helium doped with 104 ppm nitrogen

Flow Rate 20 ml/min

Pyrolysis Temperature 900°C

Pyrolysis Time 1 minute

Trap for Condensibles Liquid nitrogen

Figure 2

CHROMATOGRAM OF A TYPICAL LUNAR SOIL PYROLYSIS

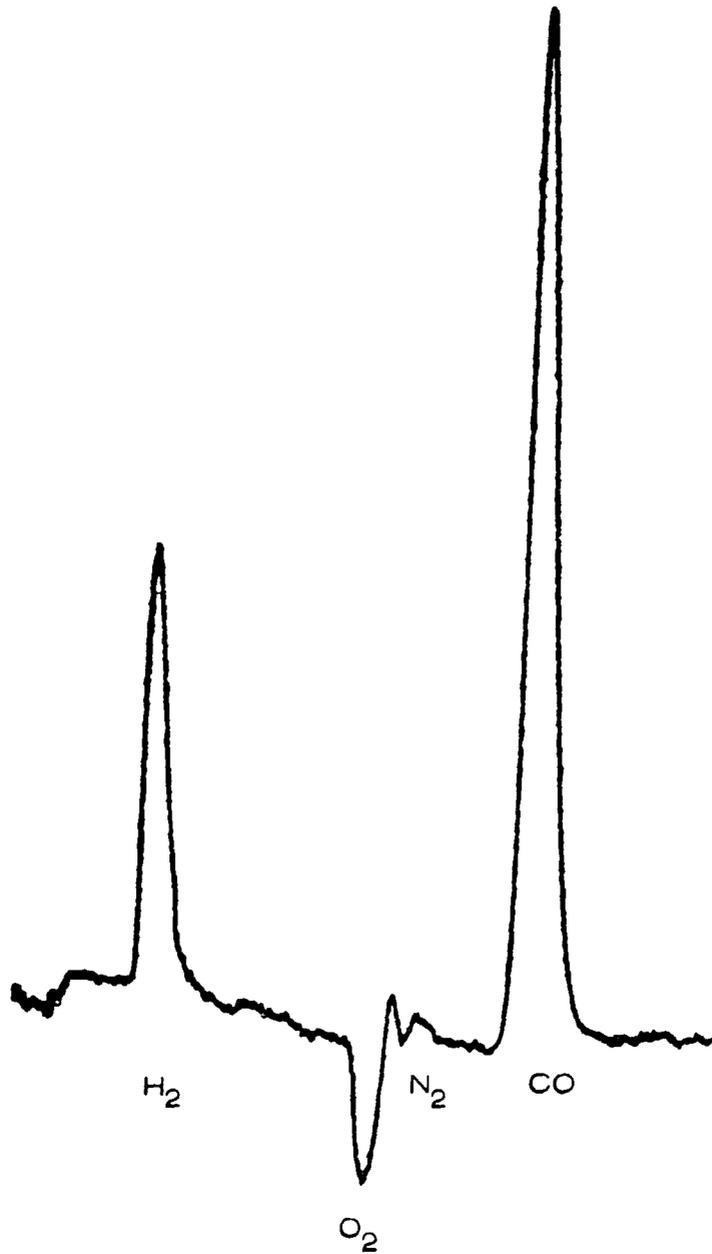
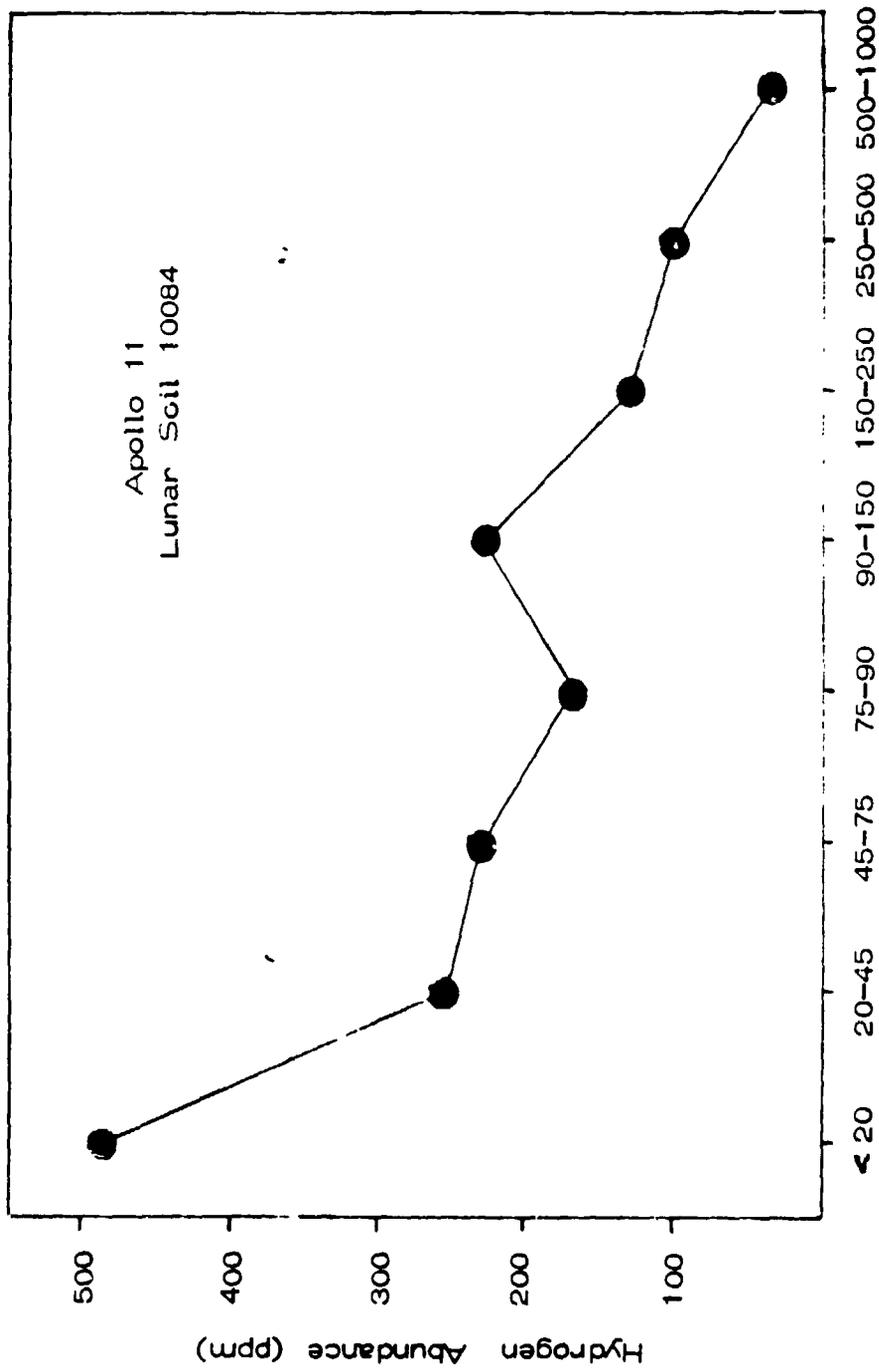


Figure 3

DISTRIBUTION OF HYDROGEN
WITH RESPECT TO PARTICLE SIZE

Apollo 11
Lunar Soil 10084



Particle Size (μm)

Figure 4

DISTRIBUTION OF HYDROGEN
WITH RESPECT TO PARTICLE SIZE.

Apollo 17
Lunar Soil 71501

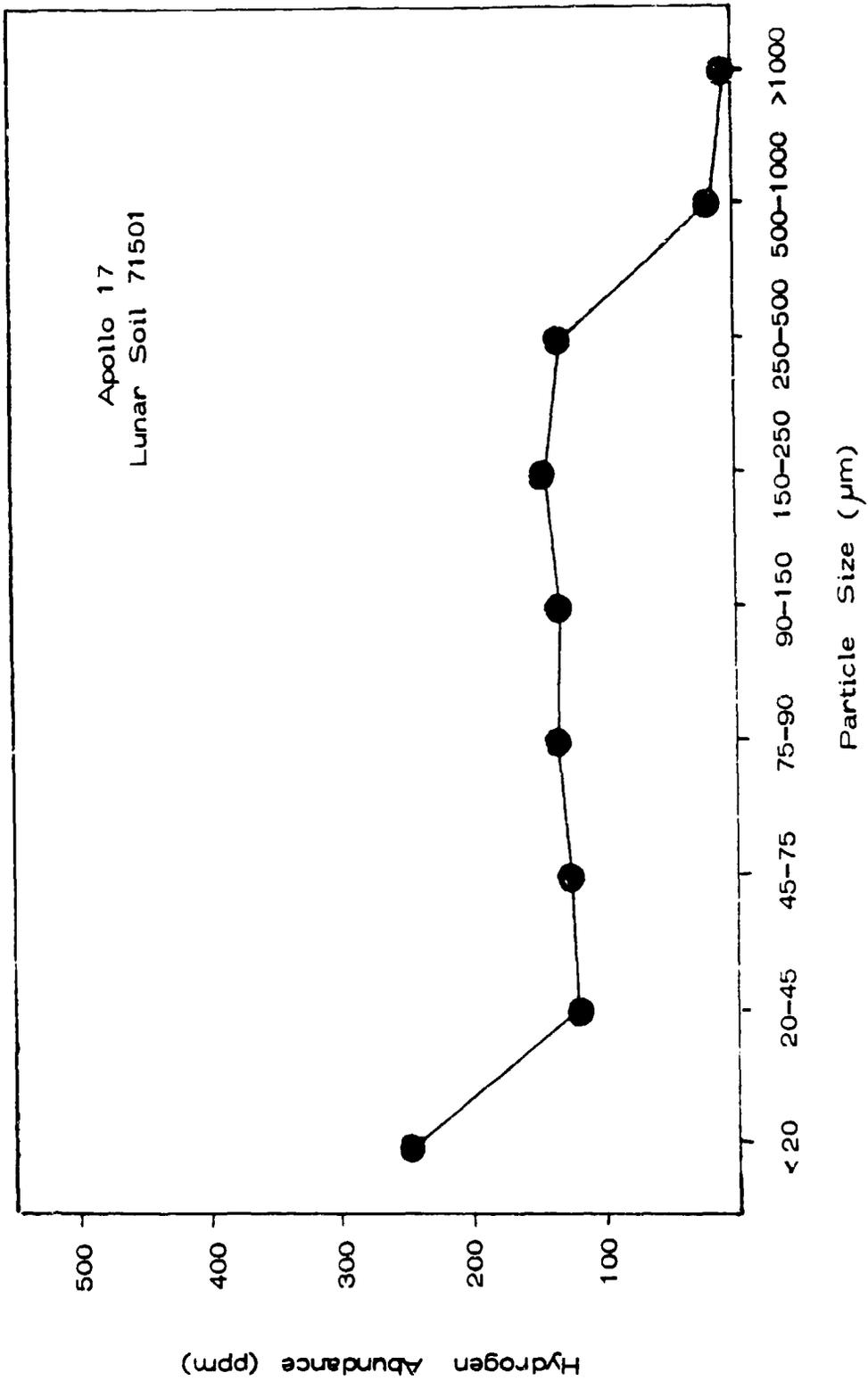


Figure 5

Table 1. CONCENTRATIONS OF HYDROGEN IN LUNAR SOILS

Sample Number	Hydrogen Concentration ppm
10084	59
14003	106
14163	67
14259	61
15021	70
15271	38
15601	54
61221	19
64421	60
66041	76
73141	50
75111	47