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The research conducted on grant NsG-541 during the period November 1964-May 1965, consisted of four basic aspects of investigations.

1. The saponifiable and nonsaponifiable Soxhlet and cold solvent extracts of a number of soils, Recent sediment cores from the Pacific Ocean, sedimentary rocks (Precambrian to Tertiary), and the Orgueil carbonaceous meteorite have been studied by thin-layer chromatography, together with infrared and ultraviolet spectroscopy. Some extracts were further characterized by determining their C^{13} / C^{12} isotope ratios.

The thin-layer chromatograms were developed with n-hexane-ether-acetic acid 70:30:1 (v/v/v) on Silica Gel G layers and photographed under ultraviolet light before and after the application of Rhodamine 6G spray reagent. Before spraying it was possible to locate the naturally fluorescent components (aromatic hydrocarbons and/or heterocyclic compounds). Significantly, the R_f values of most of these naturally fluorescent components appear to be the same within each group of sediments; this was found to be particularly true among the soils. The naturally fluorescent components appeared to be different and were more polar in the marine sediments investigated and remained unseparated at the origin, whereas in the soils and rocks most of the fluorescent substances migrated in this solvent system. The meteorite showed a different pattern of its naturally fluorescent components. Thin-layers visualized with Rhodamine 6G showed that all samples contained saturated hydrocarbons and fatty acids. This was confirmed by the infrared spectra. The ultraviolet spectra of marine sediments exhibited absorption bands at 220-230 m μ and at 270-285 m μ ranges.

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Most of the soils' showed similar absorption bands but generally the soils also contained bands at higher wavelengths. The sedimentary rocks contained a variety of dissimilar bands from 220 to 340 μ .

2. The thin-layer chromatographic method for the identification of hydrocarbons in geological samples has been further developed with known compounds and applied to petroleum and the Orgueil meteorite. Straight chain, cyclic, and aromatic hydrocarbons were separated on Silica Gel G or Silica Gel and 10% magnesium silicate adsorbent using a hexane developing system. Many aromatic hydrocarbons fluoresced under ultraviolet light. Other classes of hydrocarbons were visualized with Rhodamine 6G, antimony pentachloride, or a formaldehyde-sulfuric acid mixture.

In general, the R_f value depended on the degree of unsaturation in the compound. Increased unsaturation resulted in increased polarity thus permitting separation of many aromatic hydrocarbons. Unsaturation differences in the standards, 1-phenyldecane and 1-cyclohexyldecane influenced the migration of these compounds. Subsequent elution of the separated components from the adsorbent facilitated identification of the individual components by other methods such as spectroscopy or gas chromatography.

Information obtained from a single thin-layer chromatogram of a sample often provided data for preparative thin-layer or column chromatography in isolating larger fractions of the sample components. Adsorbent purity was critical because of the non-polar nature of these hydrocarbons. The technique as developed with known compounds has been applied to the Orgueil meteorite. Components separated from thin-layers were further analyzed by a combined

gas chromatographic-mass spectrometric method. The method is expected to be applicable to other geochemical problems as well which require hydrocarbon analysis. Elemental sulfur or sulfur compounds often present in natural samples did not interfere with the hydrocarbon identification.

3. A combined ultramicrochemical carbohydrate analytical method has been successfully applied to the acid hydrolysis products of organic matter of geological interest, such as peat. The method consists of the combination of three revised analytical procedures. (1) The colorimetric reaction of the reducing sugars with Benedict's modification of the Fehling solution which consists of adding 5 ml of an aqueous solution of Cu_2SO_4 , Na_2CO_3 and sodium citrate to 0.5 ml of the hydrolysate and boiling the solution for 3 minutes. As low as 50 μg quantities of sugars give a characteristic green color at 525 $\text{m}\mu$ wavelength whereas the reagent blank is blue at 460 $\text{m}\mu$. (2) Ascending thin-layer chromatography on Kieselguhr G layers developed with a 150:150:45:30 (v/v/v/v) solution of pyridine, ethyl acetate, water and acetic acid and visualized with anisaldehyde spray reagent. This procedure can detect 0.05 μg of sugars although the spots are usually faint. (3) Gas-chromatography of the hydrolysates made sufficiently volatile by the preparation of the trimethylsilyl derivatives of the sugars by a reaction with a solution of pyridine, hexamethyldisilazane and trimethylchlorosilane, 10:2:1 (v/v/v). Quantities of sugars as low as 1-5 μg can be detected. The positive identification of carbohydrates in rock organic matter and in Recent sediments such as peat is a difficult undertaking but this combined method was found, at least, to provide a sufficient indication of their presence in peat. Similar indications, as of this time unconfirmed, have also been found in hydrolyzed organic substances extracted from

the Orgueil carbonaceous meteorite.

4. A method has been developed for the structural studies of bituminous coal, inorganic polymers, and "polymeric-type" organic matter in carbonaceous meteorites incorporating ozonolysis, separation of the oxidized products by means of vapor phase chromatography, and finally, mass spectrometry. Confirmatory data regarding the constitution and structure of the compounds has been obtained through the use of infrared, ultraviolet, and nuclear magnetic resonance analysis.

Lower molecular weight substances were first removed from the pulverized (60 mesh) sample by Soxhlet extraction with benzene-methanol 6:4 (v/v), and the residue was treated with alkaline H_2O_2 . The residue was subsequently ozonized in a suspension of a KOH solution, the resulting ozonides treated with alkaline hydrogen peroxide, acidified with HCl, the acidic components extracted with acetone, methylated with ethereal diazomethane, and finally separated on a gas chromatographic column. Effluent fractions were individually collected in capillaries and subjected to infrared, ultraviolet, nuclear magnetic resonance, and mass spectrometry. Acidic fractions as high as 9.5 weight percent of the original coal samples were found. Well defined infrared spectra were obtained on the ester mixtures as well as on the individual chromatographic fractions, and chromophores were indicated on all ultraviolet spectra. Although nuclear magnetic resonance data is restricted because of quantitative considerations, integrations which were obtained are in agreement with the infrared and mass spectral interpretations. Coal structural fragments such as possibly 5-methyl 6-cyclohexylmethylene 1,2,4 trimellitic trimethyl ester were indicated

by this analytical method. A "polymer" fragment having similar chromatographic character has also been found in the Orgueil meteorite samples. This substance has not yet been analyzed by mass spectrometry.

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